COUPLED THERMODYNAMIC MODELING AND EXPERIMENTAL STUDY OF Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ SYSTEM

by: Elmira Moosavi-Khoonsari July 2015

Department of Mining and Materials Engineering McGill University Montreal, Canada

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DEDICATION

"To acquire knowledge, one must study; but to acquire wisdom, one must observe." Marilyn Vos Savant

To mom and dad; I can never pay back my parents for their endless love, support, and conviction which will always inspire me in my life. They taught me to dream big and work hard to make that happen,

To my beloved husband, Farzad; for his uncountable sacrifices, continuous encouragement, and enormous patience. My appreciations for understanding and companionship during late nights of study,

To my beautiful daughter, Vanda; the light of my life. I am so grateful to have her,

To my brother, Arman; for unbreakable bond and love,

In memory of my grandmothers; they will be always in my heart.

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ABSTRACT

The significance of the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system stems from its applications in industrial processes and natural phenomena. This system in whole or in part was studied for the cooling system of fast breeder reactors, the desulfurization of hot metal and liquid steel, the production of bioactive glasses, coal-combustion slags, the reduction process of bauxite with soda for the production of Al₂O₃, and the production of solid-state electrodes for electrochemical cells. It also possesses many well-known minerals such as wüstite, spinel, corundum, aegirine, etc. which are of importance in geology. However, phase equilibria in this system are indeed very complex due to the change of Fe oxidation state with oxygen partial pressure and the substitution of Fe³⁺ by Al³⁺ in solid solutions. Moreover, the high vapor pressure of sodium, hygroscopicity, high viscosity of SiO₂-rich melts, and high fluidity of Na₂O- and FeO-rich melts make the experimental study of this system quite challenging. As a result, experimental results in this system were often inconsistent and limited in terms of composition and temperature. Therefore, the construction of a coherent thermodynamic database for the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system is essential to optimize existing material processes and to develop new processes and advanced materials.

All solid and liquid phases of two binaries, six ternaries and two multicomponent sub-systems in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system were critically evaluated and optimized in the current study. Using proper thermodynamic models considering the crystal structure of each phase reduces the number of model parameters and thus, enhances the predictive ability of models especially in high order systems. The molten oxide phase was modeled using the Modified Quasichemical Model which takes into account second-nearest-neighbor cation ordering. Extensive solid solutions such as meta-oxides, β "-alumina and pyroxene were treated within the frame work of Compound Energy Formalism with the consideration of their sublattice crystal structures. The wüstite solid solution was modeled using polynomial expansions of the excess Gibbs energy. The sulfide dissolution in the molten oxide phase was modeled using the Modified Quasichemical Model in quadruplet approximation taking into account both first and secondnearest-neighbor short range ordering, simultaneously.

Experimental data in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system were very limited. Hence, key phase diagram experiments and thermodynamic optimization were conducted in this system. Phase diagram experiments were performed using the quenching method followed by Electron Probe Micro-Analysis and X-Ray Diffraction for phase identification. Two- and three-phase equilibria of this system including solid and liquid phases were determined, and the presence of β "-alumina solid solution with a large miscibility gap was revealed for the first time in this work.

The developed database was applied to predict the sulfide dissolution in the Na₂O-FeO-Fe₂O₃-CaO-MgO-MnO-Al₂O₃-SiO₂ molten oxide phase which is of high importance for the production of low sulfur steels. Based on the present thermodynamic modeling results, it was shown, for the first time, that the sulfide capacity of Na₂O-containing oxide melts is not always a unique property of a given melt composition, and can vary with the gas composition in equilibrium with the oxide melt.

RÉSUMÉ

L'importance du système Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ découle de ses applications dans les procédés industriels et les phénomènes naturels. Le système en tout ou en partie a été étudié pour le système de refroidissement des réacteurs à neutrons rapides, la désulfuration de la fonte et de l'acier liquide, la fabrication de verres bioactifs, l'étude des scories de charbon à combustion, le procédé de réduction de la bauxite par de la soude pour la production d'Al₂O₃ et la production d'électrodes à l'état solide pour les cellules électrochimiques. Il possède également de nombreux minéraux bien connus tels que la wüstite, le spinelle, le corindon, l'aegyrine, etc., qui sont d'importance en géologie. Cependant, les équilibres de phase sont très complexes en raison du changement d'état d'oxydation du fer avec la pression partielle d'oxygène et la substitution de Fe³⁺ par Al³⁺ dans les solutions solides. En outre, la pression de vapeur élevée de sodium, l'hygroscopicité des phases, la haute viscosité des liquides riches en SiO₂ et la grande fluidité des liquides riches en Na₂O et FeO rendent l'étude expérimentale de ce système assez difficile. En conséquence, les résultats expérimentaux sont souvent incompatibles et limités en termes de composition et de température. Par conséquent, la construction d'une base de données thermodynamiques cohérente pour le système Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ est essentielle pour optimiser les processus de fabrication de matériaux existants et le développement de nouveaux procédés et de matériaux avancés.

Toutes les phases solides et liquides de deux binaires, six ternaires et deux sous-systèmes à plusieurs composants dans le système Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ ont été évalués de façon critique et optimisés. En utilisant des modèles thermodynamiques appropriées tenant en compte la structure cristalline de chaque phase, le nombre de paramètres du modèle peut être réduit ce qui permet d'améliorer la capacité de prédiction du modèle en particulier dans des systèmes d'ordre supérieur. La phase liquide a été modélisée en utilisant le Modèle Quasichimique Modifié qui tient en compte l'ordre à courte distance du deuxième cation voisin le plus proche. Les solutions solides étendues telles que les méta-oxydes, l'alumine β " et le pyroxène ont été traités avec le Formalisme d'Énergie des Composés et l'examen des structures cristallines de leur sous-réseau. La solution solide wüstite a été modélisée avec des expansions polynomiales de l'énergie d'excès de Gibbs. La dissolution des sulfures dans la phase liquide a été modélisée en utilisant le Modèle Quasichimique Modifié avec l'approximation en quadruplet en tenant compte simultanément de l'ordre à courte distance du premier et du deuxième cation voisin le plus proche.

Les données expérimentales dans le système Na₂O-FeO-Fe₂O₃-Al₂O₃ étaient très limitées. Des expériences ciblées dans le diagramme de phase et une optimisation thermodynamique ont donc été réalisées dans ce système. Les expériences été effectuées en utilisant le procédé de trempe et les phases ont été identifiées à l'aide de micro-analyses par sonde électronique et par diffraction des rayons X. Les équilibres à deux et à trois phases de ce système, y compris les phases solides et liquides, ont été déterminées et la présence de solution solide d'alumine β " avec une grande lacune de miscibilité a été révélé pour la première fois.

La base de données développée a été appliquée à prédire la capacité de dissolution du sulfure dans la phase liquide Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ ce qui est important pour la production d'aciers à basse teneur en soufre. La modélisation thermodynamique a été montré, pour la première fois, que la capacité de dissolution des sulfures dans les liquides d'oxydes contenant du Na₂O n'est

pas toujours une propriété unique d'un liquide d'une composition donnée et peut varier avec la composition du gaz en équilibre avec le liquide d'oxydes.

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PREFACE AND CONTRIBUTIONS OF AUTHORS

All the work presented hereafter was performed at High Temperature Thermochemistry Laboratory, at Department of Mining and Materials Engineering, at McGill University. The present dissertation includes six chapters which have been submitted for publications:

Chapter 5; Critical Evaluation and Thermodynamic Optimization of the Na₂O-FeO-Fe₂O₃ System by Elmira Moosavi-Khoonsari and In-Ho Jung, *Metallurgical and Materials Transactions B*, 2015 (accepted),

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Chapter 7; Coupled Experimental and Thermodynamic Optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃ System: Part 1. Phase Diagram Experiments by Elmira-Moosavi-Khoonsari, Pierre Hudon, and In-Ho Jung, *Journal of the American Ceramic Society*, 2015 (accepted),

Chapter 8; Coupled Experimental and Thermodynamic Optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃ System: Part 2. Thermodynamic Optimization by Elmira-Moosavi-Khoonsari and In-Ho Jung, *Journal of the American Ceramic Society*, 2015 (accepted),

Chapter 9; Critical Evaluation and Thermodynamic Optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ System by Elmira Moosavi-Khoonsari and In-Ho Jung, submitted to *Journal of the European Ceramic Society*, 2015,

Chapter 11; Thermodynamic Modeling of Sulfide Capacities of Na₂O-Containing Oxide Melts by Elmira Moosavi-Khoonsari and In-Ho Jung, submitted to *Metallurgical and Materials Transactions B*, 2015.

For all the chapters, I, Elmira Moosavi-Khoonsari, was the main investigator, in charge of literature review, concept formation, thermodynamic modeling, experimental investigations including data collection and characterizations, as well as manuscript composition. Professor In-

Ho Jung supervised the thermodynamic modeling part and manuscript composition. For Chapter 7, Dr. Pierre Hudon guided the experimental work in early stages of the research, and contributed to the edition of the manuscript.

ORIGINAL CONTRIBUTIONS TO KNOWLEDGE

This was the first attempt to critically evaluate and optimize thermodynamic properties and phase equilibria of the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system from metallic Fe saturation to atmospheric pressure. Discrepancies among experimental data in the system were often resolved, and a comprehensive and self-consistent thermodynamic database was constructed, based on thermodynamic principles. The developed database is also consistent with other databases in FactSage thermochemical software. Unexplored thermodynamic properties and phase diagrams of the system may be predicted from the current optimization. The main original contributions to knowledge are listed below:

- No thermodynamic properties of the Na₂O-FeO-Fe₂O₃ liquid were experimentally investigated. According to the present modeling results, strong negative interactions in the Na₂O-FeO (in equilibrium with metallic Fe) and Na₂O-Fe₂O₃ (in air) liquid solutions were revealed.
- Based on this optimization, iso-activity lines of SiO₂ (solid standard state) and Na₂O (liquid standard state) were predicted in the Na₂O-FeO-SiO₂ system in equilibrium with Fe.
- Phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air and in equilibrium with metallic Fe were measured. The liquidus of the meta-oxide solid solution, the homogeneity range of Na-β"-alumina, and two- and three-phase equilibria between solids and the liquid were determined.
- The current optimization indicated that the Na₂O-FeO-SiO₂ flux with maximum about 20 wt.% Al₂O₃ may be used as a liquid agent for the desulfurization and dephosphorization of steel.
- It was demonstrated that the sulfide capacity is not always a unique property of a given slag composition containing a noticeable amount of Na₂O.

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Introduction

The Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system is very important for iron and steelmaking, glassmaking, the cement production, ceramics and combustion industries as well as geochemistry. The molten oxide phase, many solid solutions such as monoxide, spinel, corundum, meta-oxides, Na- β "-alumina, pyroxene, mulite, etc. and plenty of stoichiometric compounds are stable in this system. The knowledge of phase diagrams and chemical equilibria is fundamental to understand industrial processes and natural phenomena involving complex chemical reactions and phase transformations. Besides, the high vapor pressure of Na₂O and accurately controlling oxygen partial pressure to define the valence state of Fe oxide in liquid and solids make the experimental investigation of the above system very challenging. Moreover, extensive amounts of phase diagram experiments are required, which are costly and time-consuming. Available thermodynamic property and phase diagram data are also sometimes inconsistent and insufficient in terms of composition and temperature.

Nowadays, so called CALPHAD (Calculation of Phase Diagrams) approach is widely used in Materials Engineering. The CALPHAD thermodynamic database is developed via the critical evaluation and optimization of all available thermodynamic property and phase diagram data in the literature. As a result, discrepancies between experimental data would be resolved. When experimental data are very limited, a coupled experimental study and thermodynamic modeling approach can be used. In this approach, the preliminary thermodynamic database constructed from sub-systems may be employed to predict phase diagrams and thermodynamic properties of higher order systems. Based on such predictions, key experimental compositions and temperatures are chosen for phase diagram measurements. Accordingly, phase diagrams of the entire system would be determined with a minimum amount of experiments.

CALPHAD type modeling can be used to develop consistent and comprehensive thermodynamic databases from unary, binary to multicomponent systems. By coupling thermodynamic databases

and kinetic calculations, process simulations could be performed, which aid in improving and developing industrial processes while reducing experimentation.

The present study aimed at extending the Na₂O-containig thermodynamic database in FactSage software (<u>www.factsage.com</u>) [1]. All available thermodynamic property and phase diagram data in the literature were simultaneously evaluated and optimized to obtain a set of model equations for Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the assessment of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back calculated. In this way, all data are rendered self-consistent and consistent with thermodynamic principles.

The database of the Na₂O-CaO-MgO-Al₂O₃-SiO₂ sub-system is already available in our research group. Hence, the main task was to extend the existing database to FeO and Fe₂O₃ sides. Two binaries, six ternaries and two multicomponent sub-systems in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system were optimized. Phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air and in equilibrium with metallic Fe were also experimentally measured, due to lack of phase diagram information data in the literature, using the equilibration/quenching method followed by Electron Probe Microanalyzer (EPMA) and X-Ray Diffraction (XRD) for phase analysis. The experimental procedure and phase identification techniques are elaborated in Chapter 4. Gibbs energies of all solid and liquid solutions were described using thermodynamic models properly representing their structures. The liquid solution was treated using the one-sublattice Modified Quasichemical Model (MQM) [2] in the pair approximation. This model best suits liquid solutions showing a Short Range Ordering (SRO) tendency such as molten silicates. Solid solutions were described using the Compound Energy Formalism (CEF) [3] considering the crystal structure of each solution. All thermodynamic models used in the present study show high predictability in multicomponent systems, which will be discussed in *Chapter 3*. Thermodynamic optimization results in each sub-system are presented in Chapters 5, 6, 8-10.

At the end, as an example of the current database application, the sulfide capacity of Na₂Ocontaining slags used in the hot metal desulfurization route was calculated. Since Na₂O is a very strong desulfurizer, Na₂O-based fluxes are considered to be one of potential desulfurization agents in steelmaking industry.

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MAIN GOAL AND ORGANIZATION

2.1. Main goal

The present study was aimed at constructing a comprehensive and consistent thermodynamic database for Na₂O-Fe_tO-containing oxide systems, which was a part of a wide thermodynamic database development project for the multicomponent system Na₂O-FeO-Fe₂O₃-CaO-MgO-MnO-Al₂O₃-SiO₂-P₂O₅. The consortium project was funded by eleven industrial partners worldwide: (CRD grant from the Natural Sciences and Engineering Research Council of Canada in collaboration with Tata Steel Europe, Posco, RIST, Hyundai Steel, Nucor Steel, RioTinto Iron and Titanium, Nippon Steel and Sumitomo Metals Corp., JFE Steel, Voestalpine, and RHI).

Many binary, ternary and multicomponent sub-systems (including all solid and liquid phases) in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system were critically evaluated and optimized during the course of the current research. The task was fulfilled using a coupled thermodynamic modeling and experimental study approach. All oxide systems were rendered self-consistent and consistent with other databases in FactSage. As a result, the optimized database can be compiled with other databases to enhance the accuracy of calculations and range of applications.

2.2. Organization

This study is presented as below:

 Chapter 3 briefly explains about the approach of thermodynamic optimization and all thermodynamic models, used to describe all solid and liquid phases present in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system.

- *Chapter 4* presents the materials preparation and experimental procedures as well as characterization techniques which were used to measure phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air ($P_{O_2} = 0.21$ atm) and in equilibrium with metallic Fe ($a_{Fe} = 1$).
- *Chapter 5* shows results of the critical thermodynamic evaluation/optimization of the binaries Na₂O-FeO and Na₂O-Fe₂O₃, and the ternary system Na₂O-FeO-Fe₂O₃.
- Chapter 6 reveals results of the critical thermodynamic evaluation/optimization of the Na₂O-Fe₂O₃-SiO₂ system.
- *Chapter* 7 presents results of experimental phase diagram studies performed in the Na₂O-Fe₂O₃-Al₂O₃ system in air and in equilibrium with metallic Fe.
- *Chapter 8* is dedicated to the thermodynamic evaluation/optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system, carried out mainly based on experimental data collected in the current research.
- *Chapter 9* belongs to the thermodynamic evaluation/optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system. This is a result of compiling all binary and ternary model parameters obtained from the optimization of each individual sub-system, elaborated in chapters 5 to 8.
- Chapter 10 presents results of thermodynamic evaluation/optimization of the Na₂O-FeO-Fe₂O₃-X (X = CaO and MgO) systems.
- *Chapter 11* is dedicated to thermodynamic modeling of the sulfide dissolution in Na₂Ocontaining oxide melts. From the current models with model parameters, sulfide capacities of many melt compositions were predicted and compared with experimental data.
- *Chapter 12* summarizes results from this research, and provides some suggestions for future work.

THERMODYNAMIC MODELING

3.1. Critical evaluation/optimization

In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the evaluation of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back-calculated. In this way, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from low order to high order systems can be applied to industrial processes.

The evaluation/optimization procedure is as below:

- 1. The system of interest is defined.
- 2. All available literature data are collected;

a) Thermodynamic data including phase equilibria (phase diagrams, phase equilibria between solid, liquid and gas), calorimetric data (heat capacity, enthalpy of formation and enthalpy of mixing), vapor pressures (obtained by Knudsen cell, Langmuir method), chemical potentials (obtained by electromotive force measurements), activities, etc.,

b) Structural data including cationic distributions between sublattices, lattice parameters, etc.,

c) Physical properties including magnetism, conductivity, molar volume, etc. might be also helpful for the evaluation of the system,

d) Data from higher order systems of which the system of interest is a sub-system may be useful, especially if enough data are not available to determine thermodynamic properties of the system. The interpolation from higher order systems to lower order sub-systems is possible.

3. Considering the structure of each solution phase, a proper thermodynamic model is selected. This is of high significance in the thermodynamic database development, especially for multicomponent systems because a model based on the real structure of the phase can usually provide good predictions of thermodynamic properties of higher order systems from lower order systems.

4. Reliability of literature data are assessed before the optimization. It happens experimental data from different sources might be different with each other by more than experimental error limits. Furthermore, different types of thermodynamic property and phase equilibrium data could be inconsistent with each other. Hence, all experimental data must be critically and simultaneously assessed, according to their experimental techniques, sample preparation, and analytical methods. Possible experimental errors must be taken into account for the evaluation. Even though it is hard to judge the accuracy of experimental results based on experimental techniques, the reliability and compatibility of data may be assessed during the optimization of different types of experimental results under one set of Gibbs energy functions.

5. After the preliminary assessment of experimental results, model parameters for each phase are optimized based on reliable experimental data to construct the database for a given system. At this stage, the optimization software (for example based on a least-square regression code) may be applied for the optimization of the system. The optimization of model parameters continues until back-calculation reproduces all reliable experimental data within experimental error limits.

6. Thermodynamic property and phase equilibrium data of interest are back-calculated. Based on thermodynamic models and optimized model parameters, any type of thermodynamic calculations becomes feasible. In the present study, the FactSageTM(version 6.4) thermochemical software [1] was used for thermodynamic calculations.
3.2. Equilibrium phases and thermodynamic models

3.2.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound (species) is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{3-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{3-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(3-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given stoichiometric compound from pure elements at 298 K (ΔH_{298K}^{o} of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy at 298 K, and C_{p} is the heat capacity.

There are six binary stoichiometric compounds in the Na₂O-SiO₂ system: Na₁₀SiO₇, Na₄SiO₄, Na₆Si₂O₇, Na₂SiO₃, Na₂Si₂O₅ and Na₆Si₈O₁₉. Three binary compounds including CaFe₄O₇, CaFe₂O₄ and Ca₂Fe₂O₅ exist in the Fe₂O₃-CaO system in air. In the FeO-Fe₂O₃-SiO₂ system, there is only a binary stoichiometric compound, Fe₂SiO₄ (fayalite). In the Na₂O-FeO-Fe₂O₃ system, six binary compounds, Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, Na₈Fe₂O₇, Na₂FeO₂ and Na₄FeO₃, and one ternary stoichiometric phase, NaFe₂O₃, are considered at 1 atm total pressure. In addition, four ternary stoichiometric compounds, Na₂FeSiO₄, Na₈Fe₆Si₁₅O₄₀, NaFeSi₂O₆ and Na₅FeSi₄O₁₂, are taken into account in the Na₂O-FeO-Fe₂O₃ and Na₂O-FeO-Fe₂O₃-SiO₂ systems, but due to the lack of experimental data regarding their stability ranges and thermodynamic properties, they were not considered for the optimization (see *Chapters 5 and 6*).

3.2.2. Solution phases

Using suitable models, thermodynamic properties and phase equilibria can be predicted in composition and temperature regions where no experimental data are available, and extrapolation and interpolation become also possible. For a reasonable prediction even at high order systems, models should be based on the structure of solutions to adequately represent the configurational entropy of solution. In this study, the liquid solution phase was modeled based on the Modified Quasichemical Model and solid solutions were treated based on the Regular Solution Model or the Compound Energy Formalism.

The standard Gibbs energy of a pure component *i* is written as:

$$g_i^o = h_i^o - Ts_i^o \tag{3-4}$$

where g_i^o , h_i^o , and s_i^o represent the standard molar Gibbs energy, enthalpy and entropy of *i*, respectively, and *T* is the absolute temperature.

When components 1 and 2 are mixed to form a solution, the energy of the solution relies on interactions between constituents 1 and 2. In the case of an ideal solution when there are no interactions between 1 and 2, the solution Gibbs energy is written as:

$$G^{m} = (n_{1}g_{1}^{o} + n_{2}g_{2}^{o}) - T\Delta S^{conf}$$
(3-5)

where G^m is the Gibbs energy of solution, g^{o_i} is the molar Gibbs energy of component *i*, and ΔS^{conf} is configurational entropy obtained by random mixing of n_1 moles of 1 and n_2 moles of 2 on the same sublattice:

$$\Delta S^{conf} = -R(n_1 \ln X_1 + n_2 \ln X_2)$$
(3-6)

For ideal solutions, interactions between 1 and 2 are zero. However, interactions between components of a solution might not be zero, which are quantified as the molar excess Gibbs energy of the solution (g^{Ex}) . Therefore, the Gibbs energy of the non-ideal solution is given as follows:

$$G^{m} = (n_{1}g_{1}^{o} + n_{2}g_{2}^{o}) - T\Delta S^{conf} + (n_{1} + n_{2})g^{Ex}$$
(3-7)

 g^{Ex} is often expanded as a polynomial function of composition:

$$g^{E} = \sum q_{12}^{ij} X_{1}^{i} X_{2}^{j}$$
(3-8)

where X_1 and X_2 are mole fractions of components 1 and 2 in the solution, and q^{ij}_{12} (= $a + bT + cT^2$ +) are excess interaction parameters which can be functions of temperature. For a regular solution, only q_{12}^{11} is required to describe thermodynamic properties of the solution.

Thermodynamic properties of a binary solution which does not show large deviations from ideality can be well predicted using the polynomial expression given in Eq (3.8). However, large arbitrary model parameters are usually required to predict thermodynamic properties of higher-order systems from their lower order sub-systems. Binary systems may also require large number of interaction parameters in this simple polynomial-based model. This is related to the inability of the model to appropriately describe the configurational entropy of the solution. In such cases, a lot of large arbitrary temperature and composition dependant excess model parameters are often required. Therefore, the structure of the solution must be considered in the selection of solution model.

In the present research, solutions such as liquid oxide, monoxide, meta-oxides, Na- β "-alumina, pyroxene, etc. were described using different thermodynamic models, according to their crystal structures. Structural details and models used to treat each solution are explained in *Chapters 5, 6, 8 and 9*.

3.2.2.1. Liquid oxide phase: NaO_{0.5}-FeO-FeO_{1.5}-CaO-MgO-AlO_{1.5}-SiO₂

In the present study, the Modified Quasichemical Model (MQM) [2] was applied to treat the liquid oxide phase. Short range ordering (SRO) in the solution is taken into account by considering second-nearest-neighbor (SNN) pair exchange reactions of cationic species in the liquid oxide phase, and oxygen is a common anionic species. Therefore, the liquid components in the MQM

for the current research were NaO_{0.5}, FeO, FeO_{1.5}, CaO, MgO, AlO_{1.5} and SiO₂ because cations like Na⁺, Fe²⁺, Fe³⁺, Ca²⁺, Mg²⁺, Al³⁺ and Si⁴⁺ were considered in the pair exchange reaction given below. In addition, the NaFeO2 (associate of Na2O and Fe2O3) and NaAlO2 (associate of Na2O and Al₂O₃) components were taken into account in the liquid solution. Significant amounts of NaFe⁴⁺ and NaAl⁴⁺ were observed, especially in the Na₂O-Fe₂O₃-SiO₂ melts by Mysen et al. [3] using Mössbauer spectroscopy and Raman spectroscopy. Mysen et al. reported that Fe³⁺ configures in the tetrahedral framework as the NaFeO₂ complex, similar to the NaAlO₂ complex in the Na₂O-Al₂O₃-SiO₂ melts. They also reported that the structure of the Na₂SiO₃-NaFeSi₂O₆ melt becomes very similar to that of Na₂SiO₃-SiO₂ with increasing the degree of polymerization toward the NaFeSi₂O₆ corner, which supports the formation of NaFeO₂ associate in the melt. In summary, Si⁴⁺ forming the tetrahedral structure in silicate melts is replaced by NaFe⁴⁺ and NaAl⁴⁺ in the Na₂O-Fe₂O₃-SiO₂ and Na₂O-Al₂O₃-SiO₂ melts, respectively; this is known as a charge compensation effect [4]. Therefore, it is necessary to take into account NaFe⁴⁺ and NaAl⁴⁺ in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ liquid solution. Hence, the MQM with NaO_{0.5}, FeO, FeO1.5, CaO, MgO, AlO1.5, SiO2, NaFeO2 and NaAlO2 species was used to describe the Na2O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ liquid solution.

In the MQM, the following quasichemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B);$$
 Δg_{AB} (3-9)

where A and B are cationic species in the solution and (A - B) represents a SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the change in the non-configurational Gibbs energy due to the formation of 2 moles of (A-B) pairs. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{o} + n_{B}g_{B}^{o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(3-10)

where n_i and g_i^o are the number of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{config} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{config} = -R \left(n_A \ln X_A + n_B \ln X_B \right) - R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right]$$
(3-11)

where X_A and X_B are the mole (or site) fractions, X_{AA} , X_{BB} and X_{AB} are pair fractions and Y_A and Y_B are coordination-equivalent fractions, which are given as the following:

$$X_A = n_A / n_A + n_B = 1 - X_B \tag{3-12}$$

$$X_{ij} = n_{ij} / n_{AA} + n_{BB} + n_{AB}$$
(3-13)

$$Y_A = n_A Z_A / n_A Z_A + n_B Z_B \tag{3-14}$$

It should be noted that Eq. (3-11) is accurate only in one-dimentional lattice (Ising Model), and it provides an approximation in three dimensional lattices.

To implement the model for the optimization of experimentally measured phase diagrams, Δg_{AB} is expanded as an empirical function of composition in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge l} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge l} g^{0j}_{AB} X^{j}_{BB}$$
(3-15)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature.

The composition at which the SRO occurs is system dependant. To produce such SRO, the coordination numbers of components A and B are allowed to vary with the composition:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right)$$
(3-16)

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right)$$
(3-17)

where Z_{AA}^{A} and Z_{AB}^{A} are the values of Z_{A} when all nearest neighbors of an atom A are atoms A and when all nearest neighbors of an atom A are atoms B, respectively. At the end, the maximum SRO composition is defined by the (Z_{AB}/Z_{BA}) ratio [2].

3.2.2.2. Solid solutions

The Compound Energy Formalism (CEF) was advanced by Hillert [5]. Phases exhibiting ranges of homogeneity with two or more sub-lattices can be treated within the framework of CEF. For the $(A,B)_P(D,E)_Q$ solution, containing P moles of the first sublattice and Q moles of the second sublattice per one mole of formula, for example, one may assume four component compounds A_PD_Q , A_PE_Q , B_PD_Q , and B_PE_Q rather than elements, and the Gibbs energy of the solution can be described with reference to Gibbs energies of the end-members, G_{AD} , G_{AE} , G_{BD} and G_{BE} (the stoichiometric numbers are omitted). In the CEF, the Gibbs energy per mole of solution, structurally formulated as $(A,B)_P(D,E)_Q$, is given below:

$$G = y_{A}y_{D}G_{AD} + y_{A}y_{E}G_{AE} + y_{B}y_{D}G_{BD} + y_{B}y_{E}G_{BE}$$

+ $PRT(y_{A} ln y_{A} + y_{B} ln y_{B}) + QRT(y_{D} ln y_{D} + y_{E} ln y_{E})$
+ $(\sum_{k=D,E} y_{A}y_{B}y_{k}L_{AB:K} + \sum_{k=A,B} y_{k}y_{D}y_{E}L_{K:DE})$ (3-18)

where y_i and y_j represent the site fractions of constituents *i* and *j* on the first and second sublattices, respectively. The logarithmic terms represent the random mixing of elements on each sublattice. Interactions between elements on different sub-lattices are taken into account by Gibbs energies of end members G_{ij} , and interactions between elements on the same sub-lattice assuming the other sublattice is occupied only by k species is taken into account by excess terms, $L_{ij:k}$ or $L_{k:ij}$. L parameters can be constant or functions of composition. The compositional dependence of L parameters is often described using the Redlich-Kister polynomials.

Sometimes, G_{ij} is the Gibbs energy of a real stoichiometric compound, however if no real endmember *ij* exists, G_{ij} becomes the model parameter representing interactions between different species on different sublattices. The CEF is expandable to multicomponent systems and solutions with many sublattices. Within the framework of this formalism, many different models can be developed with the consideration of structural concepts. A very important factor to distinguish models is the way Gibbs energies of imaginary end-members are determined. Numerous solid solutions such as wüstite, spinel, meta-oxides, Na- β "-alumina, aegirine (clinopyroxene), nepheline and carnegieite, corundum, mullite, etc. exist in the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system. Sodic wüstite, meta-oxides, Na- β "-alumina and aegirine (clinopyroxene) were newly modeled in this optimization, and previous descriptions of cubic spinel [6], corundum [6], nepheline [7], carnegieite [7], and mullite [8] were taken without any further modification. Unfortunately, regarding the extension of solid solutions involving CaO and MgO to the Na₂O-Fe_tO side, no data are available in the literature. However, this should be further investigated in the future.

1) Wüstite solid solution: (Fe²⁺, Fe³⁺, Al³⁺, Na⁺)O, wüstite FeO with limited solubility of Fe₂O₃, Al₂O₃ and Na₂O.

2) Spinel solid solution: $(Fe^{2+}, Fe^{3+}, Al^{3+})^{T}[Fe^{2+}, Fe^{3+}, Al^{3+}, Va]_{2}^{O}O_{4}$, magnetite Fe₃O₄ and hercynite FeAl₂O₄ with excess solubility of γ -Fe₂O₃ and γ -Al₂O₃.

3) Intermediate-temperature meta-oxide solid solution: $(NaFe^{4+}, NaAl^{4+}, Si^{4+})O_2$, a complete solid solution between β -NaFeO₂ and α -NaAlO₂ with limited solubility of SiO₂.

4) High-temperature meta-oxide solid solution: $(Na^+, Va)[Fe^{3+}, Al^{3+}, Si^{4+}]O_2$, a complete solid solution between γ -NaFeO₂ and β -NaAlO₂ with limited solubility of SiO₂.

5) Na- β "-alumina solid solution: (Na⁺)₂[Al³⁺, Fe³⁺]₁₂O₁₉, Na₂Al₁₂O₁₉ largely extending to Na₂Fe₁₂O₁₉ (unstable) side with a miscibility gap in the middle.

6) Corundum solid solution: $(Al^{3+}, Fe^{3+})_2O_3$, a solid solution between Al_2O_3 and Fe_2O_3 with a large miscibility gap.

7) Nepheline solid solution: low-temperature NaAlSiO₄ with excess solubility of SiO₂, modeled using the MQM.

8) Carnegieite solid solution: high-temperature NaAlSiO₄ with excess solubility of SiO₂, modeled using the MQM.

9) Mullite solid solution: $(Al^{3+})_2^{O}[Al^{3+}, Si^{4+}]^T \{O^{2-}, Va\}_5^V$, $Al_6Si_2O_{13}$ with excess solubility of Al_2O_3 and SiO_2 .

10) Aegirine clino-pyroxene solid solution: $(Na^+)^{M2}[Fe^{3+}, Al^{3+}]^{M1}\{Al^{3+}, Fe^{3+}, Si^{4+}\}^BSiO_6$, a complete solid solution between NaFeSi₂O₆ (aegirine) and metastable NaAlSi₂O₆ (jadeite) at 1 atm.

In the above descriptions, cations shown within a set of brackets occupy the same sublattice, and Va represents vacancy.

Wüstite solid solution

The wüstite (FeO-rich monoxide) solution has a halite (rock-salt) structure with the space group Fm3m. A general formula based on MO oxides was proposed for monoxide solution where M^{2+} is a divalent cation such as Fe²⁺, Ca²⁺, Mg²⁺, Zn²⁺, etc. [9]. There is also limited solubility of oxides with M₂O₃ structure where M is a trivalent cation such as Al³⁺ and Fe³⁺. Moreover, there is limited solubility of Na₂O with the monovalent cation Na⁺ in the monoxide solution. It is obvious that in the case of MO oxides, divalent cations simply mix on the cationic sites while for the solution including trivalent and monovalent cations of M₂O₃ and M₂O types, respectively, the defect formation must be considered. In the case of Na solubility in wüstite, it is possibile that NaAl⁴⁺ or NaFe⁴⁺ are the species dissolving in wüstite however, no evidence was found in the literature.

In-situ spectroscopic measurements performed on the $(Mg_{1-x}Fe_x)_{1-\delta}O$ (magnesio-wüstite) solution [10, 11] revealed that divalent cations $(Mg^{2+} \text{ and } Fe^{2+} \text{ in this case})$ randomly distribute on the cationic sublattice, and trivalent cations (Fe³⁺ in this case) form defect associates (Fe³⁺-Va-Fe³⁺) consisting of two Fe³⁺ cations and a cationic vacancy. Therefore, the $(Mg_{1-x}Fe_x)_{1-\delta}O$ solution could be structurally formulated as $(Mg^{2+}, Fe^{2+}, Fe^{3+}-Va-Fe^{3+})_{1-\delta}O$ where Va represents vacancy. It should be noted that Va are always associated with Fe³⁺, which means that Fe³⁺ and Va do not distribute randomly on the cationic sites but that is the associates of Fe³⁺ and Va mixing randomly with Mg²⁺ and Fe²⁺. However, there are still some arguments about the point defect structure of $(Mg_{1-x}Fe_x)_{1-\delta}O$. The structure of magnesio-wüstite solution was also mostly studied for small values of x. There is lack of structural information for large values of x.

In the present work, wüstite is the extension of the wüstite ternary solid solution $(Fe^{2+}, Fe^{3+}, Al^{3+})O$ previously optimized by Decterov et al. [12]. The solution was modeled as a simple random mixing of Fe²⁺, Fe³⁺, Al³⁺, and Na⁺ on cationic sites while all anionic sites are occupied by oxygen. In the Na₂O-FeO-Fe₂O₃-Al₂O₃ system, the wüstite solid solution can be structurally formulated as below:

$$(Fe^{2+}, Fe^{3+}, Al^{3+}, Na^{+})(O)$$
 (3-19)

This model is structurally equivalent to the following model:

$$(Fe^{2+}, Fe^{3+}-Va, Al^{3+}-Va, Na^{+})(O)$$
 (3-20)

This means that Va introduced by the dissolution of trivalent cations M^{3+} are always associated with the trivalent cations in the form of M^{3+} -Va pairs and do not contribute to the configurational entropy. The Gibbs energy per mole of the quaternary monoxide solid solution using the symmetric 'Kohler-like' approximation is expressed as follows:

$$G^{m} = \sum_{i} X_{i} G_{i}^{o} + RT \sum_{i} X_{i} \ln X_{i} + \sum_{i} \sum_{j} X_{i} X_{j} \left(\frac{X_{i}}{X_{i} + X_{j}}\right)^{m} \left(\frac{X_{j}}{X_{i} + X_{j}}\right)^{n} q_{ij}^{mn} + G_{ternary}^{Ex}$$
(3-21)

where G_i^o is the Gibbs energy of the component such as FeO, FeO_{1.5}, AlO_{1.5} and NaO_{0.5}, X_i is the mole fraction of the same component, and q_{ij}^{mn} are binary regular or sub-regular model parameters between *i* and *j* species where *m* and *n* (*m*, *n* \ge 0) represent the powers of the mole fraction of *i* and *j* species, respectively. The q_{ij}^{mn} terms of the FeO-FeO_{1.5} solution were previously optimized by Decterov et al. [12]. Binary parameters q_{ij}^{mn} of the FeO-NaO_{0.5} and FeO_{1.5}-NaO_{0.5} systems were optimized in the present study, and no ternary excess parameters $G_{ternary}^{Ex}$ were required (see *Chapter 5*).

Meta-oxide solid solutions

There are two meta-oxide solid solutions; high-temperature meta-oxide with tetragonal crystal structure, a complete solid solution between γ -NaFeO₂ and β -NaAlO₂, and intermediate-temperature meta-oxide with orthorhombic crystal structure, a complete solid solution between β -NaFeO₂ and α -NaAlO₂ [13-15]. High-temperature and intermediate-temperature meta-oxide solutions have also noticeable excess solubility of SiO₂ up to about 20 and 10 mol %, respectively [16].

Dissolution mechanisms of SiO₂ in high- and intermediate-temperature meta-oxides are different in terms of crystal structure. Grey et al. [17] investigated the dissolution of SiO₂ in the β - and γ' -NaFeO₂ phases using XRD Rietveld refinement. They revealed that Si replaces Fe in β -NaFeO₂ (intermediate-temperature meta-oxide), and this is charge-compensated by the loss of Na from a proximate tetrahedron. From the viewpoint of configurational entropy, this can be mimicked as the replacement of NaFe pair by Si. Hence, the sublattice structure of intermediate-temperature meta-oxide can be written as following:

$$(NaFe^{4+}, NaAl^{4+}, Si^{4+})O_2$$
 (3-22)

According to Grey et al. [17], in the γ' -NaFeO₂ solution (which is considered to be a part of the γ -NaFeO₂ high-temperature meta-oxide solution) with a collapsed high cristobalite structure, Si replaces Fe in the tetrahedral framework (M site). This is charge-balanced by taking away Na from the cavity framework (Na site). On the contrary to the β -NaFeO₂ solution, where Fe and neighboring Na are replaced by Si and Va, such a neighbor pair restriction was not observed in the γ' -NaFeO₂ solution, and a more random replacement of cationic pairs was reported. Therefore, high-temperature meta-oxide solid solution can be structurally formulated as:

$$(Na^+, Va)^{Na}[Al^{3+}, Fe^{3+}, Si^{4+}]^MO_2$$
 (3-23)

where Va forms in the Na sublattice with the replacement of Fe by Si on the M site.

These sublattice structures were already successfully implemented in the form of CEF to describe the phase diagrams of the NaAlO₂-SiO₂ [18], NaFeO₂-SiO₂ (see *Chapter 6*) and NaFeO₂-NaAlO₂

(see *Chapter 8*) solid solutions, present in the Na₂O-Al₂O₃-SiO₂, Na₂O-Fe₂O₃-SiO₂ and Na₂O-Fe₂O₃-Al₂O₃ systems, respectively. In the current study, all previously optimized Gibbs energies of end-members and interaction parameters for each binary solution were combined together to predict the Gibbs energy of the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ quaternary meta-oxide solution. No additional parameters were used in sub-ternary systems.

<u>Na-β"-alumina solid solution</u>

Based on the present experimental data (see *Chapter 7*), large solubility of Fe³⁺ was observed in Na₂Al₁₂O₁₉ Na- β "-alumina by replacing Al³⁺. This solution can be structurally written as Na₂[Al³⁺,Fe³⁺]₁₂O₁₉. Therefore, one-sublattice model described in Eq. (3-18) was applied to treat the solution. The Gibbs energy of the Na₂Al₁₂O₁₉ end-member was directly taken from the Gibbs energy of Na- β "-alumina. As the end-member Na₂Fe₁₂O₁₉ is unstable in the Na₂O-Fe₂O₃ system in air, its Gibbs energy is one of main model parameters determining the solubility of Fe³⁺ in the solution. The Gibbs energy of the Na₂Fe₁₂O₁₉ end-member was determined as $G_{Na_2Fe_{12}O_{19}}^o = 2G_{NaFeO_2}^o + 5G_{Fe_2O_3}^o + G_{add}$, where G_{add} is the model parameter. For model parameters see *Chapter 8*.

Aegirine clino-pyroxene solid solution

NaFeSi₂O₆ (aegirine) and NaAlSi₂O₆ (jadeite) both crystallize in the *C2/c* space group of the monoclinic structure, and form the clino-pyroxene solid solution. The most well-known clino-pyroxene is CaMgSi₂O₆ (diopside) which has the (Ca, Mg)^{M2}[Mg]^{M1}{Si}^BSiO₆ structure. Trivalent cations such as Fe³⁺ and Al³⁺ substitute for divalent cations and Si⁴⁺. This is known as a coupled substitution in the pyroxene solution:

$$[X^{3+}]^{M1} + \{X^{3+}\}^{B} = [M^{2+}]^{M1} + \{Si^{4+}\}^{B}$$
(3-24)

where M and X represent divalent and trivalent cations, respectively. Therefore, for the clinopyroxene solid solution in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system, the following sublattice structure can be considered:

$$(Na^{+})^{M2}[Fe^{3+}, Al^{3+}]^{M1}\{Fe^{3+}, Al^{3+}, Si^{4+}\}^{B}SiO_{6}$$
(3-25)

The Fe^{2+} species can also enter the M2 and M1 sites. However, it was not taken into account in the present study because $Fe_2Si_2O_6$ is metastable, and the solubility of $Fe_2Si_2O_6$ in the clino-pyroxene is very limited in the present system even under reducing oxygen partial pressures.

Schairer and Yoder [19] investigated the NaFeSi₂O₆-NaAlSi₂O₆ join in air using the quenching method and XRD for phase analysis. They reported the presence of NaFeSi₂O₆ (aegirine) or its solid solution (pyroxene) as the secondary solid phase after the primary solid phase, hematite solid solution, for the melt compositions between 0 and 55 mol % NaAlSi₂O₆. Yoder [20] reinvestigated the NaFeSi₂O₆-NaAlSi₂O₆ phase diagram, and reported the formation of pyroxene solid solution rich in aegirine but, the solubility of Al was not specified. Gilbert [21] studied the single-phase pyroxene samples of NaAlSi₂O₆ containing 0 to 53 mol % NaFeSi₂O₆ at high pressure. Samples were prepared under 40 kbar at 1673 K. XRD analysis revealed a linear change in lattice parameters of prepared pyroxene samples, meaning NaFeSi₂O₆ and NaAlSi₂O₆ form an ideal substitutional solution where Fe³⁺ (ionic radius = 0.64 Å) replaces Al³⁺ (ionic radius = 0.51Å). It should be noted that NaAlSi₂O₆ is not stable at 1 atm, but its Gibbs energy at 1 atm was relatively well determined from the extrapolation of stability data at high pressures.

The Gibbs energy of the clino-pyroxene solid solution was described using the CEF considering the site occupancy of cations in Eq. (3.25). As M2 site is occupied only by Na⁺, the solution can be modeled considering the cation distribution only on M1 and B sites. The Gibbs energy of the solution per formula unit in the framework of the CEF is described using Eq. (3.18). G^{Ex} is expressed using the Redlich-Kister power series considering interaction energies between cations *i* and *j* on one sublattice when the other sublattice is occupied by *k*:

$$G^{Ex} = \sum_{i} \sum_{j} Y_{i}^{M I} Y_{j}^{M I} Y_{k}^{B} \sum_{m} {}^{m} L_{ij;k} (Y_{j}^{M I} - Y_{i}^{M I})^{m} + \sum_{i} \sum_{j} Y_{k}^{M I} Y_{i}^{B} Y_{j}^{B} \sum_{m} {}^{m} L_{k;ij} (Y_{j}^{B} - Y_{i}^{B})^{m}$$
(3-26)

Figure 3.1 is the schematic presentation of composition lines between the end-members of the clino-pyroxene solid solution according to the present model. As seen, two of the end-members are charge-neutral, and four of them have (-1) charge. Therefore, neutral compositional line resides between the NaFeSi₂O₆ and NaAlSi₂O₆ end-members. In the CEF, the most important model parameters are Gibbs energies of end-members. Among six end-members in this solution (see Fig. 3.1), the Gibbs energies of the charge-neutral end-members NaFeSiSiO₆ and NaAlSiSiO₆ are identical to the Gibbs energies of NaFeSi₂O₆ and NaAlSi₂O₆ and NaAlSi₂O₆ compounds, respectively. The Gibbs energies of the NaFeAlSiO₆ (-1) and NaAlFeSiO₆ (-1) end-members can be determined by the combination of Eqs. (3-27) and (3-28) as following:

$$I_{FeAl} = G_{FeAl} - G_{AlFe} \tag{3-27}$$

$$\Delta_{FeAl} = (G_{FeAl} + G_{AlFe}) - (G_{FeFe} + G_{AlAl})$$
(3-28)

where G_{FeAl} , G_{AlFe} , G_{FeFe} and G_{AlAl} are the Gibbs energies of NaFeAlSiO₆ (-1), NaAlFeSiO₆ (-1), NaFeFeSiO₆ (-1) and NaAlAlSiO₆ (-1) end-members, respectively. The parameter I_{FeAl} determines the preference of Fe³⁺ and Al³⁺ for either the M1 or B sites. In the current study, both I_{FeAl} and Δ_{FeAl} were set to be zero to obtain an ideal distribution of Fe³⁺ and Al³⁺ between the M1 and B sites. No G^{Ex} parameters were used for the NaFeSi₂O₆-NaAlSi₂O₆ clino-pyroxene solution, and it was treated as an ideal solution. It should be noted that all charged end-members have (-1) negative charge, and thus, their Gibbs energies do not influence the solution with neutral-charged compositions in the present optimization. That is, the Gibbs energies of NaFeSi₂O₆ and NaAlSi₂O₆ are the most important model parameters for the aegirine clino-pyroxene solution.

3.2.3. Metallic and gas phases

To calculate the metallic saturation condition, solid and liquid Fe from FACT pure substance database [1] were considered. Gibbs energies of gas species were taken from FACT pure substance database [1].

3.3. Extrapolation techniques

Thermodynamic properties of ternary and higher order systems may be estimated from binary and ternary model parameters, respectively, using 'geometric' models. This was elaborated by Pelton [22].

The molar excess Gibbs energy of a binary 1-2 solution is written as below:

$$G_{12}^{Ex} = \alpha_{12} X_1 X_2 \tag{3-29}$$

The term α_{12} can be expanded as a polynomial in mole fraction:

$$\alpha_{12} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} X_1^i X_2^j$$
(3-30)

where q_{12}^{ij} are empirical parameters which can be functions of temperature. In the case, the MQM is used, the equivalent fraction Y_1 and Y_2 can be used rather than mole fraction. Eq. (3-30) is often written in the 'Redlich-Kister' form:

$$\alpha_{12} = \sum_{i\geq 0}{}^{i}L_{12}(X_1 - X_2)^i$$
(3-31)

3.3.1. Extension to ternary systems

The Gibbs energy of a ternary solution can be expressed as:

$$g_{sol} = \sum g_i^o x_i - T \Delta S^{mix} + g^{Ex}$$
(3-32)

where g_{sol} and g_i^o are the molar Gibbs energies of the solution and pure component i, respectively, and ΔS^{mix} is the entropy of mixing. g^{Ex} may contain the excess Gibbs energy extrapolated from binary model parameters and ternary excess parameters. Several 'geometric' models are suggested to predict thermodynamic properties of ternary systems. That is, depending on the extrapolation model, the value of g^{Ex} can be different. The most well-known models, shown in Fig 3.2, are Muggianu, Kohler and Toop. The two formers are symmetric and the Toop models are asymmetric. The use of an inappropriate extrapolation technique may not give an accurate estimation of the ternary Gibbs energy from that of binary sub-systems. In all geometric models, the excess Gibbs energy of a ternary solution at any composition (g_P^{Ex}) may be predicted based on binary interaction parameters or the excess Gibbs energy of binary sub-systems at points a, b and c (Fig. 3.2). The excess Gibbs energy of a ternary solution can be written as:

$$g_P^E = \alpha_{12(a)} X_1 X_2 + \alpha_{23(b)} X_2 X_3 + \alpha_{13(c)} X_1 X_3 + (ternary \ terms)$$
(3-33)

where $\alpha_{12(a)}$, $\alpha_{23(b)}$, and $\alpha_{13(c)}$ are the binary ' α -functions' assessed at points a, b and c. Ternary terms can be expanded as polynomial functions where empirical coefficients may be set as zero or small non-zero values to better reproduce ternary experimental data. If at a constant temperature, all three binary ' α functions' are constant, independent of composition (regular solution), all 'geometric' models are identical. In the asymmetric models, α_{12} and α_{13} are considered constant along lines with constant X_1 . This means replacing component 2 by component 3 has no influence on the energy, α_{12} , of forming of 1-2 nearest neighbor pairs, and in a similar way for 1-3 pairs. Therefore, asymmetric models are physically more reasonable if components 2 and 3 are chemically similar whereas component 1 is chemically different. For example, the Na₂O-FeO-SiO₂ and Na₂O-NaAlO₂-NaFeO₂ systems were modeled using the 'Toop-like' approximation with SiO₂ and Na₂O as asymmetric components, respectively. If g^{Ex} is very strong, and α_{12} and α_{13} are also strong functions of composition, asymmetric and symmetric

models end in very different results. Currently in FactSage, for liquid solutions (treated with the MQM) and the monoxide solid solution (treated with the random mixing model), there is freedom to choose any 'geometric' model to predict thermodynamic properties of ternary and multicomponent systems from optimized model parameters of lower order systems. However, for the CEF employed to describe Gibbs energies of most solid solutions, 'Muggianu' model is used by default.

If 'Kohler' approximation is applied to treat the 1-2 binary system, α_{12} is written as a simple polynomial function of composition:

$$\alpha_{12} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} \left(\frac{X_1}{X_1 + X_2} \right)^i \left(\frac{X_2}{X_1 + X_2} \right)^j$$
(3-34)

If 'Toop-like' approximation is chosen for the 1-2 subsystem, α_{12} is given below:

$$\alpha_{12} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} X_1^i (1 - X_1)^j$$
(3-35)

If α_{12} is estimated using 'Muggianu' model, then:

$$\alpha_{12} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} \left(\frac{1 + X_1 - X_2}{2} \right)^i \left(\frac{1 - X_1 + X_2}{2} \right)^j$$
(3-36)

For each approximation, the Redlich-Kister polynomial expression for 1-2 sub-system was provided by Pelton [22].

3.3.2. Extension to multicomponent system

Binary and ternary excess parameters are used to predict thermodynamic properties of quaternary and higher order systems based on a general and complete extension of the Kohler-Muggianu-Toop formalism to multicomponent systems which was developed by Pelton [22]. Each ternary system can be treated by 64 possible geometric models. Therefore, it is important to invent a logical way of expanding these approximations to multicomponent systems. Consider a five-component system where ternary subsystems were predicted based on the approximations depicted in Fig. 3.3. For example, the 'Toop-like' approximation was applied to model the 1-2-3 and 1-2-4 ternary subsystems with 2 (X_2 = constant) and 1 (X_1 = constant) as asymmetric components, respectively, and 1-2-5 system was treated using the 'Kohler' model, etc.

A new composition variable may be defined as following:

$$\xi_{ij} = X_i + \sum_k X_k \tag{3-37}$$

where the summation is over all components *k* of *i*-*j*-*k* ternary systems where α_{ij} is treated using a 'Toop-like' model along lines with constant *X_j*. In Fig. 3.3:

The importance of these variables is explained here. The selection of 'Toop-like' model for α_{12} in the 1-2-3 and 1-2-4 systems means the formation energy of 1-2 nearest neighbor pairs is considered constant while the component 1 is replaced by the component 3 in the 1-2-3 ternary sub-system and as the component 2 is replace by the component 4 in the 1-2-4 sub-system. Therefore, the assumption of α_{12} being constant at constant $\xi_{12} = X_1 + X_3$ and $\xi_{21} = X_2 + X_4$ when all other mole fractions (X_5 in this case) are held constant is reasonable. In a similar way, α_{13} remains constant at constant $\xi_{13} = X_1$ and $\xi_{31} = X_3 + X_4$ when X_2 and X_5 are held constant. The same approach is applied to the other α_{ij} functions.

Another function is defined for an α_{ij} function treated using 'Kohler', 'Muggianu', or 'Toop' approximation in ternary sub-systems:

$$\sigma_{ij} = \sigma_{ji} = 1 - \sum_{k} X_k \tag{3-39}$$

where the summation is over all components *k* of the *i-j-k* ternary sub-systems where α_{ij} is described using a 'Kohler' model. In the example in Fig. 3.3:

$$\begin{array}{ll}
\alpha_{12} = 1 - X_5 & \alpha_{24} = 1 - X_1 - X_5 \\
\alpha_{13} = 1 & \alpha_{25} = 1 - X_1 \\
\alpha_{14} = 1 & \alpha_{34} = 1 & (3-40) \\
\alpha_{15} = 1 - X_2 & \alpha_{35} = 1 \\
\alpha_{23} = 1 - X_4 - X_5 & \alpha_{45} = 1 - X_1 - X_3
\end{array}$$

The α_{ij} function may be then written by replacing X_1 and X_2 by the functions $\left(1 + \frac{\xi_{ij} - \xi_{ji}}{\sigma_{ij}}\right)/2$ and

$$\left(1 + \frac{\xi_{ji} - \xi_{ij}}{\sigma_{ij}}\right) / 2, \text{ respectively. For instance, for the case of } \alpha_{12}:$$

$$\alpha_{ij} = \sum_{i \ge 0} \sum_{j \ge 0} q_{12}^{ij} \left(\frac{1 + \frac{\xi_{12} - \xi_{21}}{\sigma_{12}}}{2}\right)^{i} \left(\frac{1 + \frac{\xi_{21} - \xi_{12}}{\sigma_{12}}}{2}\right)^{j}$$
(3-41)

Ternary terms

The ternary terms in Eq. (3.33) may be introduced using the function below:

$$q_{123}^{ijk}X_1^iX_2^jX_3^k \tag{3-42}$$

where $i \ge 0, j \ge 0$ and $k \ge 0$, and q_{123}^{ijk} is an empirical coefficient. The procedure provided below is applied to extend these ternary terms to higher order systems:

If a 'Kohler' or 'Muggianu' model is used to treat the α_{12} in the 1-2-3 sub-system, ternary terms may be included as follows:

$$X_{1}X_{2}\left(q_{12(3)}^{ijk}\left(\frac{1+\frac{\xi_{12}-\xi_{21}}{\sigma_{12}}}{2}\right)^{i}\left(\frac{1+\frac{\xi_{21}-\xi_{12}}{\sigma_{12}}}{2}\right)^{j}X_{3}\left(1-\xi_{12}-\xi_{21}\right)^{k-1}\right)$$
(3-43)

If a 'Toop-type' approximation is chosen to model the α_{12} in the 1-2-3 subsystem, ternary terms may be included as below:

$$X_{1}X_{2}\left(q_{12(3)}^{ijk}\left(\frac{1+\frac{\xi_{12}-\xi_{21}}{\sigma_{12}}}{2}\right)^{i}\left(\frac{1+\frac{\xi_{21}-\xi_{12}}{\sigma_{12}}}{2}\right)^{j}\frac{X_{3}}{\xi_{21}}\left(1-\frac{X_{2}}{\xi_{21}}\right)^{k-1}\right)$$
(3-44)

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Fig. 3.1: Schematic diagram for the end-members of clino-pyroxene solid solution in the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system.



Fig. 3.2: Geometric models for estimating ternary thermodynamic properties from optimized binary data (from Pelton [22]).



Fig 3.3: Five-component system presenting the geometric models chosen for all ternary subsystems (from Pelton [22]).

Chapter 4

KEY PHASE DIAGRAM EXPERIMENTS

4.1. Experimental study of the Na₂O-Fe₂O₃-Al₂O₃ phase diagram in air

4.1.1. Starting materials

Starting materials consisting of mixtures of Na₂CO₃ (99.95 wt. %), Fe₂O₃ (99.998 wt. %) and Al₂O₃ (99.99 wt. %) from Alfa Aesar (USA) were prepared in batches of 100 mg by mechanical mixing in an agate mortar filled with 2-propanol alcohol for 1 h. It is hard to find a good source for Na₂O because it is highly hygroscopic and tends to form Na₂O₂ in air [1]. That is, Na₂CO₃ is often chosen as the source of Na₂O. The powders' characteristics including the purity and particle size are provided in Table 4.1. The particle size is of importance for the homogeneity of batches and reaction kinetics as fined-grain powders have better surface areas. Extreme precautions were taken into account to obtain starting materials with target compositions and as homogenized as possible since experimental runs were performed using only a few milligrams of each batch. The reagent grade powders of Al₂O₃ and Fe₂O₃ were separately fired in a Pt crucible (height = 34 mm, upper diameter = 32 mm, and base diameter = 19 mm), cooled down in a desiccator, and stored in a drying oven at 383 K prior to synthesizing the starting materials mixtures. Ground mixtures were then decarbonated in a Pt crucible in air by firing at 1023 K for 5 to 28 h depending on the concentration of Na₂CO₃ in the mixtures, cooled down in a desiccator, and stored in a drying oven at 383 K. Compositions of starting materials are listed in Table 4.2.

4.1.1.1. Decarbonation

Required decarbonation durations were estimated in preliminary experiments using Differential Scanning Calorimetry and Differential Thermogravimetry (DSC/DTG). Before experiments, the furnace was cleaned by heating in air at 1773 K for about 4 h. All condensates and dirt was baked off. About 20 mg of starting material was placed in a Pt-Rd crucible (OD = 6.8 mm) in STA 449 F3 Jupiter instrument. The samples were heated in air from 298 to 1023 K at 10 K/min with a purge rate of 20 ml/min, and the weight loss was monitored as a function of time (Fig. 4.1). Full decarbonation was estimated from the required mass loss of the mixture, calculated prior to the DSC/DTG experiments. As an example, for sample NAF0 (see Table 4.2), decarbonation duration of about 25 h was required to lose all of CO₂ in the mixture (about 18% of sample total mass). Upon heating, the sodium carbonate underwent the reaction $Na_2CO_3 \rightarrow Na_2O + CO_2(g)$, where CO_2 was released from the sample and only $Na_2O + Fe_2O_3 + Al_2O_3$ mixture remained. In the actual starting sample preparation for main experiments, mixtures were weighed before and after decarbonation in a box furnace to further confirm the completion of the dissociation of Na₂CO₃ to $Na_2O + CO_2(g)$. Since decarbonation was performed in the solid state, all the weight loss was assumed to result from the loss of CO₂ rather than Na₂O; the evaporation of Na₂O should be less significant at this temperature which is much lower than its melting temperature 1405 K. The alkalis' loss below 1173 K could be considered very negligible [1].

4.1.2. Experimental procedure

About 20 mg of starting material was tightly packed into each Pt capsule (length = 10 mm, inner diameter = 2.873 mm, outer diameter = 3 mm), shown in Fig. 4.2. Samples contained in open Pt crucibles were brought to the target temperatures (1698 or 1583 K) with a heating rate of 10 K/min, kept at equilibrium in air for 1 h to 1 week, and quenched in liquid N₂ (water was not employed due to the hygroscopic nature of the run products). Experiments were conducted in a ST-1700C box furnace (Sentro Tech, USA; inner dimensions: 10 cm x 10 cm x 20 cm) equipped with Pt₃₀Rh-Pt₆Rh (type B) thermocouples. This type of thermocouple is commonly used to measure the temperature up to 1973 K. The samples were placed in the hot spot of the furnace as much close

as possible to the tip of thermocouple. Temperature of the furnace was checked by melting diopside $(CaMgSi_2O_6; melting point = 1664.5 \text{ K})$ in air and PID-controlled within ±1 K.

The target temperatures were selected to avoid the formation of FeAlO₃ phase stable between 1593 and 1683 K in Fe₂O₃-Al₂O₃ system in air. Preliminary experiments were performed to find equilibration times for samples in this study. The duration of equilibrium was checked for several samples by annealing the samples at the target temperatures for 1, 5, 24, 48, 72 h and 1 week. For the samples containing the single-phase liquid and 'solid + liquid' two-phase regions, the phase equilibria were obtained within 1 h. However in the sub-solidus regions, significantly longer durations were required to reach the equilibrium state depending on the composition and temperature. Unfortunately, as the present experiments were employed in open capsules to make sure that the samples were equilibrated in air, the loss of Na₂O could not be prevented for long time annealing experiments. Although overall compositions of final samples might be slightly changed from their starting compositions, the composition of each equilibrium phase at the final stage can be used for the construction of equilibrium phase diagram in this study.

As quenching medium, a cold Cu plate was used at the beginning. However, the glass microstructure at equilibrium temperature could not be retained and the phase composition analysis was not satisfactory. Using liquid N_2 , the phase composition results were reasonable although quench crystals were still observed in the solidified liquid region. It should be noted that no reaction was observed between Fe₂O₃ and Pt crucibles under the present experimental conditions.

4.1.2.1. Thermocouples calibration

Diopside (CaMgSi₂O₆) is among substances often used to calibrate thermocouples at Geophysical Laboratory. A material must melt sharply at a known temperature, be very pure, and have the melting point within the temperature range where the thermocouples are going to be used, to be suitable for the thermocouples calibration [1].

The glassy diopside was kindly donated by Dr. Pierre Hudon, from High Pressure Laboratory at McGill University. The starting material consisting of required proportions of crystalline CaO, MgO (from Baker), and ultra pure SiO₂ (from Dynasil 4000) was prepared in a batch of 5 g by mechanical mixing in an agate mortar filled with 2-propanol alcohol for 75 min. Prior to preparing the starting material, CaCO₃ (from E. M. Industries), used as the source of CaO, was decarbonated at 1273 K for 12 h. MgO was also dried at 1323 K for 2 h, and then at 1773 K for 1 h. The CaO + MgO + SiO₂ mixture was fired in a Pt crucible at 1773 K for 1 h, and then rapidly quenched in water. The glass was removed from the crucible by gently tapping it with a hammer. The glass was crushed in an agate mortar without alcohol, refused at 1773 K for 1 h, quenched and reground until a homogeneous glass was obtained. The chemical composition and homogeneity of the diopside was checked using Electron Probe Micro-Analyzer (EPMA).

In the present study, to prepare crystalline diopside, the glass was fired at 1073 K for 24 h (in a box furnace), cooled down in a desiccator, crushed under 2-propanol alcohol in an agate mortar, and then stored in a drying oven at 383 K. The X-Ray Diffraction (XRD) result showed that the sample was fully crystalline as seen in Fig. 4.3(a).

The quenching method was adopted as the calibration technique for the thermocouples. About 20 mg of crystalline diopside powder was packed inside the Pt capsule sealed using arc welding. The capsule contained the sample was placed in the hot zone of the furnace very close to the tip of the thermocouples, and the temperature was raised to 1673 K with a heating rate of 10 K /min, kept at this temperature for 1 h, and quenched in water. The sample was cast in epoxy, and the longitudinal section was polished for the optical observation and XRD phase analysis. XRD result, illustrated in Fig. 4.3(b), and optical observation revealed that diopside was fully melted at 1673 K. The equilibration temperature was lowered by 5 to 10 degree Kelvin, and the same procedure was repeated until the melting point (1664.5 K) was bracketed to ± 2 K. The B-type thermocouples were calibrated by checking on the melting point of diopside.

4.1.3. Analytical techniques

After quenching, encapsulated quenched samples were cast in epoxy and longitudinal polished

sections of the charges were made for phase identification. Due to the hygroscopic nature of the Na₂O-containing products and to minimize water absorption as much as possible, specimens were polished using lapping oil and low water content 2-propanol alcohol (H₂O < 0.02 wt. %), and quickly transferred to the EPMA for phase composition analysis. EPMA is considered as a very powerful instrument for chemical analysis of glasses and crystals. Crystalline phases with grains as small as 5 μ m may be chemically analyzed by EPMA [1]. XRD was also employed for the phase identification if required.

EPMA analyses were conducted with the JEOL 8900 probe at McGill University using wavelength-dispersive spectrometry (WDS). The samples were C-coated for a thickness of 50 nm. An accelerating voltage of 15 kV was used with a 20 nA beam current and counting times of 20 s on peaks and 10 s on backgrounds. The beam size was usually maintained in the range 5 - 15 μ m. For any beam size, the Na₂O loss was monitored during the counting times. Raw data were reduced with the ZAF correction using crystalline hematite (Fe) and albite (Na and Al) standards. All phases were analyzed in each sample and a minimum of 10 analyses were carried out on each phase.

It happened the total mass of a phase, especially the liquid, analyzed by EPMA was not within the commonly acceptable standard error range (98 – 102 wt%). This could be pertinent to the H₂O and CO₂ absorption from the atmosphere, and/or the porous nature of the phase. Interestingly if a sample was left unprotected in the atmosphere for about 20 min, the surface was fully covered by water.

Quench crystals (mainly Fe-rich oxides) exsoluting from the original liquid during quenching were often found in the solidified liquid region in most samples despite all efforts made to quench them quickly. This is most probably due to the low viscosity of Na₂O- and Fe₂O₃- rich liquid. These quench crystals, of course, were not considered stable for the phase analysis, and they were counted as part of the liquid for the phase composition analysis.

XRD patterns were obtained using the Bruker Discover D8 X-ray diffractometer (Co-K α radiation, λ =1.79 Å) equipped with HiSTAR 2D area detector at McGill University. All X-ray patterns were

identified using databases in the XPert-High Score software (2012).

4.2. Experimental study of the Na₂O-FeO-Al₂O₃ phase diagram at Fe saturation

4.2.1. Starting materials

The general procedure of the preparation of the starting materials for experiments at Fe saturation is similar to that in air. The starting powder mixtures were prepared after mixing and decarbonation of reagent grade Na₂CO₃ (99.95 wt. %), Fe₂O₃ (99.998 wt. %) and Al₂O₃ (99.99 wt. %) powders from Alfa Aesar (USA). Since FeO has a very high tendency to oxidize in air, Fe₂O₃ with a higher oxidation state was chosen as the source of FeO, and the compositions of starting materials were then adjusted. About 100 mg of Na₂O + Fe₂O₃ + Al₂O₃ mixtures were then mechanically mixed in desired proportions with Fe powder (99.9% grade from Alfa Aesar) in an agate mortar filled with 2-propanol alcohol for 1 h. The alcohol was then driven off from the starting materials in an oven at 110 °C. Compositions of the starting materials are given in Table 4.3. The amount of Fe was carefully calculated to make sure that there would be small amount of Fe even after reduction of Fe₂O₃ by the reaction Fe₂O₃ + Fe \rightarrow 3FeO.

4.2.2. Experimental procedure and analytical techniques

To minimize the absorption of water and the oxidation of Fe, starting materials were, immediately after preparation, tightly packed into low carbon Fe capsules (length = 15 mm, inner diameter = 3 mm, outer diameter = 6 mm). These Fe capsules were made from Fe tubing that was crimped at one end and arc welded under argon to avoid oxidation in air of the iron metal; the composition of low carbon Fe, analyzed by EPMA, is 99.4 wt. % Fe, 0.03 wt. % Mn, 0.01 wt. % Ni, 0.01 wt. % Cr, and 0.01 wt. % Si. Once filled with starting materials, capsules were quickly crimped to remove excess air as much as possible and sealed by arc welding under argon. The use of sealed Fe capsules is to assure that the starting materials are saturated with Fe. Experiments were performed

in a DelTech® vertical tube furnace equipped with a dense alumina tube (length = 122 cm, outer diameter = 63 mm, and inner diameter = 57 mm). Temperatures were measured using $Pt_{30}Rh$ -Pt₆Rh (type B) thermocouples and PID-controlled within ± 1 K. The argon gas at the rate of 20 ml/min was first passed through a Mg turning furnace to reduce its oxygen content from 27×10^{-5} to about 5 x 10⁻¹⁴ bar at 723 K and then passed through the vertical tube furnace to avoid oxidation of the Fe capsules during the entire experimental period. Sealed Fe capsules containing materials were wrapped in Ta foil, put in a porous alumina boat, suspended with a Mo wire, and then placed in the hot zone of the vertical tube furnace; the Ta foil was employed to prevent reaction between the Fe capsules and alumina boats. The experimental set-up for Fe-saturated samples is illustrated in Fig. 4.4. Samples were isothermally heated at 1473 K for 12 h. At this step, large amount of Fe₂O₃ can be already reduced to FeO by reacting with Fe powder. As mentioned above, extra Fe powder was added to the starting materials to guarantee Fe saturation conditions. After 12 h at 1473 K, samples were brought to the target temperatures (1673 or 1573 K) with a heating rate of 3 K/min, kept at equilibrium for 1 h, and quenched in water. The preliminary experiments showed that 1 h at the target temperature was sufficient to reach the equilibrium state because a large quantity of liquid phase of low viscosity was available.

The furnace was calibrated using the $Pt_{30}Rh-Pt_6Rh$ (type B) external thermocouples (sample thermocouples), positioned at every centimeter along the length of the alumina tube for fixed set points (1573 and 1673 K) at the hot zone. As a result, a temperature profile along the entire length of the tube inside the furnace was obtained.

Fe crucibles seemed to be the best choice under the present experimental conditions. However, experimental runs failed sometimes due to the breakage of sealed Fe capsules from the weld zone. This was mostly related to the high equilibration temperatures which were well above the sintering temperature of the Fe. The Al₂O₃ crucible could not be a suitable choice because compositions of samples would then shift toward the Al₂O₃ saturation due to the dissolution of crucible or trap of Al₂O₃ particles in the samples. The reaction between Pt and Fe under reducing atmosphere is also very significant so that all Fe could be absorbed by Pt. Therefore, Pt crucibles could not be also used.

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Powder	Purity (wt%)	Particle size (µm)
Na ₂ CO ₃	99.95	Granular
Fe ₂ O ₃	99.998	~ 1
$Al_2O_3(\alpha)$	99.99	1
Fe	99.9	< 10

Table 4.1: Characteristics of powders used in the present study (they were provided by Alfa Aesar, USA).

Table 4.2: Compositions of starting materials in the Na₂O-Fe₂O₃-Al₂O₃ system in air.

Starting	Composi	tion (mole	fraction)
material	Na ₂ O	Al_2O_3	Fe ₂ O ₃
NAF0	0.69	0.13	0.18
NAF1	0.58	0.14	0.28
NAF2	0.51	0.24	0.25
NAF3	0.45	0.25	0.30
NAF4	0.36	0.44	0.20
NAF5	0.05	0.80	0.15
NAF6	0.38	0.06	0.56
NAF7	0.15	0.53	0.32
NAF8	0.27	0.22	0.51
NAF9	0.44	0.11	0.45
NAF10	0.36	0.42	0.22
NAF11	0.25	0.39	0.36
NAF12	0.34	0.34	0.32
NAF13	0.05	0.48	0.47

Table 4.3: Compositions of starting materials in the Na₂O-FeO-Al₂O₃ system at Fe saturation.

Starting	Composition (mole fraction)			
material	Na ₂ O	Al ₂ O ₃	FeO	
NAf1	0.36	0.22	0.42	
NAf2	0.19	0.27	0.54	
NAf3	0.31	0.52	0.17	
NAf4	0.14	0.45	0.41	
NAf5	0.13	0.31	0.56	
NAf6	0.17	0.36	0.47	
NAf7	0.17	0.03	0.80	
NAf8	0.22	0.33	0.45	
NAf9	0.09	0.19	0.72	



Fig. 4.1: Total weight loss of sample NAF0 versus time in DSC/DTG experiment in air at 1023 K (heating rate = 10 K/min, purge rate = 20 ml/min).



Fig. 4.2: (a) Open Pt and (b) sealed Fe capsules, used for experiments in air and at Fe saturation, respectively.



Fig. 4.3: XRD patterns of diopside (CaMgSi₂O₆) (a) crystal and (b) glass (with the background).



Fig. 4.4: Experimental set-up for Fe-saturated samples.
Chapter 5

PAPER 1: CRITICAL EVALUATION AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃ SYSTEM

Elmira Moosavi-Khoonsari and In-Ho Jung, *Metallurgical and Materials Transactions B*, 2015 (accepted).

5.1. Abstract

A complete literature review, critical evaluation and thermodynamic optimization of experimental phase diagrams and thermodynamic properties of the Na₂O-FeO-Fe₂O₃ system were performed at 1 bar total pressure. A set of optimized model parameters obtained for all phases present in this system reproduces available and reliable thermodynamic properties and phase equilibria within experimental error limits from 298 K (25 °C) to above liquidus temperatures for all compositions and oxygen partial pressures from metallic saturation to 1 atm. The liquid phase was modeled based on the Modified Quasichemical Model by considering the possible formation of NaFeO₂ associate in the liquid state. Complicated subsolidus phase relations depending on the oxygen partial pressure and temperature were elucidated and discrepancies among experimental data were resolved.

5.2. Introduction

The Na₂O-FeO-Fe₂O₃ system is important for various industrial applications. In the blast furnace of ironmaking process, the presence of alkali metals like Na and K can result in the accretion of alkali-rich oxides which damages the blast furnace refractory and disintegration of pellets and coke during the ironmaking process [1,2]. In the cooling system of fast breeder reactors, the corrosion of steel liners happens by the oxygen contaminated sodium with the formation of Na-Fe-O type

oxides [1-6]. The recent bioactive glass ceramics contain a considerable amount of Na₂O, FeO and Fe₂O₃ with SiO₂ to control the dissolution rate under human body condition [7]. In the coal, biomass and waste combustion, the slag containing a large amount of Na₂O, FeO and Fe₂O₃ is also frequently produced [8] and can cause a serious problem for the refractory corrosion. To analyze these industrial problems, optimize the processes and eventually design new materials and processes, understanding of the Na₂O-FeO-Fe₂O₃ system is a prerequisite.

Many studies on phase equilibrium relations and thermodynamic properties of the Na₂O-FeO-Fe₂O₃ system were conducted. However, available experimental results are often inconsistent and incomplete in terms of temperature and composition. Accurately controlling the oxygen partial pressure to determine the valence of Fe oxide, the high vapor pressure of sodium and the hygroscopic nature of soda-rich components are among challenges bringing about difficulties in better understanding of this system.

So far, no complete and consistent thermodynamic assessment of the Na₂O-FeO-Fe₂O₃ system including all phase diagrams and thermodynamic properties of all phases has been performed. The only attempt was made by Renaud [9] but it was limited to parts of this system. Therefore, this study focuses on the critical thermodynamic evaluation and optimization of the Na₂O-FeO and Na₂O-Fe₂O₃ binary systems and the Na₂O-FeO-Fe₂O₃ ternary system based on all available experimental phase equilibrium and thermodynamic data. All thermodynamic calculations were performed using the FactSage thermochemical software [10]. The present thermodynamic database development project for the seven component system Na₂O-FeO-Fe₂O₃-SiO₂-Al₂O₃-CaO-MgO which can fulfill the needs of various applications in pyrometallurgy, glassmaking, cementmaking, combustion, nuclear industry and geochemistry.

5.3. Phases and thermodynamic models for the Na₂O-FeO-Fe₂O₃ system

Figure 5.1 is the schematic presentation of stoichiometric compounds and solid solutions reported

in the Na₂O-FeO-Fe₂O₃ system. There are stoichiometric Na₂O and Fe₂O₃ phases, total fifteen Na-Fe-O stoichiometric compounds (Na₃Fe₅O₉ (also known as Na₁₀Fe₁₆O₂₉), Na₄Fe₆O₁₁, NaFeO₂, Na₄Fe₂O₅, Na₁₄Fe₆O₁₆, Na₃FeO₃, Na₈Fe₂O₇, Na₃₄Fe₈O₂₉, NaFe₅O₈, Na₅FeO₄, Na₂FeO₂, Na₁₀Fe₄O₉, Na₄FeO₃, NaFe₂O₃ and Na₉Fe₂O₇), two solid solutions (FeO wüstite and Fe₃O₄ spinel) and the liquid solution in this system. Although most of the Na-Fe-O stoichiometric compounds are found on the Na₂O-Fe₂O₃ (Fe³⁺ valence oxide) and Na₂O-FeO (Fe²⁺ valence oxide) joins, two compounds Na₉Fe₂O₇ and NaFe₂O₃ have the both Fe²⁺ and Fe³⁺ oxides. Among them, only seven compounds Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, Na₈Fe₂O₇, Na₂FeO₂, Na₄FeO₃ and NaFe₂O₃ were properly considered in the present study due to the instability of the other compounds at 1 atm total pressure or lack of their thermodynamic properties and thermal stability ranges. The thermodynamic models applied to describe the solid phases and the liquid solution are summarized below.

5.3.1. Solid oxide phases

5.3.1.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{5-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{5-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(5-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given compound from pure elements at 298 K (25 °C) (ΔH_{298K}^{o} of elemental species stable at 298 K (25 °C) and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy of formation at 298 K (25 °C), and C_{p} is the

heat capacity of a compound.

The Gibbs energies of the solid and liquid Na₂O, FeO and Fe₂O₃ and Na-Fe-O stoichiometric compounds were described using these thermodynamic equations. All available Na-Fe-O compounds are listed in Table 5.1. As mentioned above, the thermodynamic properties of only seven of them were properly evaluated due to the limited thermodynamic data and phase stability information.

5.3.1.2. Wüstite solid solution

The *Wüstite* (FeO-rich monoxide) solution has a rock-salt structure. This solid solution is the extension of the binary *wüstite* solution FeO-FeO_{1.5} previously optimized by Decterov et al. [11]. It was modeled as a simple random mixing of Fe^{2+} , Fe^{3+} , and Na^+ on cation sites while all anion sites are occupied by oxygen anions. The Gibbs energy per mole of the ternary solution using the symmetric 'Kohler-like' approximation is expressed as follows:

$$G_m = \sum_i X_i G_i^o + RT \sum_i X_i \ln X_i + \sum_i \sum_j X_i X_j \left(\frac{X_i}{X_i + X_j}\right)^m \left(\frac{X_j}{X_i + X_j}\right)^n q_{ij}^{mn} + G_{ternary}^{ex}$$
(5-4)

where G_i^o is the Gibbs energy of the component like FeO, FeO_{1.5} and NaO_{0.5}, and X_i is the mole fraction of the same component, and q_{ij}^{mn} are binary regular or sub-regular model parameters between *i* and *j* species where *m* and *n* (*m*, *n* \ge 0) represent the powers of the mole fraction of *i* and *j* species, respectively. The q_{ij}^{mn} terms of the FeO-FeO_{1.5} solution were previously optimized by Decterov et al. [11]. The binary parameters q_{ij}^{mn} of the FeO-NaO_{0.5} and FeO_{1.5}-NaO_{0.5} systems were optimized in the present study, and no ternary excess parameter $G_{ternary}^{ex}$ was required.

5.3.1.3. Spinel solid solution

 Fe_3O_4 is spinel solution having two distinct cationic sites (tetrahedral and octahedral sites) for Fe^{2+} and Fe^{3+} . The cationic distribution between these sublattices is important for determining the physical and thermodynamic properties of spinel. In addition, the vacancies exist in octahedral sites to extend the spinel solution toward Fe₂O₃. The solution was described using the Compound Energy Formalism (CEF) considering the solution structure of $(Fe^{2+}, Fe^{3+})^T [Fe^{2+}, Fe^{3+}, Va]_2^O O_4$, where T and O represent tetrahedral and octahedral sites, respectively and Va represents vacancy [13]. Less than 0.05 metal fraction of Na (Na/(Na+Fe)) solubility in the spinel Fe₃O₄ was reported [1, 12]. However, this was not taken into account in the present study due to the lack of structural information how Na⁺ cations dissolve in the spinel solution. That is, the previous description of Fe₃O₄ spinel solution [13] was adopted in the current optimization without any further modification.

5.3.2. Liquid oxide phase

In the present work, the liquid oxide phase was described using the Modified Quasichemical Model (MQM) [14]. Short range ordering (SRO) in the molten oxide solution is taken into account by considering second-nearest-neighbor (SNN) pair exchange reactions of cation species in the molten oxide, and oxygen is a common anionic species. The liquid components in the MQM in the current study were NaO_{0.5}, FeO, and FeO_{1.5} because cations such as Na⁺, Fe²⁺ and Fe³⁺ were considered in the pair exchange reaction given below. In addition, the NaFeO₂ component (associate of Na₂O and Fe₂O₃) was taken into account in the liquid oxide solution as significant amounts of NaFe⁴⁺ are observed in the liquid state, especially in the Na₂O-Fe₂O₃-SiO₂ system [15]. In the SiO₂-rich compositions, Si⁴⁺ can be replaced by NaFe⁴⁺ which is known as a charge compensation effect [16] and thus, it is necessary to take into account NaFe⁴⁺ in the Na₂O-Fe₂O₃ system to develop a consistent model for the liquid phase. The same kind of species like NaAlO₂ [16] and KAlO₂ [16] were also considered in the Na₂O(K₂O)-Al₂O₃-SiO₂ system for the same reason. Therefore, the MQM considering NaO_{0.5}, FeO, FeO_{1.5} and NaFeO₂ was used to describe the molten oxide in the Na₂O-Fe₂O-Fe₂O₃ system.

In the MQM, the following quasichemical reactions in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B)$$
: Δg_{AB} (5-5)

where A and B are cationic species in the solution and (A - B) represents a second-nearestneighbour A-B pair containing an oxygen anion in-between. The Gibbs energy of the above reaction Δg_{AB} is the model parameter which can be expanded as an empirical function of composition. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{o} + n_{B}g_{B}^{o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(5-6)

where n_i and g_i^{o} are the number of moles and molar Gibbs energies of the pure components and n_{AB} is the number of moles of (A – B) bonds at equilibrium. ΔS^{config} is the configurational entropy for the random distribution of (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{config} = -R \left(n_A \ln X_A + n_B \ln X_B \right) - R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right]$$
(5-7)

 Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge I} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge I} g^{0j}_{AB} X^{j}_{BB}$$
(5-8)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature.

In the present study, cationic species (A or B in Eq. (5-5)) are Na⁺, Fe²⁺, Fe³⁺ and NaFe⁴⁺. Thus, six possible quasichemical reactions can be considered. The Gibbs energies of liquid NaO_{0.5} (1/2 Na₂O), FeO and FeO_{1.5} (1/2 Fe₂O₃) were taken from the FACT pure substance database [17]. In the MQM, the short range ordering composition of liquid solution can be determined by the coordination number (Z_{ij}) of each species. In the current study, the coordination number of Na⁺, Fe²⁺ and Fe³⁺ were taken from the previous study stored in FactSage FToxide slag database [17] to keep the consistency of the database, and that of NaFe⁴⁺ was considered as the same value as Si⁴⁺ because NaFe⁴⁺ replaces Si⁴⁺ in the silicate slags. The Gibbs energy of liquid NaFeO₂ was the model parameter in the present work. Among the six possible quasichemical reactions, only the Gibbs energies (Δg_{AB}) of Na-Fe²⁺ and Na-Fe³⁺ reactions were used in this study to describe each Na₂O-FeO and Na₂O-Fe₂O₃ binary solutions along with the previously optimized Fe²⁺-Fe³⁺ reaction for the FeO-Fe₂O₃ binary solution [11]. The rest of reactions were considered as ideal

solutions where $\Delta g_{AB} = 0$. The Gibbs energy of the Na₂O-FeO-Fe₂O₃ liquid solution (in terms of components: NaO_{0.5}, FeO, FeO_{1.5} and NaFeO₂) was calculated from binary and ternary parameters using a geometric model [18]. There are four ternary systems within the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂ solution. All ternary systems except NaO_{0.5}-FeO-FeO_{1.5} were treated using the symmetric 'Kohler' type interpolation. The NaO_{0.5}-FeO-FeO_{1.5} system was treated using the asymmetric 'Toop' type interpolation technique with NaO_{0.5} as an asymmetric component because in this ternary system, NaO_{0.5}-FeO and NaO_{0.5}-FeO_{1.5} have strong negative deviations from an ideal solution while FeO-FeO_{1.5} is close to an ideal solution. The details of the ternary geometric interpolation model can be found elsewhere [18].

5.3.3. Metallic and gas phases

In order to calculate the metallic saturation condition (Fe and Na), the metallic solid and liquid Fe and Na from FACT pure substance database [17] were considered. The mutual solubility of both Na and Fe in the solid and liquid states is nearly zero [19] thus, the pure liquid Na and Fe can be reasonably used for the metallic saturation condition. The Gibbs energies of gas species were also taken from FACT pure substance database [17].

5.4. Critical evaluation and optimization

All of the experimental data reported in the Na₂O-FeO-Fe₂O₃ system under oxygen partial pressures ranging from metallic saturation to air were critically evaluated and one set of the optimized thermodynamic model parameters were obtained to reproduce all reliable thermodynamic properties and phase diagram data within the experimental error limits. The optimized model parameters for the stoichiometric compounds and solutions are listed in Tables 5.2 and 5.3, respectively. All experimental thermodynamic properties of stoichiometric compounds are also listed in Table 5.2 for the comparison to the present optimization results. In addition, the standard enthalpies and entropies of formation at 298 K (25 °C) of stoichiometric

compounds estimated by Lindemer et al. [20] are compared in Table 5.2. Lindermer et al. [20] reviewed all available thermodynamic data of solid compounds in the Na-Fe-O system as a part of their efforts to review all alkali metal oxide systems for nuclear applications. As Fe can have both Fe^{2+} and Fe^{3+} valence states in the liquid and solids and their amounts can change with the oxygen partial pressure in the Na-Fe-O system, strictly speaking, it is impossible to find a condition having only the Na₂O-Fe₂O₃ or Na₂O-FeO sub-system. However, for the convenience, the Na-Fe-O system is described as two sub-systems Na₂O-Fe₂O₃ in air and Na₂O-FeO at metallic saturation below. In the present thermodynamic modeling, the entire Na-Fe-O system from metallic saturation to 1 atm oxygen partial pressure was optimized simultaneously to obtain a set of model parameters for all phases.

5.4.1. The Na₂O-Fe₂O₃ system in air

5.4.1.1. Phase diagram

The phase diagram of the Na₂O-Fe₂O₃ system in air calculated from the present models with optimized parameters is shown in Fig. 5.2(a), and the related invariant reactions are listed in Table 5.4 along with all available experimental data. Knick and Kohlmeyer [21] investigated the melting behavior of the system between Fe₂O₃ and NaFeO₂ using differential thermal analysis (DTA). The melting was performed in top covered Pt crucibles and three bubbles of oxygen were blown into the crucibles every second to avoid the reduction of Fe³⁺ to Fe²⁺. They did not specify the oxygen partial pressure but partial reduction of Fe₂O₃ to Fe₃O₄ was observed, which can occur at oxygen partial pressure of about 0.21 atm. Their attempt to study the Na₂O-rich part of the system failed most probably because the starting material Na₂CO₃ did not thoroughly dissociate to Na₂O and CO₂. The solubility of CO₂ in Na₂O-rich part of the phase diagram up to 1473 K (1200 °C) using equilibration and quenching method followed by XRD. According to the phase diagram determined by Knick and Kohlmeyer [21], the only stable intermediate compound is NaFeO₂. On the other hand, Thery [22] revealed that two polymorphs Na₃Fe₅O₉ and NaFeO₂ formed in the Fe oxide-rich part of the system, six compounds

Na₁₄Fe₆O₁₆, Na₄Fe₂O₅, Na₃FeO₃, Na₈Fe₂O₇, Na₃₄Fe₈O₂₉ and Na₅FeO₄ were reported. However, Na₁₄Fe₆O₁₆, Na₄Fe₂O₅ and Na₃₄Fe₈O₂₉ were not considered for the current optimization due to the lack of data. Na₅FeO₄ is not stable under 1 atm total pressure. Therefore, Na₈Fe₂O₇ and Na₃FeO₃ are the only compounds properly taken into account in the Na₂O-rich part.

As can be seen in Fig. 5.2(a), the experimental data of Knick and Kohlmeyer [21] were well reproduced in the present study. The thermal stability region and phase transition of solid stoichiometric compounds were determined based on various studies as shown in the phase diagram. The phase diagrams under the oxygen pressures of 1 and 100 atm are also shown in Fig. 5.2(b), but the difference in the phase diagrams is insignificant except the disappearance of spinel Fe₃O₄ at the Fe oxide-rich region. It should be noted that the liquidus at the Na₂O-rich region is purely prediction due to the lack of reliable experimental data.

5.4.1.2. Thermodynamic properties of stable compounds

The thermodynamic properties of all intermediate compounds are summarized in Table 5.2. The compound NaFeO₂ is the most well investigated among all solids in the entire Na₂O-FeO-Fe₂O₃ system. In this study, therefore, the thermodynamic properties of NaFeO₂ were first fixed based on the experimental data and then the Gibbs energies of other stoichiometric solid phases and the model parameters of liquid phase were optimized.

The thermodynamic data of NaFeO₂ are presented in Figs. 5.3(a-c). NaFeO₂ occurs in three polymorphs α , β and γ [22-28]. α -NaFeO₂ with the rhombohedral crystal structure is stable from the room temperature up to 870 K (597 °C), transforms to β with the orthorhombic structure stable up to 1270 K (999 °C), and β transforms to γ with the tetragonal structure. It eventually melts at 1620 K (1347 °C) [27, 28]. Later, Grey and Li [29] and Grey et al. [30] reported the formation of the 4th polymorph (δ) with the cubic crystal structure which is stable from 1498 K (1225 °C) up to the melting temperature 1620 K (1347 °C). The present thermodynamic optimization considered only three polymorphs α , β , and γ of NaFeO₂ due to the lack of thermodynamic data such as transition enthalpy from γ to δ . If δ -NaFeO₂ exists, its thermodynamic properties will be very close to those of γ -NaFeO₂.

Margrave and Grimley [31] measured the heat content of NaFeO₂ between 298 K (25 °C) and 1400 K (1127 °C) using a drop calorimeter. Christensen et al. [27] also measured the high-temperature heat content by means of a drop calorimeter and derived heat content equations as functions of temperature for three polymorphs of NaFeO₂ and liquid NaFeO₂. The both enthalpy measurements are consistent with each other as can be seen in Fig. 5.3(a). King [32] measured the low-temperature heat capacity of NaFeO₂ from 53 K (-220 °C) to 298 K (25 °C) using an adiabatic calorimeter as plotted in Fig. 5.3(b) and derived its entropy at 298 K (25 °C) (88.34 J/mol-K). The enthalpy of formation of α -NaFeO₂ at 298 K (25 °C) was measured by Koehler et al. [28] using an acid solution calorimeter. The Gibbs energy of formation of NaFeO₂ was investigated by several researchers using electromotive force (emf) measurements [2, 4, 33, 34]. However, as it is presented in Fig. 5.3(c), the emf results are quite inconsistent with each other due to unknown reasons.

In the present work, the standard entropy of formation of α-NaFeO₂ at 298 K (25 °C) was first fixed according to the study performed by King [32]. The heat capacities of all three polymorphs of NaFeO₂ were assumed to be the same because no significant difference was derived from the heat content data. In the evaluation of heat capacity, the both of the low-temperature heat capacity data obtained by King [32] and the heat content data collected by Margrave and Grimley [31] and Christensen et al. [27] were simultaneously considered. The enthalpies of transition from α to β (nearly 0 kJ/mol) and β to γ (2.177 kJ/mol) were determined based on the experimental data reported by Christensen et al. [27]. Subsequently, the Gibbs energy of NaFeO₂ was calculated from these data. The standard enthalpy of formation at 298 K (25 °C) was then determined based on the calorimetric data obtained by Koehler et al. [28] and the Gibbs energy data measured using emf (Fig. 5.3(c)). The experimental data of Koehler et al. [28] are in agreement with the emf data collected by Yamaguchi et al. [2]. However, the other emf data are inconsistent with the enthalpy of formation at 298 K (25 °C) reported by Koehler et al. [28]. Although it is hard to explain the large discrepancies between emf results, it is worthy to mention that the emf data of Yamaguchi et al. [2] for other compounds were also mostly well reproduced in the present study in comparison to other emf results. This will be discussed below. In the current optimization, the melting enthalpy of NaFeO₂ and the heat content of the melt with temperature (ie. heat capacity) were also well

reproduced as it is shown in Figs. 5.3(a) and (b), which indicates that the enthalpy of the Na_2O -Fe₂O₃ liquid was well modeled.

Na₃Fe₅O₉ was reported in two different stoichiometries [2, 22, 25, 34-38]. Thery [22], El-Shobaky et al. [25], and Zhang et al. [38] determined the chemistry as Na₁₀Fe₁₆O₂₉ while Rooymans [35], Romers et al. [36], Makukhin et al. [37], Yamaguchi et al. [2], and Kale and Srikanth [34] defined it as Na₃Fe₅O₉. Using XRD, Rooymans [35] reported that Na₃Fe₅O₉ crystallizes in the monoclinic system. This system was later confirmed by Romers et al. [36] and the space group was also established as C2/c. There are also inconsistencies in the temperature stability range of Na₃Fe₅O₉ compound in the literature. In the current study, the temperature stability range was fixed according to the phase diagram measured by Thery [22]. The lower limit of temperature measured by Thery [22] is very close to the latest work performed by Kale and Srikanth [34] (They did not specify the upper temperature limit of the stability).

The Gibbs energy of formation of Na₃Fe₅O₉ from its constituent oxides was studied using emf measurements [2, 34,38], illustrated in Fig. 5.4. Makukhin et al. [37] also investigated the Gibbs energy of formation of Na₃Fe₅O₉ from β-NaFeO₂ and Fe₂O₃ with the aid of emf measurements in the temperature range between 1223 K (950 °C) and 1373 K (1100 °C). However, the Gibbs energies of formation of $Na_3Fe_5O_9$ determined based on the emf data are quite inconsistent with each other. The results of Zhang et al. [38] and Kale and Srikanth [34] are similar but largely different from the data of Yamaguchi et al. [2]. As Zhang et al. [38] considered the Na₁₀Fe₁₆O₂₉ stoichiometry, their Gibbs energy value was simply divided by three to obtain the Gibbs energy of Na₃Fe₅O₉ in the present assessment. In the current study, the heat capacity of Na₃Fe₅O₉ was first determined from the sum of the heat capacities of 1.5 Na₂O and 2.5 Fe₂O₃ and then ΔH_{298K}^{o} and S_{298K}^{o} were defined to reproduce its thermal stability region in Fig. 5.2. It should be mentioned that the experimental heat capacity of NaFeO₂ was very close to the sum of the heat capacities of 0.5 mol Na₂O and 0.5 mol Fe₂O₃. This indicates that the heat capacity estimation of a compound from the heat capacities of its constituent oxides is reasonable. The optimized Gibbs energy is very close to the results collected by Yamaguchi et al. [2] as can be seen in Fig. 5.4. It is impossible to reproduce the temperature dependency of the emf data obtained by Kale and Srikanth [34] and Zhang et al. [38] together with the phase diagram.

Using XRD, Brachtel and Hoppe [39] reported that Na₈Fe₂O₇ belongs to the monoclinic P_21/c space group. Stuve et al. [40] determined the low-temperature heat capacity of Na₈Fe₂O₇ at the temperature range between 6 K (-267 °C) and 310 K (37 °C) using an adiabatic calorimeter. They also measured ΔH_{298K}^o of this compound from its constituent oxides using an acid solution calorimeter, and also heat content from 298 K (25 °C) to 1200 K (927 °C) using a drop calorimeter. Based on these data, they computed ΔH_{298K}^o , S_{298K}^o and the standard Gibbs energy of formation of this compound. In the present work, S_{298K}^o of Na₈Fe₂O₇ (437.96 J/mol-K) was taken from Stuve et al. [40]. The low- and high-temperature heat capacities of Na₈Fe₂O₇ measured by Stuve et al. [40], illustrated in Fig. 5.5, were considered simultaneously to obtain a proper heat capacity function at high temperatures. When ΔH_{298K}^o reported by Stuve et al. [40] was used without any modification, this compound was stable in the Na₂O-FeO system at metallic saturation, which is inconsistent with the phase diagram data. Therefore, ΔH_{298K}^o of Na₈Fe₂O₇ was adjusted to make sure it does not form at the Fe saturation condition but appears in the phase diagram in air.

The formation of Na₃FeO₃ was reported by different researchers [41-46] and its crystal structure was determined by means of XRD [45, 46]. The low-temperature polymorph (α) belongs to the monoclinic *P2*₁/*n* space group [45] and the high-temperature polymorph (β) crystallizes in the monoclinic *I*a space group [46]. Using DTA/TG, Sofin and Jansen [46] reported this compound decomposed at about 1023 K (750 °C). Huang et al. [43] performed high-temperature mass spectroscopy experiments regarding the reaction below:

$$Na_4 FeO_3 = Na_3 FeO_3 + Na (g)$$
(5-18)

where Na₄FeO₃ is stable on the Na₂O-FeO join at metallic saturation. Based on the vapor pressure of Na(g) and previously reported Gibbs energy data of Na₄FeO₃, they derived the Gibbs energy of Na₃FeO₃. Lindemer et al. [20] estimated the enthalpy of formation of Na₃FeO₃ at 298 K (25 °C). In the present study, the Gibbs energy of Na₃FeO₃ was determined based on the experimental data of Huang et al. [43] and the Gibbs energy of Na₄FeO₃ which will be discussed in 5.4.2. Fig. 5.6 shows the vapor pressure of Na in equilibrium with Na₄FeO₃ and Na₃FeO₃ together. In the current optimization, the heat capacity of Na₃FeO₃ was first estimated from the sum of heat capacities of its constituent oxides (1.5 mol Na₂O and 0.5 mol Fe₂O₃). The ΔH_{298K}^o and S_{298K}^o of the compound were then adjusted to reproduce the experimental data. In particular, S_{298K}^o of Na₃FeO₃ was modified from 165.56 J/mol-K (the sum of entropies of its constituent oxides) to 133.43 J/mol-K to reproduce the experimental data. As it is observed in the Na₂O-Fe₂O₃ phase diagram in air (Fig. 5.2(a)), the decomposition of Na₃FeO₃ occurs at about 1050 K (777 °C) which is well consistent with the DTA/TG results of Sofin and Jansen [46]. The present optimization results are compared with the data of Lindemer et al. [20] in Table 5.2. It should be noted that Na₃FeO₃ is also stable below 763 K (490 °C) in the Na₂O-FeO system at Fe saturation. This will be discussed in the section 5.4.2.

5.4.1.3. Thermodynamic properties of other compounds

There are five other compounds on the Na₂O-Fe₂O₃ join. There are lack of thermodynamic and phase diagram data for these compounds. Therefore, it was difficult to accurately evaluate their Gibbs energies. In the present study, their thermodynamic data were roughly estimated assuming that they are unstable under oxygen partial pressure up to 1 atm. Due to insufficient experimental data, the heat capacity of each compound was estimated from the sum of the heat capacities of stoichiometric amounts of Na₂O and Fe₂O₃. The same approach was taken for S_{298K}^o . ΔH_{298K}^o was then tuned to determine the temperature stability range of each phase. That is, to make sure these phases are unstable at 1 atm oxygen partial pressure, ΔH_{298K}^o of each unstable phase was adjusted to be 1 kJ/mol more positive than ΔH_{298K}^o making the phase just appear in the Na₂O-Fe₂O₃ phase diagram at 1 atm oxygen partial pressure. The detailed experimental data available for each compound are discussed below.

Brachtel and Hoppe [47] reported that Na₅FeO₄ has the orthorhombic crystal structure with the space group *Pbca*. Furukawa et al. [5] and Huang et al. [44] both reported that this compound formed even at low oxygen pressures. However, neither equilibrium thermal stability region nor thermodynamic properties were experimentally measured for Na₅FeO₄.

Collongues and Thery [24], Hua et al. [48] and Huang et al. [49] reported the formation of $Na_4Fe_6O_{11}$ but its crystal structure remains undetermined. Huang et al. [49] studied the equilibrium vapor pressure over the mixture 2Na₂CO₃ + 3Fe₂O₃ using the Knudsen Effusion Mass Spectrometry (KEMS) in the temperature range from 913 K (640 °C) to 1023 K (750 °C) and determined ΔH_{298K}^o of Na₄Fe₆O₁₁. They implied that this solid phase would be stable at high temperatures (> 1270 K (997 °C)) and decompose to other oxides such as Na₃Fe₅O₉ and NaFeO₂ at low temperatures. However, the exact thermal stability of the compound was not determined. The existence of this phase above 1270 K (997 °C) is inconsistent with the experimental results by Zhang et al. [38], El-Shobaky et al. [25] and Yamaguchi et al. [2], illustrated in Fig. 5.2(a). Therefore, in the present study, it was assumed that this phase is unstable at oxygen partial pressures up to 1 atm. Na₄Fe₂O₅ and Na₁₄Fe₆O₁₆ compounds were synthesized and their crystal structures were determined by Brachtel and Hoppe [50-52] using XRD. The former belongs to the monoclinic $P2_1/n$ space group, and the latter crystallizes in the triclinic $P1^-$ space group. Neither thermodynamic properties nor temperature stability regions were experimentally measured for these compounds. Tschudy [41] and Lykasov and Pavlovskaya [12] reported the formation of Na₃₄Fe₈O₂₉ (which stoichiometry is very close to Na₈Fe₂O₇) and NaFe₅O₈, respectively. However, no experimental data are available about their crystal structures, thermodynamic properties and temperature stability regions. Therefore, the compounds Na₃₄Fe₈O₂₉, Na₁₄Fe₆O₁₆, Na₄Fe₂O₅ and NaFe₅O₈ were ruled out from the current evaluation.

5.4.2. The Na₂O-FeO system at metallic saturation

5.4.2.1. Phase diagram

The optimized Na₂O-FeO phase diagram at metallic saturation is presented in Fig. 5.7 along with experimental data [1, 3, 4, 12, 43]. When mole fraction of Na₂O is less than about 0.75, the system is saturated with Fe. For Na₂O concentrations higher than 0.75, the system can be saturated with metallic Na if Na evaporation is suppressed. The mutual solubility between liquid Fe and Na is very limited. The most comprehensive phase diagram study was done by Dai et al. [1, 33]. They investigated the liquidus and solidus of the entire Na₂O-FeO system at Fe saturation using DTA.

The oxide mixtures were contained in sealed Pt capsules in DTA experiments and the products were analyzed using XRD. They also performed quenching experiments using sealed Pt capsules and Fe capsules followed by XRD. The melting temperatures of stoichiometric compounds were determined using a heating microscope. The solid NaFeO₂ compound containing ferric oxide (Fe³⁺) was even stable in the Na-Fe-O system at Fe saturation due to its high stability (negative Gibbs energy). Two other compounds, Na₂FeO₂ and Na₄FeO₃, were also found. The Na₂FeO₂ phase melted congruently at 1086 K (813 °C) and the other two solids NaFeO₂ and Na₄FeO₃ were found to melt peritectically at 1230 K (957 °C) and 915 K (642 °C), respectively. Moreover, they observed a considerable solubility of Na₂O in the wüstite solid solution against NaFeO₂ compound using the both DTA and emf measurements; the maximum solubility of Na₂O in the wüstite was reported to be about 14 mol % at 1248 K (975 °C). They also mentioned that the liquid in this system supercooled easily which caused large scatters in the experimental results.

Although Dai et al. [1] did not report the formation of NaFe₂O₃ phase, the existence of this compound between the wüstite solid solution and NaFeO₂ under Fe saturation was reported by many researchers [12, 53-55]. Using the equilibration and quenching method, Claude et al. [53] determined the maximum solubility of Na₂O in the wüstite in equilibrium with Fe under the oxygen pressure of 1.2×10^{-15} atm to be 10.5 mol % at 1273 K (1000 °C). More recently, Lykasov and Pavlovskaya [12] also measured the Na₂O solubility in the wüstite in reduced oxygen partial pressures using emf data. Subsequently, they estimated the maximum solubility of Na₂O in the wüstite solution as 8.8 and 8.9 mol % at 1070 K (797 °C) and 1270 K (997 °C), respectively, but these data were not exactly at Fe saturation condition.

The calculated invariant points of the Na₂O-FeO system at metallic saturation are compared with the experimental data of Dai et al. [1] in Table 5.5. According to the optimized Na₂O-FeO phase diagram at metallic saturation, illustrated in Fig. 5.7, five intermediate compounds are stable in this system: (a) NaFe₂O₃ with Fe²⁺ and Fe³⁺, (b) NaFeO₂ and Na₃FeO₃ with Fe³⁺ and (c) Na₂FeO₂ and Na₄FeO₃ with Fe²⁺. Among them, the Gibbs energy of NaFeO₂ was well investigated as discussed in the section 5.4.1.2. The Gibbs energies of other four compounds were also relatively well investigated and will be discussed below. Therefore, in the present thermodynamic modeling, Gibbs energies of all these solid compounds were first determined based on the experimental data and then, the model parameters of the Na₂O-FeO liquid solution were defined to reproduce the

phase diagram data by Dai et al. [1] presented in Fig. 5.7. There is no experimental study confirming the formation of Na₃FeO₃ phase below 763 K (490 °C) at Fe saturation. However, based on the experimental data in Fig. 5.6, the stability of Na₃FeO₃ against Na₄FeO₃ in equilibrium with Fe can be calculated and this results in the formation of Na₃FeO₃ in the Na₂O-FeO system at Fe saturation, illustrated in Fig. 5.7. It should be noted that the Na₃FeO₃ phase appears at the same position as Na₂FeO₂ in the Na₂O-FeO phase diagram in Fig. 5.7.

The model parameters of the wüstite solution were also determined to reproduce the experimental phase relations corresponding to the wüstite solution and shown in Fig. 5.8. Lykasov and Pavlovskaya [12] investigated the reduction of Fe₃O₄ and Na₂O mixtures with the variation of oxygen partial pressures recorded by an emf cell at the temperature range between 1070 K (797 °C) and 1270 K (997 °C). They characterized equilibrium phase assemblages of some quenched samples using XRD, and found several phase equilibrium regions. They also reported a certain amount of Na₂O solubility in the Fe₃O₄ spinel (maximum ~ 5 mol % Na₂O). The solution behavior of Na₂O in the spinel is not well known thus, this was not considered in the present study. The phase stability near the wüstite region was also investigated by Claude et al. [53] and Balkhi et al. [54, 55]. In both of the cases, the equilibrium partial pressure of oxygen was fixed to be 1.2×10^{-10} ¹⁵ atm at 1273 K (1000 °C). The oxygen partial pressure they used in their experiments was controlled by the Fe and wüstite (Fe_{0.97}O with no Na₂O) equilibration. Therefore, the partial pressure of oxygen in their experiments [53-55] was in fact higher than that over the assemblage of Fe and wüstite solid solution containing Na₂O; the activity of FeO decreases with increasing Na₂O and consequently the oxygen partial pressure over 'Fe + wüstite solution (containing Na₂O)' should be lower than that over 'Fe + wüstite solution (with no Na₂O)'.

Therefore, the experimental data of Claude et al. [53] and Balkhi et al. [54, 55] are not really at Fe saturation condition but at the oxygen partial pressure slightly higher than Fe saturation condition. It should be also noted that NaFeO₂ used as a starting material in the experiments by Claude et al. [53] and Balkhi et al. [54, 55] (these two studies were from the same laboratory) was not pure. Since NaFeO₂ was synthesized in Al₂O₃ crucibles, it contained a certain amount of Al₂O₃ impurity to form Na(Fe,Al)O₂. The present modeling results are in good agreement with the experimental data with the exception of the Na₂O solubility in the spinel solution. The compositions where the phase assemblages were not determined by Claude et al. [53] and Balkhi et al. [54, 55] correspond

to the phase regions containing NaFe₂O₃ or NaFeO₂. It should be mentioned that the phase diagram in Fig. 5.7 at metallic Fe saturation region relates to the phase boundary lines of Fe in Fig. 5.8. As mentioned earlier, the solubility of Na₂O in the wüstite solution at Fe saturation is about 0.25 Na metal fraction (Na/Na+Fe) (about 14 mol % Na₂O) at 1273 K (1000 °C). Although NaFe₂O₃ is unstable at 1273 K (1000 °C) at Fe saturation, this can be stable at higher oxygen partial pressures as it is presented in Fig. 5.8.

5.4.2.2. Thermodynamic properties of stable compounds

Using XRD, Balkhi et al. [54, 55] determined that NaFe₂O₃ occurs in two polymorphs depending on the partial pressure of oxygen: (a) α -NaFe₂O₃ with the space group *R3m* (*R32*) of the rhombohedral system was synthesized at a reduced oxygen partial pressure condition and (b) β -NaFe₂O₃ was synthesized at a less reduced oxygen partial pressure condition and belongs to the hexagonal *P321* (*P3m1*, *R3m1*) space group. They also reported that this phase is relatively unstable at the room temperature and easily hydrolyses [54]. Later, Lykasov and Pavlovskaya [12] reported that this compound is stable in the Na-Fe-O system at reduced oxygen conditions. With the aid of emf measurements, they measured the oxygen partial pressures over three phase equilibria, 'spinel + wüstite (containing Na₂O) + NaFe₂O₃' and 'spinel + NaFeO₂ + NaFe₂O₃ can be determined from these oxygen partial pressure data. As shown in Fig. 5.9, both oxygen partial pressures were reasonably reproduced in the present calculations. If the solubility of Na₂O in the spinel solution is properly considered, the agreement will be better.

Wu [3] and Shaiu [4] reported the existence of Na₂FeO₂ with the aid of XRD. However, its crystal structure remains undetermined. Lindemer et al. [20] estimated the ΔH_{298K}^o and S_{298K}^o of this compound based on the equilibrium reaction $2Na_4FeO_3 + Fe = 3Na_2FeO_2 + 2Na(g)$ reported by Horsley [56]. Dai et al. [33] measured ΔH_{298K}^o of Na₂FeO₂ using acid solution calorimetry and subsequently estimated its Gibbs energy of formation with temperature. The accuracy of acid solution calorimetry data obtained by Dai et al. [33] will be discussed below for Na₄FeO₃ compound as well. Fig. 5.10 depicts the calculated Gibbs energy of formation of Na₂FeO₂ from its

constituent elements along with experimental data by Shaiu [4] and Wu [3]. The slopes of the reported Gibbs energy data dependent on the entropy of Na₂FeO₂ are largely inconsistent with each other. In the current study, ΔH_{298K}^o and S_{298K}^o of Na₂FeO₂ were determined from the Gibbs energy data in Fig. 5.10 after the estimation of its C_P from the heat capacities of Na₂O and FeO. As can be seen in Table 5.2, ΔH_{298K}^o fixed in the present optimization is -755.4 kJ/mol, which is significantly different from the experimental value, -802.9 kJ/mol, measured by Dai et al. [1]. The experimental data obtained by Dai et al. [1] cannot be consistent with the emf results in Fig. 5.10. The accuracy of Dai et al. [1] data is questionable and will be also discussed for Na₄FeO₃ below. The present results are consistent with the results of Shaiu [4]. It should be noted that Wu [3] himself also pointed out the entropy value (the slope in Fig. 5.10) derived from his emf results is unrealistic.

The existence of Na₄FeO₃ was reported by many researchers [1, 3, 4, 41, 43, 56-61]. The structure of this compound was determined to be monoclinic Cc space group by Rieck and Hoppe [60]. Its ΔH_{298K}^o was originally measured by Gross and Wilson [57] using an acid solution calorimeter. Later, Tyzack [62] and Dai et al. [33] also utilized the same technique to obtain the enthalpy of formation of this compound at 298 K (25 °C). As can be seen in Table 5.2, the two sets of data reported by Gross and Wilson [57] and Tyzack [62] are about 44 kJ/mol more positive than that collected by Dai et al. [33]. The standard Gibbs energy of formation of Na₄FeO₃ from its constituent elements was investigated by Wu [3] and Bhat and Borgstedt [61] using emf data in the temperature range 660 K-823 K (387 °C-550 °C) and 723 K-873 K (450 °C-600 °C), respectively. Sridharan et al. [6] investigated the equilibrium oxygen partial pressure over the three-phase region 'Na(1)+Na₄FeO₃+Fe' and derived the Gibbs energy of formation of Na₄FeO₃. All experimental Gibbs energy data for Na₄FeO₃ are plotted in Fig. 5.11. Although there are some scatters among the experimental data, they are generally consistent with each other in terms of the absolute value. The data reported by Wu [3] have a less steeper slope with temperature than the others similar to the case of Na₂FeO₂. In the present study, the thermodynamic properties of Na₄FeO₃ were determined based on these data in Fig. 5.11 and the enthalpy of formation at 298 K (25 °C) measured using acid calorimetry. It was found that ΔH_{298K}^o of Na₄FeO₃ from Gross and Wilson [57] and Tyzack [62] are much consistent with the emf data than the data from Dai et al.

[33]. As mentioned earlier, this is also the reason; we suspect the accuracy of ΔH_{298K}^o measured for Na₂FeO₂ by Dai et al. [33].

5.4.2.3. Thermodynamic properties of other compounds

Amann [63] reported the existence of $Na_{10}Fe_4O_9$ phase having the hexagonal structure with the space group *R3m*. There are neither phase equilibrium relations nor thermodynamic data available for this compound in the literature. Therefore, this solid phase was ruled out from the current thermodynamic optimization.

5.4.3. The Na₂O-FeO-Fe₂O₃ system

The optimized liquid projection of the Na₂O-FeO-Fe₂O₃ system is shown in Fig. 5.12, and the related invariant reactions are listed in Table 5.6. The calculated isopleths of the Fe₃O₄-NaFeO₂ and FeO-NaFeO₂ systems are presented in Figure 5.13. Dai et al. [1] performed DTA on starting mixtures of Na₂O, FeO, and Fe₂O₃ contained in sealed Pt capsules. They also carried out equilibration and quenching experiments using sealed Pt capsules, followed by XRD. However, no specific experimental results were reported in their paper. As seen in Figures 5.12 and 5.13, the liquidus temperatures and the primary phase regions from Dai et al. [1] were reasonably reproduced considering experimental difficulties including supercooling and evaporization of materials.

In the Fe₃O₄-NaFeO₂ section (Fig. 5.13(a)), Dai et al. [1] determined a eutectic point at about 86 mol% NaFeO₂ at 1419 K (1146 °C) and the probable existence of wüstite phase just below the primary crystallization field of spinel phase. However, Dai et al. [1] presented the existence of wüstite phase with reservation. In the current study, the eutectic reaction of Liquid \rightarrow spinel + NaFeO₂ is calculated at 79 mol % NaFeO₂ at 1389 K (1116 °C), which is somewhat lower than the experimental results of Dai et al. [1]. This is partially due to the ignorance of the Na₂O solubility in the spinel solution (0.02 ~ 0.05 Na metal fraction (Na/Na+Fe)) [1, 12]. The existence

of wüstite phase with the liquid cannot be calculated in this optimization. Even in the schematic liquidus projection of the Na-Fe-O system provided by Dai et al. [1], the primary crystallization region of wüstite phase is far from the Fe₃O₄-NaFeO₂ join. Therefore, it is hard to believe the presence of wüstite just below the crystallization field of spinel solution on this join.

In the FeO-NaFeO₂ section (Fig. 5.13(b)), Dai et al. [1] determined a eutectic point at about 61.3 mol% NaFeO₂ at a temperature around 1389 K (1116 °C) whereas the calculated eutectic point occurs around 58 mol% NaFeO₂ at about 1323 K (1050 °C). They could not also observe the formation of the NaFe₂O₃ compound while based on the literature data explained above, this compound is stable in the Na₂O-FeO-Fe₂O₃ system.

5.4.4. Fe³⁺/Fe²⁺ ratio in molten oxides

Ban-Ya et al. [65] studied the variation of Fe³⁺/Fe²⁺ in the Na₂O-FeO-Fe₂O₃ liquid up to about 30 mol % Na₂O under CO₂ atmosphere at 1883 K (1610 °C). The analyses of Fe²⁺, Fe_{tot} and Na₂O concentrations in the quenched liquid were performed using wet chemical analysis. According to the experimental data, the Fe³⁺/Fe²⁺ ratio increases with increasing Na₂O content in the Na₂O-FeO-Fe₂O₃ liquid. As it is illustrated in Fig. 5.14, the calculated results from the present study can reasonably reproduce the experimental data. However, the present modeling predicts the maximum of Fe³⁺/Fe²⁺ at about 25 mol % Na₂O in the melt. As in the current thermodynamic modeling, three different species, FeO, Fe₂O₃ and NaFeO₂, were considered in the liquid phase, the number of moles of Fe₁O, n_{Fe_1O} , and Na₂O, n_{Na_2O} , in the melt were calculated from the number of moles of these modeling species: $n_{Fe_1O} = n_{FeO} + 3n_{Fe_2O_3} + 3/2n_{NaFeO_2}$ and $n_{Na_2O} = n_{Na_2O} + 1/2n_{NaFeO_2}$. Ban-Ya et al. [65] reported similar maximum trends in the Na₂O-FeO-Fe₂O₃-SiO₂ system. The predicted Fe³⁺/Fe²⁺ ratios in the Na₂O-FeO-Fe₂O₃ melt at 1883 K (1610 °C) for partial pressures of oxygen equal to 1.0 and 1.0E-6 atm are also presented in Fig. 5.14. The noticeable peak of Fe³⁺ is clear in air, but the Fe³⁺ amount naturally decreases with decreasing the oxygen partial pressure.

5.4.5. Prediction of phase equilibria and thermodynamic properties

Based on the present thermodynamic modeling, the phase diagrams (predominance diagrams) of the Na-Fe-O system with the variations of oxygen and Na partial pressures were calculated at 1073 K (800 °C) and 1273 K (1000 °C) and the results are presented in Figs. 5.15(a) and (b), respectively. This type of diagrams can be important to understand the condensed phases from the gas phase containing Na under various oxygen partial pressures. It is easily observed that NaFeO₂ phase has a wide stability region from metallic saturation to above 1 atm oxygen partial pressure. Of course, the liquid phase is stable at high Na(g) pressure. The ternary phase diagrams of the Na-Fe-O system at 1 atm total pressure at 1073 K (800 °C) and 1273 K (1000 °C) are also depicted in Figs. 5.16(a) and (b), respectively.

No thermodynamic properties of the Na₂O-FeO-Fe₂O₃ liquid were investigated. According to the present modeling results, it is possible to calculate any thermodynamic property of the liquid. In Figs. 5.17(a) and 5.18(a), the predicted mixing Gibbs energy and enthalpy of the Na₂O-FeO-Fe₂O₃ melt at 1773 K (1500 °C) at metallic saturation and in air are illustrated, respectively. Both liquid solutions, Na₂O-FeO at metallic saturation and Na₂O-Fe₂O₃ in air, show a strong negative deviation from the ideal solution. In particular, the enthalpy of mixing in air reaches at least -100 kJ/mol. It should be noted that the calculation result is very accurate as it is observed in Fig. 5.3 showing the melting enthalpy of NaFeO₂ phase in air. In comparison to the mixing enthalpy of the CaO-SiO₂ melt which is about -50 kJ/mol at the orthosilicate composition and 1873 K (1600 °C), the mixing enthalpy of the Na₂O-FeO-Fe₂O₃ melt is considered very negative. The activities of Na₂O and FeO in the Na₂O-FeO liquid solution calculated at metallic saturation are also shown in Fig. 5.17(b).

In general, interactions between binary network modifier components in the molten state, for example, between alkali oxides (Na₂O, K₂O and Li₂O) and alkali earth oxides (CaO, MgO, BaO and SrO), are small and therefore, the solution behaves like an ideal solution. However, there are rather unexpected strong negative interactions in the Na₂O-FeO and Na₂O-Fe₂O₃ liquid solutions. The formation of several congruently melting stoichiometric phases in these systems also supports the strong negative interactions in the liquid state. Although there is lack of information, the K₂O-

FeO and K₂O–Fe₂O₃ solutions and Li₂O-FeO and Li₂O-Fe₂O₃ solutions would have interaction energies similar to those of Na₂O-FeO and Na₂O-Fe₂O₃ solutions.

The amounts of different liquid species in the Na₂O-Fe₂O₃ melt calculated at metallic saturation and in air are presented in Figs. 5.17(c) and 5.18(b), respectively. Although the thermodynamic properties such as the melting enthalpy of NaFeO₂ (Fig. 5.3(a)) and Fe³⁺ amount in the Na₂O-Fe₂O₃ melt (Fig. 5.14) were well reproduced, no direct experimental data are available to quantify the amount of NaFeO₂ associate in the molten oxide. The calculated amount of NaFeO₂ associate in the liquid in air is about 35 mol% at 50 mol % Na₂O composition, and it of course decreases with increasing temperature. The strong negative interaction in the Na₂O-Fe₂O₃ liquid solution shows the tendency to form a large amount of NaFeO₂ associate in the molten state. The mixing enthalpy of the Na₂O-Fe₂O₃ liquid at 50 mol% Na₂O composition is about -110 kJ/mol at 1773 K (1500 °C) as it is illustrated in Fig. 5.18(a). The expandability of the present modeling results for the NaFeO₂ associate in the melt has been already examined in the higher order system Na₂O-Fe₂O₃-SiO₂-Al₂O₃-CaO, and it should be mentioned that the current modeling can well describe the higher order liquid solution.

5.5. Summary

A critical evaluation and optimization of thermodynamic properties and phase equilibrium data of the Na₂O-FeO-Fe₂O₃ system at 1 bar total pressure were performed. Discrepancies among experimental results were resolved and a coherent database including a set of optimized model parameters was obtained. The thermodynamic models with resultant database allow, using the FactSage computational software, to calculate any phase diagram section of the Na₂O-FeO-Fe₂O₃ system for all oxygen partial pressures, compositions and temperatures. Many unexplored thermodynamic properties of the Na₂O-FeO-Fe₂O₃ liquid solution and phase diagrams were predicted from the present thermodynamic modeling results. The current thermodynamic properties and the phase diagram information can be useful to understand industrial processes involving the Na₂O-FeO-Fe₂O₃ system.

Although the optimization of all the thermodynamic properties of solids and liquid solution was performed reasonably well in comparison to the available experimental data, there are still certain limitations in terms of modeling and experimental data: (i) no proper treatment of the Na₂O solubility in the spinel solution, (ii) limited experimental phase diagram data at high Na₂O regions, (iii) lack of experimental investigation to quantify the amount of NaFeO₂ associate in the molten oxide, and (iv) limited thermodynamic data for many stoichiometric solids. These should be further investigated in future to understand the Na-Fe-O system, completely.

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Phase		Crystal system	Space group	Technique	Reference
Na5FeO4		ND*	ND	XRD	[41]
		Orthorhombic	Pbca	XRD	[47]
Na ₃₄ Fe ₈ O ₂₉		ND	ND	XRD	[41]
Na ₈ Fe ₂ O ₇		ND	ND	XRD	[40]
		Monoclinic	$P_2 l/c$	XRD	[39]
		ND	ND	XRD	[41-43, 50, 51]
Na ₃ FeO ₃	α	Monoclinic	$P2_1/n$	XRD	[45]
	β	Monoclinic	I a	XRD	[46]
Na14Fe6O16		Triclinic	P1-	XRD	[52]
Na ₄ Fe ₂ O ₅		Monoclinic	$P2_1/n$	XRD	[50, 51]
	a	Rhombohedral	ND	XRD	[22-24]
	u	ND	ND	DTA	[1]
		Orthorhombic	ND	XRD	[22-25]
	β	Orthorhombic	$Pna2_1$		[26]
NaFeO ₂		ND	ND	DTA	[1]
		Tetragonal	ND	XRD	[22]
	γ	Tetragonal	P41212		[26]
		ND	ND	DTA	[1]
	δ	Cubic	ND	XRD	[29, 30]
Na4Fe6O11		ND	ND	XRD	[24, 48]
NatoFatcOas		Tetragonal	ND	XRD	[22]
1Na10F e16O29		ND	ND	XRD	[25, 38]
		Monoclinic	ND	XRD	[35]
Na ₃ Fe ₅ O ₉		Monoclinic	C2/c	XRD	[36]
		ND	ND	EMF	[2]
NacEeOc		ND	ND	XRD	[3, 4]
Na21 CO2		ND	ND	DTA	[1]
Na ₁₀ Fe ₄ O ₉		Hexagonal	R3m	XRD	[63, 64]
		ND	ND	XRD	[3, 4, 41, 56-59]
N. F.O		Monoclinic	Сс	XRD	[60]
Na ₄ FeO ₃		ND	ND	DTA	[1]
		ND	ND	EMF	[61]
		ND	ND	XRD	[53]
		ND	ND	EMF	[12]
NaFe ₂ O ₃	α	Rhombohedral	R3m, R32	XRD	[54, 55]
	β	Hexagonal	P321, P3m1 R3m1	XRD	[54, 55]
Na9Fe2O7		Hexagonal	R3m	XRD	[63, 64]
NaFe5O8		ND	ND	EMF	[12]

Table 5.1: Crystal structures of stoichiometric compounds in the Na_2O -FeO-Fe $_2O_3$ system.

* ND: Not determined

Phase		⊿Н°298 К	S ^o 298 K	C_p	Technique ^{a)}	Reference
		(kJ/mol)	(J/mol-K)	(J/mol-K)		
Na ₂ O	α	-417.982	75.061	66.216+0.0438651T -813370.0184T ⁻² -1.40875003856E-5T ² (298 K (25 °C) – 1405 K (1132 °C))		[17]
	β	-416.225	76.779	104.6 (1405 K (1132 °C) – 1500 K (1227 °C))		[17]
	γ	-404.300	86.372			[17]
Fe ₂ O ₃		-825.787	87.728	137.00893-2907640T ⁻²		[17]
FeO		-265.832	59.496	-18.0244740968+0.0306080599496T-2533299.99432T ⁻² +1500.90000264T ^{-0.5} (298 K (25 °C) - 1644		[17]
				K (1371 °C))		
				68.1992 (1644 K (1371 °C) – 2000 K (1727 °C))		
Na ₃ Fe ₅ O ₉		-2890	346		Est	[20]
		-2899.491	375.360	$1.5 C_p (Na_2O) + 2.5 C_p (Fe_2O_3)$		This work
Na ₄ Fe ₆ O ₁	1	-3665	442		Est	[20]
		-3569.54 ± 3.95			KEMS	[49]
		-3559.339	490.549	$2 C_p (Na_2O) + 3 C_p (Fe_2O_3)$		This work
Na ₈ Fe ₂ O ₇		-2745.54 ± 4.18			SC	[40]
			437.96		AC	[40]
		-2710.378	437.964	392.78204057729+0.0808869 <i>T</i> -3552627.12022383 <i>T</i> ⁻² +1.497672E-5 <i>T</i> ²		This work
		-1155	172		Est	[20]
Na ₃ FeO ₃		-1162.6			MS	[43]
				181.7+0.03339 <i>T</i> -2967000 <i>T</i> ⁻²	Sum of oxides	[43]
		-1175.871	133.434	$1.5 C_p (Na_2O) + 0.5 C_p (Fe_2O_3)$		This work
Na ₅ FeO ₄		-1596	246.3		Est	[20]
		-1450.246	240.620	$2.5 C_p (\text{Na}_2\text{O}) + 0.5 C_p (\text{Fe}_2\text{O}_3)$		This work
NaFeO ₂			88.34 ± 0.84		AC	[32]
		-698.02 ± 1.30			SC	[28]
	α	-697.350	88.341	$110.95 \pm 0.00769337 \pm 25522007^{-2}$		This work
		Phase transformat	ions $\alpha \rightarrow \beta$:	$^{1}H_{tr} = 41.84 \text{ J/mol at } 870 \text{ K} (597 ^{\circ}\text{C}), \beta \rightarrow \gamma: \Delta H_{tr} = 2177 \text{ J/mol at } 1270 \text{ K} (997 ^{\circ}\text{C})$		
Na ₂ FeO ₂		-802.92 ± 3.73 b)	· ·		SC	[33]
1 (421 002		-780	136		Est.	[20]
		-755 435	134	$1 C_{p}(Na_{2}O) + 1 C_{p}(FeO)$		This work
NaFerOr		-968.000	1/0 00/	$0.5 C_{\rm e} (N_{20}O) + 0.5 C_{\rm e} (Ee_{\rm e}O_{\rm e}) + 1 C_{\rm e} (Ee_{\rm e}O)$		This work
Na ₄ EeO ₂		$-120670 \pm 23^{\text{b}}$	147.774	0.5 Cp (1Va2O) + 0.5 Cp (1C2O3) + 1 Cp (1CO)	SC	[57]
1 1041 003		1200.70 - 2.5	203		Fet	[20]
		-1205 56 ^{b)}	205		SC	[62]
		-1205.50 ×			SC	[32]
		-1249.76	212 625	$2C(N_{20}O) + 1C(F_{20}O)$	50	[JJ] This work
		-1203.000	212.023	$2 C_p (\operatorname{INa}_2O) + 1 C_p (\operatorname{ICO})$		THIS WOLK

Table 5.2: Thermodynamic properties of stoichiometric compounds present in the Na₂O-FeO-Fe₂O₃ system.

^{a)} KEMS: Knudsen Effusion Mass Spectrometry; MS: Mass Spectrometry; SC: Solution Calorimetry; DC: Drop Calorimetry; AC: Adiabatic Calorimetry; Est; estimation.

^{b)} Original enthalpy of formation value was given from constituent oxides Na₂O and FeO, and it is converted to elemental species base in this study.

Liquid soluti	ion (NaO _{0.5} -FeO-FeO _{1.5} -Na	aFeO ₂)
$Z_{Na Na}^{Na} = 0.68$	$Z_{Fe(II)}^{Fe(II)} = 1.2$	37744375 , $Z_{Fe(III)}^{Fe(III)} = 2.06616563$, $Z_{NaFe}^{NaFe} = 2.75488750$
$G_{NaO_{0.5}} = 1/2$	G _{Na2O}	
G _{Na2} O	298 – 1405 K (25 - 1132 °C)	$H_{298\ K} = -356602.750952, S_{298\ K} = 120.320451152, C_{P} = 66.216000736 + 0.043865102024T - 813370.10208T^{-2} - 1.4087498712E - 5T^{2}$
	1405 – 9999 K (1132 - 9726 °C)	$H_{298K} = -372790.914728, S_{298K} = 91.72246388, C_P = 104.6$
G_{FeO}	· · · · · · · · · · · · · · · · · · ·	
	298 – 1644 K (25 – 1371 °C)	$H_{_{298\ K}} = -234136.87012, S_{_{298\ K}} = 78.465514272, C_{_P} = -18.0244749336 + 0.0306080612048T - 2533299.99432T^{-2} + 1500.89966792T^{-0.5}$
	1644 – 9999 K (1371 – 9726 °C)	$H_{298\ K} = -247254.835616, S_{298\ K} = 58.4820022560, C_P = 68.199212552$
$G_{FeO_{1.5}} = 1/2G_{F}$	$\overline{r}e_2O_3$	
$G_{Fe_2O_3}$		$H_{_{298\ K}} = -805257.07504, \ S_{_{298\ K}} = 873.77363144, \\ C_P = -8760452.505600 E6T^{-2} - 146.8578519 E - 6T^2 - 146.8578519 - 146.8578519 E - 6T^2 - 146.8578519 E - 6T^2 - $
$G_{NaFeO_2} = 1/2$	$2G_{Na,O} + 1/2G_{Fe,O_3} - 99371.2$	2552+16.91756468T
$\Delta g_{Na-Fe(II)} = (-$	-158992 + 33.472T) - 96232X	$\frac{1}{NaNa} - 87864X_{Fe(II)Fe(II)}^{1} - 125520X_{NaNa}^{2} + (211764.792 - 74.596536T)X_{Fe(II)Fe(II)}^{2}$
$\Delta g_{Na-Fe(III)} = (-$	-271960 + 47.005428T) - 1253	$52X_{Fe(III)Fe(III)}^{1}$
$^{*}\Delta g_{Fe(II)-Fe(III)}$	$=-18823.816X_{Fe(III)Fe(III)}^{1}-9$	$878.424X_{Fe(II)Fe(II)}^{2}$
$q_{Na,Fe(II),Fe(III)}^{011} =$	= 83680	
$q_{Fe(II), NaFe, Na}^{001} =$	-62760	
Wüstite solut	tion (FeO-FeO _{1.5} -NaO _{0.5})	
G_{FeO}	H	$\overline{I_{298K}} = -265238.11112, S_{298K}} = 59.495798, C_{P} = -18.0244749336 + 0.0306080612048T - 2533299.99432T^{-2} + 1500.89966792T^{-0.5}$

Table 5.3: Optimized model parameters of solutions in the Na₂O-FeO-Fe₂O₃ system (J/mol and J/mol-K).

 $G_{FeO_{1.5}} = 1/2G_{Fe_2O_3}$

$G_{Fe_2O_3}$		$H_{_{298K}} = -769123.08872, S_{_{298K}} = 97.33910732, C_{_P} = 146.8584 - 5576782.0536T^{-2} + 525627886.72T^{-3}$			
$G_{\scriptscriptstyle Na_2O}$	298 - 1405 K (25 - 1132 °C)	$H_{_{298K}} = -397062.001664, S_{_{298K}} = 75.060997656, C_{_P} = 66.216000736 + 0.043865102T - 813370.0184T^{-2} - 1.4087498712E - 5T^{-2}$			
	1405 – 1500 K (1132 – 1227 °C)	$H_{298K} = -413250, S_{298K} = 46.46302$ $C_P = 104.6$			
$\Delta g_{FeO-NaO_{0.5}} = -690$	$\Delta g_{FeO-NaO_{0.5}} = -69036 + (-35762.74 + 29.0193872T)X_{FeO}^2$				
$\Delta g_{FeO_{1,5}-NaO_{0,5}} = -62760 - 96232X^{1}_{NaO_{0,5}}$					
* $\Delta g_{FeO-FeO_{15}} = -(8275.952 + 11.572944T) - 49145.264X_{FeO_{15}}^{1}$					

			Composition (mol %)			
1 [K(()]	Reaction	Na ₂ O		- Deference	
Exp.	Calc.		Exp.	Calc.	Kelerence	
1408 (1135) ± 24	1400 (1127)	$L = Fe_2O_3 + NaFeO_2(\gamma)$	36	36.0	[21]	
1373 (1100)	1369 (1096)	$Fe_2O_3 + NaFeO_2(\gamma) = Na_3Fe_5O_9$	38.5	37.5	[22]	
1033 (760)	1038 (765)	$Na_3Fe_5O_9 = Fe_2O_3 + NaFeO_2(\beta)$	38.5	37.5	[22]	
1620 (1347)	1620 (1347)	$L = NaFeO_2(\gamma)$	50.0	50.0	[27, 28]	
-	1492 (1219)	$L = NaFeO_2(\gamma) + Na_8Fe_2O_7$	-	63.5		
~1023 (750)	1052 (779)	$NaFeO_2(\beta) + Na_8Fe_2O_7 = Na_3FeO_3$	75.0	75.0	[46]	
-	644 (371)	$Na_8Fe_2O_7 = Na_3FeO_3 + Na_2O(\alpha)$	80.0	80.0		
-	1530 (1257)	$L = Na_8Fe_2O_7$	-	80.0		
-	1306 (1033)	$L = Na_8Fe_2O_7 + Na_2O(\gamma)$	-	95.6		

Table 5.4: Calculated invariant reactions of the Na_2O -Fe₂O₃ system in air.

T [K (°C)]			Composition (mol %)		
		Reaction	Na ₂ O		
Exp.	Calc.		Exp.	Calc.	
1253 (980) ± 20	1230 (957)	$L + w \ddot{u}stite = NaFeO_2(\beta)$	25.00	25.00	
-	1210 (937)	wüstite + NaFeO ₂ (β) = NaFe ₂ O ₃	-	16.67	
-	761 (488)	wüstite = spinel + $NaFe_2O_3$	-	4.34	
-	474 (201)	$NaFe_2O_3 = spinel + NaFeO_2(\alpha)$	-	16.67	
1031 (758) ± 20	1051 (778)	$L = Na_2FeO_2 + NaFeO_2(\beta)$	42.5	44.31	
1086 (813)	1086 (813)	$L = Na_2 FeO_2$	50.0	50.0	
-	763 (490)	$Na_2FeO_2 = Na_3FeO_3 + Fe$	-	50.0	
904 (631) ± 8	915 (642)	$L+Na_2FeO_2 = Na_4FeO_3$	66.7	66.67	
869 (596) ± 15	898 (625)	$L = Na_4FeO_3 + Na_2O(\alpha)$	75.4	74.22	

Table 5.5: Calculated invariant reactions of the Na₂O-FeO system at metallic saturation in comparison to the experimental data by Dai et al. [1].

Table 5.6: Calculated invariant reactions involving the liquid phase of the Na₂O-FeO-Fe₂O₃ system.

T [V (%C)]	Dhassa in amilikuinn mith limid	Comp	Composition (mol %)			
I [K(C)]	Phases in equilibrium with liquid	Na ₂ O	Fe ₂ O ₃	FeO		
1374 (1101)	spinel + Fe_2O_3 + $NaFeO_2(\gamma)$	32.9	57.3	9.7		
1309 (1036)	spinel + wüstite + NaFeO ₂ (γ)	26.6	33.2	40.2		
1270 (997)	$Na_8Fe_2O_7 + NaFeO_2(\gamma) + NaFeO_2(\beta)$	61.9	5.5	33.0		
1270 (997)	$NaFe_2O_3 + NaFeO_2(\gamma) + NaFeO_2(\beta)$	32.3	16.4	51.3		
1252 (979)	wüstite + NaFeO ₂ (β) + NaFe ₂ O ₃	32.0	14.0	54.0		
1243 (970)	$Na_8Fe_2O_7 + Na_2O(\beta) + Na_2O(\gamma)$	89.3	0.1	10.5		
1230 (957)	wüstite + NaFeO ₂ (β) + Fe(fcc)	33.8	12.8	53.4		
1185 (912)	$NaFeO_2(\beta) + Fe(bcc) + Fe(fcc)$	40.6	6.8	52.5		
1070 (797)	$Na_8Fe_2O_7 + Na_2FeO_2 + NaFeO_2(\beta)$	51.8	29.0	45.3		
1051 (778)	$Na_2FeO_2 + NaFeO_2(\beta) + Fe(bcc)$	46.7	2.7	50.6		
914 (641)	$Na_8Fe_2O_7 + Na_2FeO_2 + Na_4FeO_3$	69.7	0.0	30.2		



Fig. 5.1: Schematic presentation of solid phases reported in the Na₂O-FeO-Fe₂O₃ system. Those compounds shown in the parentheses are either unstable under 1 atm oxygen pressure or unknown (lack of thermodynamic and phase stability data).



Fig. 5.2: Calculated optimized phase diagram of the Na₂O-Fe₂O₃ system (a) oxygen partial pressure of 0.21 (in air) and (b) oxygen total pressures of 1 and 100 atm.







Fig. 5.3: Calculated (a) heat content, (b) heat capacity, and (c) standard Gibbs energy of formation of NaFeO₂ from Fe₂O₃ and Na₂O.



Fig. 5.4: Calculated standard Gibbs energy of formation of Na₃Fe₅O₉ from Fe₂O₃ and Na₂O.


Fig. 5.5: Calculated (a) heat content and (b) heat capacity of $Na_8Fe_2O_7$. High temperature C_p was proposed from heat content data measured by drop calorimetry.



Fig. 5.6: Vapor pressure of Na in equilibrium with Na₄FeO₃ and Na₃FeO₃.



Fig. 5.7: Calculated optimized phase diagram of the Na₂O-FeO system at metallic saturation.



Fig. 5.8: Calculated phase diagram near wüstite stability region at 1273 K (1000 °C). Wus, Spl, N₃F₅, NF, NF₂ and L are the abbreviations for wüstite, spinel, Na₃Fe₅O₉, NaFeO₂, NaFe₂O₃ and liquid phase, respectively.



Fig. 5.9: Calculated oxygen partial pressure versus temperature over the spinel + wüstite + NaFe₂O₃ and spinel + NaFeO₂ + NaFe₂O₃ three-phase equilibrium regions.



Fig. 5.10: Calculated standard Gibbs energy of formation of Na₂FeO₂ from its constituent elements.



Fig. 5.11: Calculated standard Gibbs energy of formation of Na₄FeO₃ from its constituent elements.



Fig. 5.12: Calculated optimized liquid projections of the Na-Fe-O system.



(a)



(b) Fig. 5.13: Calculated optimized (a) Fe₃O₄-NaFeO₂ and (b) FeO-NaFeO₂ isopleths.



Fig. 5.14: Calculated Fe^{3+}/Fe^{2+} ratio at different partial pressures of oxygen (1.0, 3.7E-3 and 1.0E-6 atm) at 1883 K (1610 °C) in the Na₂O-FeO-Fe₂O₃ liquid.



Fig. 5.15: Calculated predominance diagrams of the Na-Fe-O system at (a) 1073 K (800 °C) and (b) 1273 K (1000 °C).



Fig. 5.16: Calculated ternary phase diagrams of the Na-Fe-O system at (a) 1073 K (1000 °C) and (b) 1273 K (1200 °C). A: Na₂O (β), A': Na₂O(γ), B: Na₈Fe₂O₇, C: NaFeO₂(β), C': NaFeO₂(γ), D: Na₃Fe₅O₉, E: Fe₂O₃, F: NaFe₂O₃, G: Na₂FeO₂, and Wus: Wüstite.



(b)



Fig. 5.17: Calculated thermodynamic properties of liquid Na₂O-FeO at metallic saturation at 1773 K (1500 °C) in liquid standard state. (a) Enthalpy and Gibbs energy of mixing, (b) activities of FeO(l) and Na₂O(l) and (c) distribution of model species in liquid solution.



Fig. 5.18: Calculated thermodynamic properties of liquid Na₂O-Fe₂O₃ in air at 1773 K (1500 °C) in liquid standard state. (a) Enthalpy of mixing and (b) distribution of model species in liquid solution.

Chapter 6 PAPER 2: CRITICAL EVALUATION AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃-SiO₂ SYSTEM

Elmira Moosavi-Khoonsari and In-Ho Jung, *Metallurgical and Materials Transactions B*, 2015 (accepted).

6.1. Abstract

A complete literature review, critical evaluation and thermodynamic optimization of phase diagrams and thermodynamic properties of the Na₂O-FeO-Fe₂O₃-SiO₂ system were performed at 1 atm total pressure. A set of optimized model parameters obtained for all phases present in this system reproduces available and reliable thermodynamic properties and phase equilibria within experimental error limits from 298 K (25 °C) to above liquidus temperatures for all compositions and oxygen partial pressures from metallic Fe saturation to 1 atm. The liquid phase was modeled based on the Modified Quasichemical Model considering the possible formation of NaFeO₂ associate in the liquid state. The NaFeO₂ metaoxide solid solutions containing the excess SiO₂ were described within the framework of Compound Energy Formalism. Based on the thermodynamic models and model parameters, unexplored thermodynamic properties and phase diagrams of the Na₂O-FeO-Fe₂O₃-SiO₂ system were predicted.

6.2. Introduction

The Na₂O-based flux Na₂O-FeO-Fe₂O₃-SiO₂ was studied for the desulfurization (de-S)^[1-4] and dephosphorization (de-P) [1-3] of hot metal and liquid steel. The Na₂O-FeO-Fe₂O₃-SiO₂ system is also one of the fundamental oxide systems for the coal-combustion slag [3, 5, 6], bio-glasses [7-9], and geological Fe-bearing silicate rocks. Many investigations were performed to determine

phase equilibrium relations and thermodynamic properties of the Na₂O-FeO-Fe₂O₃-SiO₂ system [1-4, 10-26]. However, available experimental results are inconsistent and incomplete in terms of temperature and composition. Accurately controlling the oxygen partial pressure to define the valence of Fe oxide in solid and liquid states, the high vapor pressure of sodium and the hygroscopic nature of Na₂O-rich components make experimental studies of this system very challenging.

The purpose of the present study was to critically evaluate and optimize thermodynamic properties and phase diagrams of the Na₂O-FeO-Fe₂O₃-SiO₂ system. The optimization of this system was not attempted, previously. In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for the Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the evaluation of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be backcalculated. In this way, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from low order to high order systems can be applied to industrial processes.

Critical thermodynamic optimizations of the Na₂O-SiO₂ [27], FeO-Fe₂O₃ [28], FeO-SiO₂ and Fe₂O₃-SiO₂ [29] systems were already performed and stored in the FactSage FACT oxide (FToxid) database. Thermodynamic optimizations of the Na₂O-FeO, Na₂O-Fe₂O₃ and Na₂O-FeO-Fe₂O₃ systems were also conducted by the present authors [30]. In this study, the evaluation/optimization of the Na₂O-FeO-Fe₂O₃-SiO₂ system was carried out based on the previously optimized model parameters. This work is part of a wide database development project for the multi-component system Na₂O-FeO-Fe₂O₃-SiO₂-Al₂O₃-CaO-MgO, which plays a key role in many applications in ironmaking, steelmaking, glassmaking, cement production, combustion and geology.

6.3. Equilibrium phases and thermodynamic models

Figure 1 shows the main solid phases in the Na₂O-FeO-Fe₂O₃-SiO₂ system at 1 atm. The following solution phases exist in this system:

i) Liquid phase: NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-SiO₂, considering NaFeO₂ associate in the molten state,

ii) High-temperature metaoxide solid solution: $(Na^+, Va)[Fe^{3+}, Si^{4+}]O_2$, high-temperature γ -NaFeO₂ phase with the excess solubility of SiO₂,

iii) Intermediate-temperature metaoxide solid solution: $(NaFe^{4+}, VaSi^{4+})O_2$, intermediate-temperature β -NaFeO₂ phase with the excess solubility of SiO₂,

iv) Spinel solid solution: $(Fe^{2+}, Fe^{3+})[Fe^{2+}, Fe^{3+}, Va]_2O_4$, magnetite Fe_3O_4 phase with the excess solubility of γ -Fe₂O₃,

v) Wüstite solid solution: FeO-FeO_{1.5}-NaO_{0.5}, wüstite FeO solid solution with limited solubilities of Fe³⁺ and Na⁺.

Cations shown within a set of brackets for the metaoxide and spinel solutions occupy the same sublattice, and Va represents vacancy. There are also many stoichiometric phases.

6.3.1. Solid oxide phases

6.3.1.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{6-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{6-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(6-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given compound from pure elements at 298 K (25 °C) (ΔH_{298K}^{o} of elemental species stable at 298 K (25 °C) and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy of formation at 298 K (25 °C), and C_p is the heat capacity of a compound.

There are six binary stoichiometric compounds in the Na₂O-SiO₂ system: Na₁₀SiO₇, Na₄SiO₄, Na₆Si₂O₇, Na₂SiO₃, Na₂Si₂O₅ and Na₆Si₈O₁₉. In the FeO-Fe₂O₃-SiO₂ system, there is only a binary stoichiometric compound, Fe₂SiO₄ (fayalite). In the Na₂O-FeO-Fe₂O₃ system, six binary compounds, Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, Na₈Fe₂O₇, Na₂FeO₂ and Na₄FeO₃, and one ternary stoichiometric phase, NaFe₂O₃, are considered at 1 atm total pressure. In addition, four ternary stoichiometric compounds, Na₂FeSiO₄, Na₈Fe₆Si₁₅O₄₀, NaFeSi₂O₆ and Na₅FeSi₄O₁₂, are taken into account in the Na₂O-FeO-Fe₂O₃-SiO₂ system. All these stoichiometric compounds are illustrated in Fig. 6.1. There are several other stoichiometric phases reported in the Na₂O-FeO-Fe₂O₃ and Na₂O-FeO-Fe₂O₃-SiO₂ systems, but due to the lack of experimental data regarding their stability ranges and thermodynamic properties, they were not considered in the previous optimization [30] and the present study.

6.3.1.2. Solid solutions

Four solid solutions including FeO wüstite, Fe₃O₄ spinel, high- and intermediate-temperature NaFeO₂ metaoxides exist in the Na₂O-FeO-Fe₂O₃-SiO₂ system. Previous descriptions of Fe₃O₄ spinel [31] and FeO wüstite [30] solid solutions were taken in the current study without any further modification. In this work, the NaFeO₂ metaoxide solid solutions were newly modeled.

Grey et al. [11] investigated crystal structures of the β - and γ' -NaFeO₂ solid solutions using XRD Rietveld refinement to understand the dissolution behavior of the excess SiO₂ in these solutions. They revealed that in the intermediate-temperature β -NaFeO₂ solid solution, oxygen ions configure in the hexagonal close-packed structure and all tetrahedra in the crystal are the same size. Silicon replaces Fe and this is charge-compensated by the loss of Na from a proximate tetrahedron. That is, Si replaces the NaFe pair. The high-temperature γ' -NaFeO₂ solid solution has a collapsed high cristobalite structure. In the present study, this solution was considered as part of the high temperature γ -NaFeO₂ solution, which will be discussed below. In the γ' -NaFeO₂ solution, Si replaces Fe in the tetrahedral framework, which is charge-balanced by taking away Na from the cavity framework. Since no structural data are available for the dissolution of SiO₂ in the γ -NaFeO₂ is similar to that in γ' -NaFeO₂. Grey et al. [11] originally suggested two slightly different Na sites (Na1 and Na2) and two different M sites for Fe (M1 and M2) in the γ' -NaFeO₂ solid solution. However, as there are rare site preference data for Si between M1 and M2 and Va between Na1 and Na2, the most logical approach was to consider one type of M sites and one type of Na sites. Based on this structural information, two different structures were proposed for the β - and γ -NaFeO₂ solutions. It should be noted that the following pair exchange reaction was taken into account for both of solutions;

$$Fe^{3+} + Na^+ = Si^{4+} + Va$$
 (6-4)

however, the cationic ordering is different in the solutions. That is, Fe^{3+} and neighboring Na⁺ are replaced by Si⁴⁺ and Va in the β -NaFeO₂ solution, while such a neighbor pair restriction is not applied to the γ -NaFeO₂ solution, and a more random replacement of cationic pairs is observed.

The high-temperature γ -NaFeO₂ metaoxide solid solution was structurally formulated as $(Na^+,Va)^{Na}[Fe^{3+},Si^{4+}]^MO_2$ where Va forms on the Na sublattice with the replacement of Fe³⁺ by Si⁴⁺ in the M site. The Gibbs energy of the solution is described using the Compound Energy Formalism (CEF) [32]. The Gibbs energy of the high-temperature γ -NaFeO₂ metaoxide solid solution per mole of formula can be written as:

$$G^{m} = \sum_{i} \sum_{j} y_{i}^{Na} y_{j}^{M} G_{ij} - TS_{c} + G^{E}$$
(6-5)

where y_i^{Na} and y_j^M represent the site fractions of constituents *i* and *j* on the *Na* and *M* sublattices, *G_{ij}* is the Gibbs energy of an end-member (i)^{Na}[j]^M O₂ in which *Na* and *M* sites are occupied only by *i* and *j* cations, respectively, S_c is the configurational entropy assuming random mixing on each sublattice,

$$S_{c} = -R \left(\sum_{i} y_{i}^{Na} \ln y_{i}^{Na} + \sum_{j} y_{j}^{M} \ln y_{j}^{M} \right)$$
(6-6)

and G^E is the excess Gibbs energy,

$$G^{E} = \sum_{i} \sum_{j} \sum_{k} y_{i}^{Na} y_{j}^{Na} y_{k}^{M} L_{ij;k} + \sum_{i} \sum_{j} \sum_{k} y_{k}^{Na} y_{i}^{M} y_{j}^{M} L_{K;ij}$$
(6-7)

where $L_{ij;k}$ and $L_{k;ij}$ are the interaction energies between cations *i* and *j* on one sublattice when the other sublattice is occupied only by *k* cations.

To model the high-temperature γ -NaFeO₂ metaoxide solid solution, the Gibbs energies of four end-members, which are the primary model parameters, were defined first. G_{NaFe} is equal to the Gibbs energy of pure stoichiometric γ -NaFeO₂. G_{VaSi} is the Gibbs energy of imaginary γ -VaSiO₂, which was determined as $G_{VaSi} = G_{SiO_2}^o(high - temperature cristobalite) + G^{add}$, where $G^{add} > 0$. Once the Gibbs energy of one of charged end-members, G_{NaSi} , was defined, the Gibbs energy of the other charged end-member, G_{VaFe} , was fixed by assuming the reciprocal Gibbs energy of the solution is zero: $\Delta = G_{NaFe} + G_{VaSi} - G_{NaSi} - G_{VaFe} = 0$. In the present optimization, in addition to the end-member Gibb energies, excess interaction parameters were also required to reproduce the excess solubility of SiO₂ in the high-temperature γ -NaFeO₂ metaoxide solution.

The intermediate-temperature β -NaFeO₂ metaoxide solid solution was structurally formulated as (NaFe⁴⁺,VaSi⁴⁺)O₂ according to the crystal structure determined by Grey et al. [11]. The Gibbs energy of this solution was also treated based on the CEF but with one sublattice model. The Gibbs energies of two end-members were determined: G_{NaFe} is the Gibbs energy of pure stoichiometric β -NaFeO₂, and G_{VaSi} is the Gibbs energy of imaginary β -VaSiO₂ which was defined in a similar way to the Gibbs energy of γ -VaSiO₂, explained above. In this study, excess interaction parameters were also added to describe the solubility of SiO₂ in the β -NaFeO₂ phase.

In the present work, the α -NaFeO₂ phase was modeled as a pure stoichiometric compound since the solubility of SiO₂ in this polymorph was reported to be very negligible (about 1 mol %) [10].

It should be also noted that the γ' -NaFeO₂ structure is not stable at the stoichiometric NaFeO₂ composition, and the existence of δ -NaFeO₂, stable over a very narrow temperature range (less than 70 degree in Kelvin), above the γ -NaFeO₂ polymorph is still debatable [30]. Therefore, for the sake of simplicity, the γ' - and δ -NaFeO₂ solutions were treated as the extension of the γ -NaFeO₂ solid solution.

6.3.2. Liquid oxide phase

In this study, the liquid oxide phase was described using the Modified Quasichemical Model (MQM) [33]. Short range ordering (SRO) in the liquid oxide solution is taken into account by considering second-nearest-neighbor (SNN) pair exchange reactions of cationic species in the liquid oxide phase, and oxygen is a common anionic species. Therefore, the liquid components in the MQM in the present study were NaO_{0.5}, FeO, FeO_{1.5} and SiO₂ because cations like Na⁺, Fe²⁺, Fe³⁺ and Si⁴⁺ were considered in the pair exchange reaction given below. In addition, the NaFeO₂ component (associate of Na₂O and Fe₂O₃) was taken into account in the liquid solution since significant amounts of NaFe⁴⁺ were observed in the liquid state, especially in the Na₂O-Fe₂O₃-SiO₂ melts by Mysen et al. [34] using Mössbauer spectroscopy and Raman spectroscopy. Mysen et al. reported that Fe³⁺ configures in the tetrahedral framework as the NaFeO₂ complex, similar to the NaAlO₂ complex in the Na₂O-Al₂O₃-SiO₂ melts. They also reported that the structure of the Na₂SiO₃-NaFeSi₂O₆ melt becomes very similar to that of Na₂SiO₃-SiO₂ with increasing the degree of polymerization toward the NaFeSi₂O₆ corner, which supports the formation of NaFeO₂ associate in this melt. In summary, Si⁴⁺ forming the tetrahedral structure in silicate melts is replaced by NaFe⁴⁺, which is known as a charge compensation effect [35]. Therefore, it is necessary to take into account NaFe⁴⁺ in the Na₂O-Fe₂O₃-SiO₂ liquid solution. The same kind of species, NaAlO₂ and KAIO₂ [35], were also considered in the Na₂O(K₂O)-Al₂O₃-SiO₂ melts for the same reason. Hence, the MQM with NaO_{0.5}, FeO, FeO_{1.5}, SiO₂ and NaFeO₂ species was used to describe the Na₂O-FeO-Fe₂O₃-SiO₂ liquid solution.

In the MQM, the following quasichemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B);$$
 Δg_{AB} (6-8)

where A and B are cationic species in the solution and (A - B) represents a SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{o} + n_{B}g_{B}^{o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(6-9)

where n_i and g_i^{o} are the number of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{config} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{config} = -R \left(n_A \ln X_A + n_B \ln X_B \right) - R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right]$$
(6-10)

 Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge I} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge I} g^{0j}_{AB} X^{j}_{BB}$$
(6-11)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature.

In the present study, cationic species (A or B in Eq. (6-8)) are Na⁺, Fe²⁺, Fe³⁺, Si⁴⁺ and NaFe⁴⁺. Therefore, ten possible quasichemical reactions were considered. The Gibbs energies of the liquid NaO_{0.5} (1/2 Na₂O), FeO, FeO_{1.5} (1/2 Fe₂O₃) and SiO₂ were taken from the FACT pure substance database [36]. The Gibbs energy of liquid NaFeO₂ was the model parameter, previously determined in the optimization of the Na₂O-Fe₂O₃ system [30]. To keep the consistency of the database, the coordination numbers of all species were kept the same as those in the previous studies [29, 30]. Among the ten possible binary quasichemical reactions, the Gibbs energy parameters (Δg_{AB}) of the Na⁺-Si⁴⁺ [37], Fe²⁺-Fe³⁺ [28], Fe²⁺-Si⁴⁺ [29], Fe³⁺-Si⁴⁺ [29], Na⁺-Fe²⁺ [30] and Na⁺-Fe³⁺ [30] reactions for the Na₂O-SiO₂, FeO-Fe₂O₃, FeO-SiO₂, Fe₂O₃-SiO₂, Na₂O-FeO and Na₂O-Fe₂O₃ solutions, respectively, were taken from the previous optimizations without any modification. The Gibbs energy of the NaFe⁴⁺-Si⁴⁺ reaction was optimized in this study to

describe the NaFeO₂-SiO₂ pseudobinary solution. The rest of binary solutions were considered as ideal solutions where $\Delta g_{AB} = 0$.

There are ten ternary solutions within the NaO_{0.5}-FeO-FeO_{1.5}-SiO₂-NaFeO₂ system. The Gibbs energies of ternary solutions were first predicted from binary model parameters using a specific geometric model and if it was necessary, ternary model parameters were added to improve Gibbs energy descriptions of ternary solutions. The Gibbs energies of quaternary and higher order systems were then predicted without any additional model parameter. The Gibbs energy descriptions of the NaO_{0.5}-FeO₋FeO_{1.5}-NaFeO₂ and FeO₋FeO_{1.5}-SiO₂ solutions were taken from the previous optimizations performed by the present authors [30] and Jak et al. [29], respectively. In the current study, several ternary model parameters were newly added into three solutions, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO_{1.5}-SiO₂ and NaO_{0.5}-NaFeO₂-SiO₂, for a more accurate optimization of the NaO_{0.5}-FeO-FeO_{1.5}-SiO₂-NaFeO₂ system. No additional parameters were required in the other two ternary solutions, FeO-SiO₂-NaFeO₂ and FeO_{1.5}-SiO₂-NaFeO₂. Regarding geometric interpolation techniques for ternary systems, the NaO_{0.5}-FeO-FeO_{1.5} system was treated using 'Toop-type' model with Na₂O as the 'asymmetric component' [30]. The ternary systems FeO-FeO_{1.5}-SiO₂ [29], NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO_{1.5}-SiO₂, NaO_{0.5}-NaFeO₂-SiO₂, FeO-NaFeO₂-SiO₂ and FeO_{1.5}-NaFeO₂-SiO₂ were treated using 'Toop-type' approximation with SiO₂ as the 'asymmetric component'. The rest of ternary systems were treated using the symmetric 'Kohlertype' model. Details of ternary geometric models can be found elsewhere [38].

6.3.3. Metallic and gas phases

To calculate the metallic saturation condition, solid and liquid Fe from FACT pure substance database [36] were considered. The Gibbs energies of gas species were taken from FACT pure substance database [36].

6.4. Critical evaluation and optimization

In the present thermodynamic modeling, all experimental data reported in the Na₂O-FeO-Fe₂O₃-SiO₂ system under oxygen partial pressures ranging from metallic saturation to air were simultaneously and critically assessed. One set of optimized thermodynamic model parameters were then obtained for all phases to reproduce reliable phase diagram and thermodynamic property data within the experimental error limits. The optimized model parameters of stoichiometric compounds and solutions are listed in Tables 6.1 and 6.2, respectively. As Fe can have both Fe²⁺ and Fe³⁺ valence states in the liquid and solids, and Fe²⁺ and Fe³⁺ amounts change with the oxygen partial pressure in the Na-Fe-Si-O system, strictly speaking, it is impossible to find a condition having only Na₂O-Fe₂O₃-SiO₂ or Na₂O-FeO-SiO₂ subsystem. However, for the convenience, the Na-Fe-Si-O system is described below as two subsystems, Na₂O-Fe₂O₃-SiO₂ in air and Na₂O-FeO-SiO₂ at metallic saturation.

6.4.1. The Na₂O-FeO-SiO₂ system at metallic Fe saturation

6.4.1.1. Phase diagrams

Carter and Ibrahim [13] studied phase equilibria of the Na4SiO4-FeO-SiO2 system in Fe crucibles with the aid of thermal analysis (TA), heating microscopy (HM) and quenching method followed by XRD for phase analysis. Using TA, they found continuous changes in the compositions of samples, and a great tendency to form the glass phase upon cooling. Therefore, TA was considered as a less reliable technique for phase diagram measurements of this system. They determined liquidus temperatures along five binary joins including Fe₂SiO₄-Na₂Si₂O₅, Fe₂SiO₄-Na₂SiO₃, Fe₂SiO₄-Na₄SiO₄, FeO-Na₂Si₂O₅ and FeO-Na₂SiO₃ mainly using HM. The quenching method followed by XRD was only used to measure the liquidus on the Fe₂SiO₄-Na₂Si₂O₅ join. Carter and Ibrahim [13] reported the existence of only one ternary compound, Na₂FeSiO₄, under the reduced oxygen atmosphere in the composition and temperature ranges studied. No solid solubility was noticed due to none identifiable shifts in XRD patterns of stoichiometric phases. Schairer et al. [14] also investigated the Na₂O-FeO-SiO₂ phase diagram in equilibrium with metallic Fe by means of quenching method and XRD for phase analysis. Unfortunately, details of experimental data and

the experimental procedure were not provided. Only the phase diagram, constructed based on experimental results, was presented. They reported the existence of several ternary compounds with very small primary phase regions, but the crystal structure and stoichiometries of the compounds were not identified. Using chemical analysis, they also revealed that ferric iron (Fe³⁺) contents of melts were lower than 2.5 wt% except in regions close to the FeO corner, however details were not given. Ostrovskii [15] studied the Fe₂SiO₄-Na₂Si₃O₇ phase diagram in equilibrium with Fe using quenching method and petrographic microscopy. He investigated the stability field of Na₂Si₂O₅ compound, and also modified the Na₄SiO₄-FeO-SiO₂ phase diagram from Carter and Ibrahim [13] to include the Na₈Fe₆Si₁₅O₄₀ compound. He claimed that this phase is anhydrous and melts incongruently around 1035 K (762 °C) at 97 atm. In the present study, the melting behavior of Na₈Fe₆Si₁₅O₄₀ compound at 1 atm was assumed to be the same as that at 97 atm since the melting temperature of an oxide phase does not change, noticeably, in this pressure range.

The optimized liquidus projection and primary phase regions of the Na₂O-FeO-SiO₂ system in equilibrium with metallic Fe are presented in Figs. 6.2 and 6.3, respectively. The optimized phase diagrams of several joins are also illustrated in Figs. 6.4(a-f) along with experimental data from Carter and Ibrahim [13], Schairer et al. [14], and Ostrovskii [15]. The calculated invariant reactions are listed in Table 6.3. As it is seen in Figs. 6.2 and 6.3, the general features of the phase diagram determined by the experimental studies from Carter and Ibrahim and Schairer et al. are similar. However, the liquidus temperatures are different by about one hundred degree in kelvin in certain compositions as shown in Figs. 6.4(a-f). In all cases, the liquidus temperatures measured by Schairer et al. [14] are higher than those determined by Carter and Ibrahim [13]. The entire data reported by Ostrovskii [15] seem less reliable as it is observed from the discrepancy in the well-known melting temperature of the Na₂Si₃O₇ composition (Figure 4(f)). In this study, the peritectic melting of Na₈Fe₆Si₁₅O₄₀ compound at about 1035 K (762 °C) was reproduced.

Schairer et al. [14] from the Carnegie Geological Laboratory established many oxide phase diagrams using quenching method followed by petrographic microscopy or XRD for phase analysis. Therefore, it is hard to treat their data as less important or less reliable due to the lack of experimental details in their report. The HM widely used by Carter and Ibrahim [13] is not a very accurate technique for liquidus measurements in comparison with the quenching method. Nevertheless, Carter and Ibrahim [13] demonstrated that the results obtained by means of HM and

quenching method are nearly consistent with each other at least for the Na₂SiO₃-Fe₂SiO₄ join. The measured liquidus temperatures for the Na₂SiO₃-Fe₂SiO₄ section by the two groups show the largest difference among all of the sections. Hence, it is hard to conclude which set of experimental data reported in the Na₂O-FeO-SiO₂ system at Fe saturation are more accurate. Schairer et al. [14] observed several ternary compounds, which were not clearly identified, in the SiO₂-rich region while no such compounds were reported by Carter and Ibrahim [13]. If these ternary compounds really formed as equilibrium phases, the experiments of Carter and Ibrahim [13] did not probably reach the equilibrium state and had undercooling of liquidus. In addition, another possible problem is the Na evaporation during the course of experiments. Schairer et al. [14] reported that the Na loss was very significant for compositions with less than 45 wt.% SiO₂ at 1473 K (1200 °C) and higher temperatures. Ban-Ya et al. [1] also mentioned the Na loss in the melts containing about 30 to 50 mol % of SiO₂. Such problems could happen in phase diagram measurements, particularly for compositions with high concentrations of Na₂O due to the use of open crucibles.

The chemical compositions of only two ternary compounds, Na₂FeSiO₄ [13] and Na₈Fe₆Si₁₅O₄₀ [15], were determined with certainty in the Na₂O-FeO-SiO₂ system at Fe saturation. Hence, in the current optimization, only these two compounds were taken into account. As no thermodynamic data are available for both Na₂FeSiO₄ and Na₈Fe₆Si₁₅O₄₀, their S_{298K}^0 and C_P were estimated based on the Neumann-Kopp rule. That is, the S_{298K}^0 and C_P of the compounds are the same as the sum of stoichiometric amounts of S_{298K}^0 and C_P of theirs constituent oxides. Afterward, ΔH_{298K}^0 of both compounds were determined to reproduce their thermal stability regions, as shown in Figs. 6.3 and 6.4(a-f). The calculated primary phase fields and various sections of the Na₂O-FeO-SiO₂ system at Fe saturation are in agreement with experimental data considering the scatters of available experimental data. As clearly demonstrated in Figs. 6.4(a-f), it is certainly necessary to reinvestigate the phase diagram of the Na₂O-FeO-SiO₂ system at Fe saturation.

6.4.1.2. Activities of FeO

Arato et al. [17] and Goto et al. [2] determined the equilibrium oxygen partial pressures over the Na₂O-FeO-SiO₂ melts at Fe satu ration using electro motive force (EMF) measurements between 1273 K (1000 °C) and 1473 K (1200 °C). The oxygen partial pressures determined from the two experimental studies are compared with calculated results from this study in Figs. 6.5(a-b). As it is seen in Fig. 6.5(b), the data from Arato et al. [17] are limited to the liquids with very low FeO amounts. For certain compositions, Goto et al. [2] and Arato et al. [17] reported the activities of FeO rather than the oxygen partial pressures, which were converted to oxygen partial pressures based on the equation, $\sqrt{P_{O_2}} = a_{FeO(reported)} \cdot \sqrt{P_{O_2}^{refrence}}$ where $P_{O_2}^{reference}$ is the oxygen partial pressure over the pure liquid 'FeO' (Fe_{0.97}O) in equilibrium with Fe. It should be mentioned that $P_{Q_2}^{reference}$ used in the experimental studies of Goto et al. [2] are quite different from the reference values calculated based on the FactSage database. For example, $P_{O_2}^{reference}$ reported by Goto et al. [2] and Arato et al. [17] are about 1.0E-13 and 1.33E-12 atm, respectively, at 1473 K (1200 °C) while the value calculated according to the FactSage database is 1.45E-12 atm at 1473 K (1200 °C). The calculated $P_{O_2}^{reference}$ from the FactSage database is very close to that obtained from the widely accepted Gibbs energy reported by Darken and Gurry [39, 40]. The calculated results from the present study lie between the two sets of experimental data.

Ban-Ya et al. [1] and Hyun et al. [16] equilibrated the Na₂O-FeO-SiO₂ melts contained in Fe crucibles with controlled H₂O/H₂ gas mixtures at 1673 K (1400 °C). After the experiments, Fe²⁺, Fe_{tot}, Na₂O and SiO₂ contents of quenched samples were analyzed using wet chemical analysis. The total of each sample was within 98.4 \pm 1.6 wt %. Based on the oxygen partial pressures controlled by the H₂O/H₂ gas mixtures over the Na₂O-FeO-SiO₂ melts and the oxygen partial pressure over the liquid iron oxide, 'FeO(1)', in equilibrium with Fe(s), the activities of liquid 'FeO' in the melts were calculated. Liu et al.^[4] also determined the activities of liquid FeO in the Na₂O-FeO-SiO₂ melts at Fe saturation using EMF measurements at 1273 K (1000 °C), 1373 K (1100 °C) and 1473 K (1200 °C), 1473 K (1200 °C), 1373 K (1100 °C) and 1273 K (1000 °C), respectively, calculated from the present thermodynamic optimization along with the experimental

data [1, 2, 4, 16, 17]. The calculated iso-activity lines are in reasonable agreement with the experimental results within experimental uncertainty.

As it is seen in with decreasing the FeO content, the position of maxima of FeO iso-activity lines at a given FeO content changes from the low basicity (Na₂O/SiO₂) side to the high basicity side: molar ratio of Na₂O/SiO₂ = 0.4 at X_{FeO} = 0.6, 1.0 at X_{FeO} = 0.2 and 2.0 at low FeO contents. This trend is quite different from the conventional metallurgical slag systems such as CaO-FeO-SiO₂ and MgO-FeO-SiO₂ where the maxima of FeO iso-activity lines always locate at molar ratio of CaO/SiO₂ and MgO/SiO₂ = ~ 2.0, the orthosilicate composition.

No experimental data are available for the activities of SiO₂ and Na₂O in the Na₂O-FeO-SiO₂ system at Fe saturation. Based on the present optimization, the iso-activity lines of SiO₂ (solid standard state) and Na₂O (liquid standard state) were calculated in this system in equilibrium with Fe at 1673 K (1400 °C), and are presented in Fig 6.7. The activities of Na₂O and SiO₂ are mainly influenced by the basicity, Na₂O/SiO₂ ratio, and are almost independent of the iron oxide concentration of the melt.

6.4.1.3. Valency of Fe oxides in liquid

The variations of Fe³⁺/Fe²⁺ ratio with the iron oxide content in the Na₂O-FeO-SiO₂ melts saturated with Fe were calculated at 1673 K (1400 °C), and are shown in Fig. 6.8. In the present thermodynamic modeling, the amount of Fe³⁺ in the liquid solution was calculated from both FeO_{1.5} (1 mole of Fe³⁺ per 1 mole of species) and NaFeO₂ (1 mole of Fe³⁺ per 1 mole of species) liquid components. The total amount of Fe oxide, Fe₁O, was calculated from the equilibrium amounts of liquid solution species. Although there are quite scatters in the experimental data, as depicted in Fig. 6.8, the experimental results of Ban-Ya et al. [1] and Hyun et al. [16] show that the relative amount of Fe³⁺ (molar ratio of Fe³⁺/Fe²⁺) significantly increases with increasing the molar ratio of Na₂O/SiO₂. In the FeO-SiO₂ liquid saturated with Fe, the Fe³⁺ is less than 10 % of total Fe. However, with the addition of Na₂O, the Fe³⁺/Fe²⁺ ratio increases to 0.4 or 0.2 obtained by Hyun et al. [16] and Ban-Ya et al. [1], respectively, for the melts with Na₂O/SiO₂ molar ratio equal to 1.0. On the other hand, Schairer et al. [14] reported about 2.5 wt % Fe₂O₃ in the Na₂O-

FeO-SiO₂ melts in equilibrium with Fe using chemical analysis, but exact compositions of melts were not provided. The present modeling results are in reasonable agreement with the experimental data collected by Ban-Ya et al. [1] within experimental error limits, however rather lower than the data from Hyun et al. [16].

The behavior of Fe³⁺ species in the Na₂O-FeO-SiO₂ melts saturated with Fe is very interesting. Typically, the amount of Fe³⁺ in Fe saturated oxide melts is very small with the exception of pure Fe oxide regions. However, in the Na₂O-FeO-SiO₂ liquid in equilibrium with Fe, the amount of Fe³⁺ noticeably increases with increasing the Na₂O concentration. In any conventional metallurgical FeO-bearing slag containing CaO and MgO, such a behavior was not observed. The increment of Fe³⁺ with the Na₂O content might be explained by the strong interaction energy between Na₂O and Fe₂O₃ in the liquid state. The mixing enthalpy of the Na₂O-Fe₂O₃ melt is -110 kJ/mol, in comparison with -50 kJ/mol for the Na₂O-FeO melt at 1773 K (1500 °C).

6.4.2. The Na₂O-Fe₂O₃-SiO₂ system in air

6.4.2.1. Liquidus projection and primary crystalline phases

Bowen and Schairer [18] investigated the Na₂Si₄O₉-Fe₂O₃ join in air using the quenching method followed by petrographic microscopy for phase analysis. Bowen et al. [19] extended their study to the Na₂SiO₃-Fe₂O₃-SiO₂ system in air using the same techniques mentioned above. They measured the liquidus temperatures on six joins, Na₂SiO₃-Fe₂O₃, Na₂Si₂O₅-Na₁₀Fe₂Si₈O₂₄, Na₁₀Fe₂Si₈O₂₄, Fe₂O₃, Na₂SiO₃-Na₂Fe₂Si₄O₁₂, Na₂Si₂O₅-Fe₂O₃ and Na₂Si₂O₅-Na₂Fe₂Si₄O₁₂. The existences of four ternary compounds including NaFeSi₂O₆ (aegirine; formerly named as acmite), Na₅FeSi₄O₁₂, Na₄Fe₂SiO₇ and Na₁₂Fe₈Si₅O₂₈ were also reported. The NaFeSi₂O₆ compound melts incongruently at 1263 K (990 °C) and Na₅FeSi₄O₁₂ melts congruently at 1111 K (838 °C). However, the compositions of the other two compounds Na₄Fe₂SiO₇ and Na₁₂Fe₈Si₅O₂₈ were not determined with certainty.

The optimized liquidus projection and primary phase regions of the Na₂O-Fe₂O₃-SiO₂ system calculated in air are shown in Figs. 6.9 and 6.10, respectively. The calculated invariant reactions

involving the liquid phase are compared in Table 6.4 with the experimental data from Bowen et al. [19]. The experimental liquidus temperatures and the primary phase regions were well reproduced within \pm 3 mol% in composition and \pm 20 K in temperature. Among the four ternary compounds reported by Bowen and Schairer [18] and Bowen et al. [19] in this system, only NaFeSi₂O₆ and Na₅FeSi₄O₁₂ were considered as stable compounds in the present study. Collins and Mulay [24], who measured the isothermal phase diagram of the Na₂O-Fe₂O₃-NaSiO₃ system at 973 K (700 °C), did not observe the Na₄Fe₂SiO₇ and Na₁₂Fe₈Si₅O₂₈ phases. Moreover, Bowen et al. [19] might have confused the Na₁₂Fe₈Si₅O₂₈ phase with the extensive γ -NaFeO₂ metaoxide solid solution.

6.4.2.2. Thermodynamic properties of NaFeSi₂O₆

Thermodynamic properties of NaFeSi₂O₆, the most important compound in the Na₂O-Fe₂O₃-SiO₂ system in air, were well studied [20-23]. Ko et al. [20] measured the low-temperature heat capacity of NaFeSi₂O₆ using adiabatic calorimetry in the temperature range from 5 K (-268 °C) to 307 K (34°C), and derived its standard entropy of formation at 298 K (25 °C). They also determined the heat content of NaFeSi₂O₆ in the temperature range between 298 K (25 °C) and 1201 K (928 °C) in air with the aid of drop calorimetry. Using HF solution calorimetry, Bennington and Brown [21] obtained the standard enthalpy of formation of NaFeSi₂O₆ at 298 K (25 °C) from its both constituent elements and oxides. Although traces of Fe₂O₃ and other impurities (Cr, Mn and Ni; less than 0.1 wt.%) were detected in the NaFeSi₂O₆ composition, their influence on the enthalpy value was negligible. Tangeman and Lange [23] measured the heat capacity of NaFeSi₂O₆ glass in air in the temperature range between 328 K (55 °C) and 998 K (725 °C) by means of differential scanning calorimetry (DSC). Based on the enthalpy of liquid and heat content of solid NaFeSi₂O₆ obtained using drop calorimetry, Sugawara and Akaogi [22] estimated ΔH_{298K}^{o} and the fusion enthalpy of NaFeSi₂O₆.

The optimized heat capacity and heat content of NaFeSi₂O₆ are shown in Figs. 6.11(a and b), respectively, along with experimental data. In the present study, S_{298K}^0 of NaFeSi₂O₆ was taken from Ko et al. [20], and its C_P was optimized based on the low- and high-temperature calorimetry data

collected by Ko et al. [20], Tangeman and Lange [23] and Sugawara and Akaogi [22], as seen in Figs. 6.11(a and b). The C_P of glass obtained by Tangeman and Lange [23] below the glass transition temperature, about 800 K (527 °C), is in good agreement with C_P of crystalline NaFeSi₂O₆. It should be mentioned that the experimental heat capacity data of NaFeSi₂O₆ are very close to the sum of C_P of its constituent oxides. This indicates that the heat capacity estimation of a ternary compound from stoichiometric amounts of its constituent oxides is reasonable. $\Delta H_{298 \text{ K}}^{\circ}$ of NaFeSi₂O₆ was taken from Bennington et al. [21] (-2576. 8 ± 2.97 kJ/mol) and then adjusted to -2590.525 kJ/mol to reproduce its primary phase field and melting temperature reported by Bowen et al. [19] and Bowen and Schairer [18], respectively.

Thermodynamic properties of the Na₅Fe₅Si₄O₁₂ compound were not experimentally investigated. Therefore, its $S_{298\,\text{K}}^{0}$ and C_P were estimated first from the sum of $S_{298\,\text{K}}^{0}$ and C_P of its constituent oxides (5Na₂O + 2.5Fe₂O₃ + 4SiO₂), and its $\Delta H_{298\,\text{K}}^{0}$ was then optimized to reproduce its primary phase field, illustrated in Fig. 6.10.

6.4.2.3. Phase diagrams

The subsolidus phase equilibria and several pseudobinary sections of the Na₂O-Fe₂O₃-SiO₂ system in air were also investigated. Collins and Mulay [24] studied the subsolidus phase equilibria of six compositions in the Na₂O-Fe₂O₃-SiO₂ system in air at 973 K (700 °C) using the quenching method followed by XRD for phase analysis. Grey and Li [10] measured the NaFeO₂-SiO₂ phase diagram up to 20 mol % SiO₂ between 973 K (700 °C) and 1623 K (1350 °C) in air using Differential Thermal Analysis (DTA). They reported the formation of four NaFeO₂ solid solutions: (i) β-NaFeO₂ with the orthorhombic crystal structure containing 0 - 11 mol% SiO₂, (b) γ' -NaFeO₂ with the cubic crystal structure and 7.5 - 33 mol% SiO₂, (c) γ -NaFeO₂ with the tetragonal structure containing 0 - 5 mol% SiO₂ and (d) δ -NaFeO₂ with the cubic structure and 0 - 33 mol% SiO₂. Later, Grey et al. [11] determined the crystal structures of the β and γ' solid solutions using Rietveld refinement of XRD to understand the dissolution behavior of Si⁴⁺ in the β - and γ' -NaFeO₂ phases. Grey and Li [10], Grey et al. [11] and Rulmont et al. [12] reported the formation of a series of NaFeO₂ metaoxide solid solutions rather than the Na₁₂Fe₈Si₅O₂₈ compound. In this study, for the sake of simplicity, γ -, γ' - and δ -NaFeO₂ were treated as one continuous solid solution, the high-temperature γ -NaFeO₂.

Udalov et al. [25] determined the liquidus temperatures on the Na₂Si₂O₅-Fe₂O₃ join in air using steel or quartz crucibles. They used the quenching method and the phases were analyzed by XRD, Scanning Electron Microscopy (SEM) and Electron Probe Micro-Analysis (EPMA). Two critical mistakes were made in their experiments leading to a large error in the phase diagram measurements: (i) the use of Fe crucibles in air and SiO₂ crucibles which could dissolve in the melts during the experiments and (ii) the presence of inherent impurities (calcium aluminoferrite) in the composition of Fe₂O₃ starting materials.

The isothermal section of the Na₂O-Fe₂O₃-SiO₂ system calculated in air at 973 K (700 °C) is shown in Fig. 6.12(a) along with the experimental data reported by Collins and Mulay [24]. Although they reported the 'NaFeO₂ + Fe_2O_3 + Na₂SiO₃' three-phase region for all six compositions, the formation of this three-phase equilibrium region is theoretically impossible for the compositions with Na₂O:Fe₂O₃:SiO₂ molar ratios equal to 3:1:1, 4:2:1, 2:1:1 and 3:2:1. This indicates that the compositions of samples might shift to the regions with lower amounts of Na₂O due to the Na evaporation. Moreover, a very small liquid region in the Na₂O-rich section and a noticeable β -NaFeO₂ solid solution are present in the Na₂O-Fe₂O₃-SiO₂ phase diagram calculated in air at 973 K (700 °C) in the current study (Fig. 6.12(a)). It is very probable that the β -NaFeO₂ solid solution did not properly develop during the course of the experiments by Collins and Mulay [24] at low temperature. Regarding these, the Na₂O-Fe₂O₃-SiO₂ phase diagram calculated in air at 923 K (650 $^{\circ}$ C) without taking into account the NaFeO₂ metaoxide solid solutions (only pure stoichiometric NaFeO₂ compounds were considered) is illustrated in Fig. 6.12(b). As it is seen, considering the possible loss of Na₂O for the samples with high concentrations of Na₂O, the three-phase assemblage experimentally determined by Collins and Mulay [24] was reproduced in the calculated phase diagram. It is worthy to note that this ternary assemblage further confirms that the Gibbs energy of NaFeSi₂O₆ was reasonably constrained in this study. If this Gibbs energy was much negative, the 'Na₂SiO₃+NaFeO₂+NaFeSi₂O₆' three-phase region would form. In addition, the two compounds Na₁₂Fe₈Si₅O₂₈ and Na₄Fe₂SiO₇, reported by Bowen et al. [19], were not observed by Collins and Mulay [24]. Therefore, these two compounds were not taken into account in this study as mentioned before.

The phase diagrams of many sections in the Na₂O-Fe₂O₃-SiO₂ system calculated in air are depicted in Figs. 6.13(a-h) along with experimental data. In general, the optimized and experimentally measured phase diagrams are in good agreement. The NaFeO₂-SiO₂ section (Fig. 6.13(a)) shows the β - and γ -NaFeO₂ metaoxide solid solutions measured by Grey and Li [10]. Two different dissolution behaviors of SiO₂ in the γ - and β -NaFeO₂ phases were considered as discussed in section 2.1.2. Rather strong negative excess interaction parameters were required for the solid solutions to reproduce the liquidus of NaFeO₂ metaoxide solid solution in the NaFeO₂-SiO₂ section in air. The incongruent melting temperature of the NaFeSi₂O₆ compound and the liquidus temperature of the NaFe₂SiO₆ composition [19, 41-43] were well reproduced. In Fig. 6.13(c), the experimental data reported by Bowen et al. [19] and Udalov et al. [25] present a large disagreement. As explained before, the experimental results from Udalov et al. [25] are less reliable due to the use of steel or quartz crucibles. The current calculations are in agreement with the data obtained by Bowen et al. [19].

6.4..2.4. Thermodynamic properties of liquid phase

Thermodynamic properties of the Na₂O-Fe₂O₃-SiO₂ liquid in air were investigated. Sugarawa and Akaogi [22] measured the mixing enthalpies of the Na₂SiO₃-Fe₂O₃ and Na₂SiO₃-Na₂Fe₂Si₄O₁₂ melts at 1373 K (1100 °C) using drop calorimetry. They found that these two melts show nearly ideal solution behavior within the standard error of the experiments, about \pm 10 kJ/mol. DeYoung and Elliott [3] determined the activity of Na₂O in the Na₂O-Fe₂O₃-SiO₂ liquid in air using EMF data. The measurements were performed between 1253 K (980 °C) and 1373 K (1100 °C) within the composition range 20 - 35 mol% Na₂O, 0 - 27.5 mol% Fe₂O₃ and 65 - 80 mol% SiO₂. The mixing enthalpies of the Na₂SiO₃-Fe₂O₃ and Na₂SiO₃-Na₂Fe₂Si₄O₁₂ melts calculated in air are presented in Figs. 6.14(a-b), respectively, along with experimental data. The calculated enthalpies of mixing in both liquids show almost ideal behavior as reported by Sugarawa and Akaogi [22]. There is about 12 kJ/mol difference between the mixing enthalpies experimentally measured by

Sugawara and Akaogi [22] and calculated based on the previous optimization by Jak et al. [37]. There are many experimental enthalpy data in the Na₂O-SiO₂ melt which were well reproduced in the previous optimization by Jak et al. [37]. Considering the systematic difference from the Na₂O-SiO₂ binary system, the present calculations are in good agreement with experimental data within experimental error limits.

The calculated activities of Na₂O (liquid standard state) in the Na₂O-Fe₂O₃-SiO₂ melts in air are depicted in Figs. 6.15(a-h) along with the experimental data obtained by DeYoung and Elliott [3]. The calculated activities and experimental results are in good agreement in the temperature range between 1300 K (1027 °C) and 1370 K (1097 °C). The experimental data in both single-phase liquid region and two-phase regions were also well reproduced in a wide range of compositions.

Lange and Carmichael [26] measured the Fe³⁺/Fe_{tot} ratio in the Na₂O-Fe₂O₃-SiO₂ melts in air between 1199 K (926 °C) and 1856 K (1583 °C). Using EPMA, quenched samples were analyzed for SiO₂, Na₂O, and total iron as FeO. The colorimetric wet chemical analysis was employed to determine the Fe²⁺ content of samples. The concentration of Fe³⁺ was then calculated from the difference between the total iron and Fe²⁺. Experimental uncertainties are very large at low temperatures and low concentrations of Fe₂O₃. Moreover, a significant loss of Na₂O was noticed at high temperatures. The calculated Fe³⁺/Fe_{tot} ratios versus temperature for the Na₂O-Fe₂O₃-SiO₂ melts in air are illustrated in Fig. 6.16 along with the experimental data from Lange and Carmichael [26]. Typically, the amount of Fe³⁺ increases with decreasing the temperature in air due to the exchange reaction between Fe²⁺ and Fe³⁺: FeO(l) + 1/2O₂(g) = Fe₂O₃(l). That is, the equilibrium constant of this reaction rapidly decreases with increasing the temperature, similar to that of this reaction in the solid state. Although the calculated Fe³⁺ is slightly higher than the experimental data at high temperatures, the experimental data were reasonably well reproduced in the present thermodynamic optimization.

6.5. Summary

A detailed and critical assessment of thermodynamic properties and phase equilibrium data of the Na₂O-FeO-Fe₂O₃-SiO₂ system was performed at 1 atm total pressure. Discrepancies among

experimental results were resolved and a coherent thermodynamic database including a set of optimized model parameters was obtained. The present models and optimized model parameters can be used along with thermodynamic software such as FactSage to calculate any phase diagram and thermodynamic property of this system under oxygen partial pressures from Fe saturation to 1 atm. In this study, the Na₂O-FeO-SiO₂ and Na₂O-Fe₂O₃-SiO₂ liquidus projections were calculated, for the first time, at Fe saturation and in air, respectively. Thermodynamic properties of the liquid solution such as activities of SiO₂ and Na₂O were also predicted. Although the best optimized phase diagrams were calculated from the current thermodynamic modeling, more accurate phase diagram measurements at Fe saturation are required to better understand this system and validate the present calculation results.

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| Phase | $\Delta H^{o}_{298 \mathrm{K}} (\mathrm{kJ/mol})$ | <i>S^o298 к</i>
(J/mol-K) | $C_p(T)$
(J/mol-K) | Technique ^{a)} | Reference |
|------------------------------------|---|--|--|-------------------------|-----------|
| Na ₂ FeSiO ₄ | -1820.259 | 180.080 | $C_P (\text{Na}_2\text{O}) + C_P (\text{FeO}) + C_P (\text{SiO}_2(\text{Trd}))^{b)}$ | | This work |
| Na8Fe6Si15O40 | -17940.598 | 1340.074 | $C_P (\text{Na}_2\text{O}) + C_P (\text{FeO}) + C_P (\text{SiO}_2(\text{Trd}))$ | | This work |
| Na5FeSi4O12 | -5691.690 | 422.715 | 2.5 C_P (Na ₂ O) + 0.5 C_P (Fe ₂ O ₃) + 4 C_P (SiO ₂ (Trd)) | | This work |
| | | 170.570 ± 0.2 | | AC | [20] |
| NaFeSi ₂ O ₆ | -2576.800 ± 2.97 | | | SC | [21] |
| | -2546.900 ± 17 | | | Estimation | [22] |
| | -2590.525 | 171.000 | 171.44900 + 0.14880 <i>T</i> - 3611152.58187 <i>T</i> ⁻² - 5.96397E-5 <i>T</i> ² (298 – 1263 K) (25 - 990 °C) 261.984 (1263 – 5000 K) (990 – 4727 °C) | | This work |

Table 6.1: Optimized thermodynamic properties of ternary compounds present in the Na₂O-FeO-Fe₂O₃-SiO₂ system.

a) AC: Adiabatic calorimetry; SC: Solution calorimetry.
 b) Trd: Tridymite.

Table 6.2: Optimized model parameters of solutions in the Na₂O-FeO-Fe₂O₃-SiO₂ system (J/mol and J/mol-K).

Liquid solution (NaO _{0.5} -FeO-FeO _{1.5} -NaFeO ₂ -SiO ₂)*				
$Z_{Na\ Na}^{Na} = 0.68872 , \ Z_{Fe(II)\ Fe(II)}^{Fe(II)} = 1.37744 \ , \ Z_{Fe(III)\ Fe(III)}^{Fe(III)} = 2.06617 \ , \ Z_{NaFe\ NaFe}^{NaFe} = 2.75489 \ , \ Z_{SiSi}^{Si} = 2.75489 \ . \ . \ . \ . \ . \ . \ . \ . \ . \ $				
$q_{Na,Si,Fe(I)}^{013} = -167360$				
$q_{Fe(II),SiNa}^{001} = -85772$				
$q_{Na,Si,Fe(I)}^{031} = -104600$				
$q_{Na,Si,Fe(I)}^{002} = 41840$				
$\Delta g_{NaFeO_2 - SiO_2} = (-39091.11200 - 10.62820T) + (11862.47680 - 11.68717T)X_{SiSi}^4$				
$q_{Na,Si,NaFe}^{001} = -26470.076 - 3.4844352T$				
$q_{Si,Na,NaFe}^{401} = 75312$				
$q_{Na,Si,Fe(III)}^{002} = 41952.968 - 71.433432T$				
Metaoxide solid solutions				
High-temperature γ -NaFeO ₂ : (Na,Va) ^{Na} [Fe,Si] ^M O ₂				
${}^{0}L_{NaVa;Si} = -29288$				
${}^{1}L_{NaVa;Fe} = -118624.768 + 220.890096T$				
Intermediate-temperature β-NaFeO ₂ : (NaFe,VaSi)O ₂				
$^{1}L_{NaFe\ VaSi}=20920$				
${}^{4}L_{NaFe VaSi} = -205016$				

* All other model parameters can be found in the previous work [30]. The formalism of the ternary excess parameters can be found elsewhere [44].

N. *			Composition (mol %)		
N0.*	I [K (°C)]	Invariant reactions	Na ₂ O	SiO ₂	
1	1207 (934)	L+wüstite+NaFeO ₂ (β)→ NaFe ₂ O ₃	29.14	3.88	
2	1140 (867)	$L+Fe_2SiO_4+SiO_2(Trd) \rightarrow SiO_2(Qz-h)$	14.58	67.45	
3	1100 (827)	L+wüstite→Fe ₂ SiO ₄ +Na ₂ FeSiO ₄	27.96	49.76	
4	1081 (808)	$L+Na_6Si_2O_7 \rightarrow Na_2SiO_3+Na_4SiO_4$	47.11	23.33	
5	799 (526)	$L \rightarrow Na_2O(\alpha) + Na_4FeO_3 + Na_4SiO_4$	72.35	12.50	
6	1042 (769)	L+Na ₂ FeSiO4 \rightarrow Fe ₂ SiO ₄ +Na ₂ SiO ₃ (α)	30.23	54.28	
7	1041 (768)	$L+Na_{10}SiO_7 \rightarrow Na_2O(\beta)+Na_4SiO_4$	78.81	18.08	
8	1035 (762)	L+Fe ₂ SiO ₄ + SiO ₂ (Qz-h)→Na ₈ Fe ₆ Si ₁₅ O ₄₀	19.74	68.06	
9	1023 (750)	L+Na ₂ O(β)+Na ₄ SiO ₄ \rightarrow Na ₂ O(α)	78.27	17.59	
10	992 (719)	L+Na ₈ Fe ₆ Si ₁₅ O ₄₀ \rightarrow Fe ₂ SiO ₄ +Na ₂ Si ₂ O ₅ (γ)	27.00	62.32	
11	987 (714)	$L \rightarrow Fe_2SiO_4 + Na_2Si_2O_5(\gamma) + Na_2SiO_3(\alpha)$	29.87	59.03	
12	975 (702)	$L+SiO_2(Qz-h)+Na_6Si_8O_{19}+Na_8Fe_6Si_{15}O40$	23.76	69.54	
13	822 (549)	L+Na ₂ FeO ₂ →Na ₄ FeO ₃ +Na ₄ SiO ₄	66.11	12.60	
14	975 (702)	$L \rightarrow Na_8 Fe_6 Si_{15}O_{40} + Na_2 Si_2 O_5(\beta) + Na_6 Si_8 O_{19}$	23.62	69.33	
15	938 (665)	L+Na ₂ FeSiO ₄ →wüstite+Na ₂ SiO ₃ (α)	40.53	16.86	
16	911 (638)	L+Na ₂ SiO ₃ (α)→wüstite+Na ₄ SiO ₄	40.99	16.80	
17	905 (632)	$L \rightarrow NaFe_2O_3 + NaFeO_2(\beta) + Na_4SiO_4$	41.40	16.19	
18	908 (635)	L+wüstite→NaFe ₂ O ₃ +Na ₄ SiO ₄	40.95	16.61	
19	871 (598)	$L \rightarrow Na_2FeO_2 + NaFeO_2(\beta) + Na_4SiO_4$	53.68	12.62	

Table 6.3: Calculated invariant reactions involving the liquid phase of the Na₂O-FeO-SiO₂ system at Fe saturation.

* Reaction number corresponds to the composition of the invariant reaction indicated in Fig. 6.2.

** Experimental results of Carter and Ibrahim [13] and Schairer et al. [14] cannot be properly compared because Carter and Ibrahim did not consider the $Na_8Fe_6Si_{15}O_{40}$ compound, and Schairer et al. considered several undetermined crystals.

	T [K(°C)]		Invariant reactions	Composition (mol %)			
No.*				Na ₂ O		SiO ₂	
	Exp.	Calc.		Exp.	Calc.	Exp.	Calc.
1	ND	1739 (1466)	L1+L2+SiO ₂ (Crs)→SiO ₂ (Trd)	ND	1.71	ND	42.94
2	ND	1738 (1465)	L1+L2+SiO ₂ (Crs)→SiO ₂ (Trd)	ND	3.12	ND	92.15
3	ND	1697 (1424)	$L+SiO_2(Trd)+spinel\rightarrow L2$	ND	2.00	ND	41.01
4	ND	1697 (1424)	$L+SiO_2(Trd)+spinel\rightarrow L2$	ND	3.76	ND	91.07
5	ND	1662 (1389)	$L+SiO_2(Trd)+spinel\rightarrow Fe_2O_3$	ND	4.32	ND	90.45
6	ND	1269 (996)	L+Na ₈ Fe ₂ O ₇ +NaFeO ₂ (γ) \rightarrow NaFeO ₂ (β)	ND	60.64	ND	14.32
7	ND	1243 (970)	L+Na ₂ O(γ)+Na ₈ Fe ₂ O ₇ \rightarrow Na ₂ O(β)	ND	89.60	ND	7.30
8	1228 (955) ± 5	1236 (963)	L+Fe2O3→NaFeSi2O6+SiO2(Trd)	11.70	11.99	78.82	79.35
9	1140 (867) ± 3	1140 (867)	L+ SiO ₂ (Trd)+NaFeSi ₂ O ₆ →SiO ₂ (Qz-h)	16.86	16.72	76.98	76.87
10	1118 (845)	1114(841)	$L+NaFeO_2(\gamma) \rightarrow Na_2SiO_3(\alpha)+Fe_2O_3$	38.01	37.14	43.68	46.36
11	1088 (815) ± 5	1102 (829)	$L \rightarrow Fe_2O_3 + Na_5FeSi_4O_{12} + Na_2SiO_3(\alpha)$	36.00	35.82	50.58	49.32
12	1082 (809) ± 5	1098 (825)	$L \rightarrow Fe_2O_3 + NaFeSi_2O_6 + Na_5FeSi_4O_{12}$	30.78	30.78	55.88	57.12
13	ND	1081 (808)	$L{+}Na_6Si_2O_7{\longrightarrow}Na_2SiO_3(\alpha){+}Na_4SiO_4$	ND	59.97	ND	27.73
14	ND	1073 (800)	$L+Na_2O(\beta) \rightarrow Na_8Fe_2O_7+Na_{10}SiO_7$	ND	80.78	ND	17.40
15	ND	1065 (792)	$L+NaFeO_{2}(\gamma) \rightarrow NaFeO_{2}(\beta)+Na_{2}SiO_{3}(\alpha)$	ND	56.08	ND	24.71
16	1089 (816) ± 5	1059 (786)	$L+Na_2SiO_3(\alpha) \rightarrow Na_5FeSi_4O_{12}+Na_2Si_2O_5(\gamma)$	36.26	33.57	61.36	63.50
17	ND	1052 (779)	L+Na ₈ Fe ₂ O ₇ + NaFeO ₂ (β)→Na ₃ FeO ₃	ND	61.00	ND	19.97
18	ND	1051 (778)	L→Na8Fe2O7+Na10SiO7+Na4SiO4	ND	79.40	ND	18.82
19	1073 (800) ± 5	1025 (752)	$L \rightarrow NaFeSi_2O_6 + Na_5FeSi_4O_{12} + Na_2Si_2O_5(\gamma)$	30.90	28.73	64.61	66.98
20	ND	1002 (729)	$L+Na_8Fe_2O_7 {\longrightarrow} Na_3FeO_3+Na_4SiO_4$	ND	62.34	ND	22.64
21	ND	986 (713)	$L \rightarrow NaFeSi_2O_6 + Na_2Si_2O_5(\gamma) + Na_6Si_8O_{19}$	ND	23.50	ND	72.94
22	ND	977 (704)	$L \rightarrow NaFeO_2(\beta) + Na_2SiO_3 + Na_4SiO_4$	ND	59.56	ND	24.22
23	ND	944 (671)	$L \rightarrow Na_3FeO_3 + Na_4SiO_4 + NaFeO_2(\beta)$	ND	61.30	ND	21.93

Table 6.4: Calculated invariant reactions involving the liquid phase of the Na₂O-Fe₂O₃-SiO₂ system in air in comparison with the experimental data from Bowen et al. [19].

* ND: Not Determined.

** Reaction number corresponds to the composition of the invariant reaction indicated in Fig. 6.9.



Fig. 6.1: Schematic diagram of the solid phases in the Na₂O-FeO-Fe₂O₃-SiO₂ system.



Fig. 6.2: Calculated optimized liquidus projection of the Na₂O-FeO-SiO₂ system in equilibrium with metallic Fe. Temperatures are in °C. Qz, Trd and Crs represent the quartz, tridymite and cristobalite crystal structures of SiO₂, respectively. The invariant reactions indicated by numbers are listed in Table 6.3.



Fig. 6.3: Calculated primary phase regions of the Na₂O-FeO-SiO₂ system in equilibrium with metallic Fe along with experimental data [13-15]. OM: Petrographic microscopy and HM: Heating microscopy.



(a)



(b)







(f)

Fig. 6.4: Calculated optimized isopleths of the Na₂O-FeO-SiO₂ system at metallic Fe saturation along with experimental data: (a) Fe₂SiO₄-Na₂Si₂O₅, (b) Fe₂SiO₄-Na₂SiO₃, (c) Fe₂SiO₄-Na₄SiO₄, (d) FeO-Na₂SiO₃, (e) FeO-Na₂Si₂O₅, and (f) Fe₂SiO₄-Na₂Si₃O₇.



(b)

Fig. 6.5: Calculated partial pressures of oxygen over the Na₂O-FeO-SiO₂ liquid: (a) molar ratio of Na₂O/SiO₂ = 1.0 and (b) various molar ratios of Na₂O/SiO₂ at 1473 K (1200° C) along with experimental data [2, 17].



(a)



(b)



Fig. 6.6: Calculated iso-activity lines of 'FeO' (liquid standard state) in the Na₂O-FeO-SiO₂ liquid in equilibrium with metallic Fe at (a) 1673 K (1400 °C), (b) 1473 K (1200 °C), (c) 1373 K (1100 °C), and (d) 1273 K (1000 °C).



Fig. 6.7: Calculated iso-activity lines of SiO₂ (thick lines; cristobalite standard state) and Na₂O (thin lines; liquid standard state) in the Na₂O-FeO-SiO₂ liquid in equilibrium with metallic Fe at 1673 K (1400 °C).



Fig. 6.8: Calculated Fe³⁺/Fe²⁺ ratios in the Na₂O-FeO-SiO₂ liquid in equilibrium with metallic Fe at 1673 K (1400 °C) in comparison with the experimental data from Ban-Ya et al. [1] and Hyun et al. [16].



Fig. 6.9: Calculated optimized liquidus projection of the Na₂O-Fe₂O₃-SiO₂ system in air. Temperatures are in °C. Qz, Trd and Crs represent the quartz, tridymite and cristobalite crystal structures of SiO₂, respectively. The invariant reactions indicated by numbers are listed in Table 6.4.



Fig. 6.10: Calculated primary phase regions of the Na₂O-Fe₂O₃-SiO₂ system in air along with experimental data from Bowen et al. [19].



Fig. 6.11: Calculated thermodynamic properties of NaFeSi₂O₆ (aegirine): (a) heat capacity and (b) heat content.



Fig. 6.12: Calculated optimized phase diagram of the Na₂O-Fe₂O₃-SiO₂ system in air at (a) 973
K (700 °C) (fully equilibrium) and (b) 923 K (650 °C) (assuming only stoichiometric NaFeO₂ compounds). The phase assemblage of each area in the diagram is 1: liquid + β-NaFeO₂, 2: Na₄SiO₄ + Na₂SiO₃ + β-NaFeO₂, 3: β-NaFeO₂ + Na₂SiO₃ + Fe₂O₃, 4: Na₄SiO₄ + β-NaFeO₂ + Na₃FeO₃, 5: Na₄SiO₄ + Na₂SiO₃ + β-NaFeO₂ and 6: β-NaFeO₂ + Na₂SiO₃ + Fe₂O₃.







(e)



(f)



Fig. 6.13: Calculated optimized phase diagram of various sections of the Na₂O-Fe₂O₃-SiO₂ system in air along with experimental data: (a) NaFeO₂-SiO₂, (b) Na₂Si₂O₅-Na₁₀Fe₂Si₈O₂₄, (c) Na₂Si₂O₅-Fe₂O₃, (d) Na₂Si₄O₉-Fe₂O₃, (e) Na₂SiO₃-Fe₂O₃, (f) Na₁₀Fe₂Si₈O₂₄-Fe₂O₃, (g) Na₂Si₂O₅-Na₂Fe₂Si₄O₁₂, and (h) Na₂SiO₃-Na₂Fe₂Si₄O₁₂.



Fig. 6.14: Calculated enthalpy of liquid phase referenced to solid state: (a) Na₂SiO₃–Fe₂O₃ and (b) Na₂SiO₃–NaFeSi₂O₆ sections.



(a)







(c)



(d)



(e)





Fig. 6.15: Calculated activity of Na₂O (liquid standard state) at constant molar ratios of Na₂O/SiO₂ in the Na₂O-Fe₂O₃-SiO₂ liquid in air at (a) 1300 K (1027 °C), (b) 1310 K (1037 °C), K (1050 °C), (d) 1330 K (1057 °C), (e) 1340 K (1067 °C), (f) 1350 K (1077 °C), (g) 1360 K (1087 °C), and (h) 1370 K (1097 °C).



Fig. 6.16: Calculated Fe³⁺/Fe_{tot} ratios vs. temperature for different compositions in the Na₂O-Fe₂O₃-SiO₂ liquid in air. Fe_{tot} represents total Fe in the melt.

Chapter 7

PAPER 3: COUPLED EXPERIMENTAL AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃-Al₂O₃ SYSTEM: PART 1. PHASE DIAGRAM EXPERIMENTS

Elmira Moosavi-Khoonsari, Pierre Hudon, and In-Ho Jung, *Journal of the American Ceramic Society*, 2015 (accepted).

7.1. Abstract

As part of the complete thermodynamic modeling of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system, the Na₂O-FeO-Fe₂O₃-Al₂O₃ phase diagrams in air (1583 and 1698 K) and at Fe saturation (1573 and 1673 K) were investigated using the quenching method followed by EPMA and XRD phase analysis. General features of the phase diagrams in this system were well revealed for the first time. A complete meta-oxide solid solution between NaAlO₂ and NaFeO₂ was observed. An extensive solid solution of Na₂(Al,Fe)₁₂O₁₉ Na- β "-alumina was found and the existence of a miscibility gap in this solution was confirmed. Several compatibility triangles of three-phase assemblages were also identified in air and at Fe saturation.

7.2. Introduction

Phase diagram and chemical equilibrium information is indispensable for the optimization of existing material processes and the development of new processes and advanced materials. The thermodynamic understanding of the multicomponent system Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂-CaO-MgO, for example, is crucial in various industrial applications including glass-ceramics [1], cement-making [2], iron and steelmaking [3], and combustion [4]. This system is also important in geochemistry [5,6]. The Na₂O-FeO-Fe₂O₃-Al₂O₃ subsystem, alone, is of practical interest in the

sintering process of bauxite with soda for the production of Al₂O₃ [7], refractories [8], and the production of solid solution electrodes for electrochemical cells [9-11]. However, to date, no accurate phase diagram study of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system has been performed. Actually, only a few experimental investigations were conducted in air on the formation of the meta-oxide solid solutions between the NaAlO₂ and NaFeO₂ and the β -alumina group of solid solutions [7-17]. Moreover, as Fe can have both 2+ and 3+ valence states in the liquid and solid oxides and their amounts in molten oxides change with the oxygen partial pressure, phase diagram information depending on the partial pressure of oxygen is of the upmost importance for many industrial processes.

Any phase diagram study of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system is very complex because phase relations change with the oxygen partial pressure. Therefore, a study which relies on a large number of phase equilibrium experiments at various temperatures and partial pressures of oxygen is time consuming and costly. A coupled experimental phase diagram study and thermodynamic modeling approach is thus widely used by the CALPHAD community. This methodology was successfully applied, for example, to the MnO-SiO₂-TiO₂-Ti₂O₃ system [18-20], where the complex phase equilibria were well exposed with a minimum number of experiments.

The purpose of the present work was to perform a coupled experimental phase diagram study and thermodynamic modeling of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system. As the first part of this series, new key phase diagram experiments were performed in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air and at metallic Fe saturation. To determine key experimental compositions, preliminary phase diagrams were calculated using the thermodynamic databases of all the subsystems such as the binaries Na₂O-FeO [21], Na₂O-Fe₂O₃ [21], Na₂O-Al₂O₃ [22], and the ternary Na₂O-Fe₂O₃-FeO [21]. Key phase diagram compositions were typically targeted inside three-phase regions and in some two-phase assemblages. The preliminary phase diagrams were designed for additional experimental results, and other key phase diagram compositions were designed for additional experiments. This process was repeated until a sufficient amount of phase diagram data was obtained to construct the general topology of the phase diagram of the system. In the second part of this series, the thermodynamic modeling of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system based on the present key experimental results will be presented, and many unexplored phase diagram sections

will be predicted from the optimized model parameters. This study is part of a large thermodynamic database development of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂-CaO-MgO system.

7.3. Phase diagram study in air

In the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air, several solid solution phases exist: Na(Al,Fe)O₂ meta-oxide, Na₂(Al,Fe)₁₂O₁₉ Na- β "-alumina, FeAl₂O₄-Fe₃O₄ spinel, and (Al,Fe)₂O₃ corundum. The main purpose of the present study was to experimentally determine (i) the liquidus of the meta-oxide phase, (ii) the homogeneity range of the Na- β "-alumina, and (iii) two- or three-phase equilibria between solids and the liquid. So far, none of this phase diagram information has been clearly reported in the literature. The meta-oxides NaAlO₂ and NaFeO₂ both have two different polymorphs (intermediate- and high-temperature phases with orthorhombic and tetragonal crystal structures, respectively) forming complete solid solutions between each other [12-17]. The meta-oxide solution considered in this study is the tetragonal high-temperature form of the solution, which is stable above 1270 K; it is therefore called high-temperature meta-oxide (or HT meta-oxide) in this work.

7.3.1. Experimental and analytical methods

Starting materials consisting of mixtures of Na₂CO₃ (99.95 wt. %), Fe₂O₃ (99.998 wt. %) and Al₂O₃ (99.99 wt. %) from Alfa Aesar (USA) were prepared in batches of 100 mg by mechanical mixing in an agate mortar filled with 2-propanol alcohol for 1 h. Ground mixtures were then decarbonated in a Pt crucible in air by firing at 1023 K for 5 to 28 h depending on the concentration of Na₂CO₃ in the mixtures, cooled down in a desiccator, and stored in a drying oven at 383 K. The required decarbonation time for each starting composition was determined in preliminary experiments in air by monitoring the weight loss as a function of time using Differential Scanning Calorimetry and Differential Thermo-Gravimetry (DSC/DTG). In the starting sample preparation of the main experiments, mixtures were also weighed before and after decarbonation to further confirm the completion of the dissociation of Na₂CO₃ to Na₂O and CO₂. Since decarbonation was performed

in the solid state at 1023 K, all the weight loss was assumed to result from the loss of CO₂ rather than Na₂O; the evaporation of Na₂O should be less significant at this temperature which is much lower than its melting temperature of 1405 K. Compositions of the starting materials used in the present study are listed in Table 7.1.

About 20 mg of starting material was tightly packed into each open Pt capsule (length = 10 mm, inner diameter = 2.873 mm, outer diameter = 3 mm). Samples were brought to the target temperatures (1698 or 1583 K) with a heating rate of 10 K/min, kept in air for 1 to 168 h, and quenched in liquid N₂ (water was not employed due to the hygroscopic nature of the run products). Experiments were conducted in a ST-1700C box furnace (Sentro Tech, USA; inner dimensions: 10 cm x 10 cm x 20 cm) equipped with Pt₃₀Rh-Pt₆Rh (type B) thermocouples. The furnace temperature was calibrated by melting diopside (CaMgSi₂O₆; melting point = 1664.5 K) in air and PID-controlled within ±1 K.

After quenching in liquid N₂, encapsulated quenched samples were cast in epoxy and longitudinal polished sections of the charges were made for phase identification. Due to the hygroscopic nature of the Na₂O-containing products and to minimize water absorption as much as possible, specimens were polished using lapping oil and low water content 2-propanol alcohol (H₂O < 0.02 wt. %), and quickly transferred to the Electron Probe Micro-Analyzer (EPMA) for phase composition analysis. EPMA analyses were conducted with the JEOL 8900 probe at McGill University using Wavelength-Dispersive Spectrometry (WDS). An accelerating voltage of 15 kV was used with a 20 nA beam current and counting times of 20 s on peaks and 10 s on backgrounds. Raw data were reduced with the ZAF correction using hematite (Fe) and albite (Na and Al) standards. Each phase in each sample was analyzed at least 10 times. The Na evaporation during EPMA analysis was monitored depending on the beam current, size, and counting time, and it was confirmed that the present EPMA settings caused nearly no Na loss. X-ray diffractometer equipped with HiSTAR area detector and CoK α radiation at McGill University.

7.3.2. Experimental results and discussion

Experimental conditions, observed phases, and phase compositions found in the samples equilibrated in air at 1698 and 1583 K are summarized in Table 7.1. The temperatures were selected to avoid the formation of FeAlO₃, which is stable between 1593 and 1683 K in the Fe₂O₃-Al₂O₃ system in air. As general features of the current phase diagram are not well known yet, additional phase assemblages including FeAlO₃ in narrow ranges of composition and temperature require a much larger volume of experimental work, and also may cause difficulties in the analysis of experimental results. Based on equilibrium phase relations in the isothermal sections, Gibbs energies of Na- β "-alumina and liquid phases could be optimized in the thermodynamic modeling (see part II of this study). Phase assemblages relevant to FeAlO₃ can be then reasonably well predicted from thermodynamic models.

Preliminary experiments were performed to check if equilibrium was reached. This was accomplished by annealing the samples at 1698 and 1583 K for 1, 5, 24, 48, 72, and 168 h, respectively; the runs listed in Table 7.1 being the ones for which equilibrium was attained. Unfortunately, as the present experiments were performed in open capsules to make sure that the samples were equilibrated in air, the loss of Na₂O could not be prevented in long duration experiments. Although the overall compositions of the quenched samples might be slightly different from their starting compositions, the composition of each phase in a sample after quenching can be used to construct the equilibrium phase diagram in this study.

Equilibrium phases were homogeneously distributed in each sample, as shown in Fig. 7.1(a) for the representative sample NAF3-1. For the samples containing glass only (sample NAF6-1) and solid + glass (e.g. sample NAF3-1), equilibrium was reached within 1 h. However in the subsolidus regions (e.g. sample NAF4-1), longer durations were required depending on the composition and temperature.

Back Scattered Electron (BSE) images of samples quenched after equilibration at 1698 K in air are illustrated in Fig. 7.2. The high-temperature meta-oxide solid solution HT-Na(Al,Fe)O₂ in equilibrium with the glass is observed in samples NAF0-1, NAF1-1, NAF2-1 (Fig. 7.2(a)), and NAF3-1. The presence of meta-oxide solid solution and glass in these samples was also confirmed

by XRD phase analysis. Quench crystals (mainly Fe-rich oxides) exsoluting from the original liquid during quenching were often found in the solidified liquid phase of most samples despite all efforts to quench them quickly. This is most probably due to the low viscosity of the Na₂O- and Fe₂O₃-rich liquid. These quench crystals were not considered stable and were counted as part of the glass in the phase composition analysis. Sample NAF6-1 quenched only to single glass (Fig. 7.2(b)). The three-phase assemblages HT-Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉#1 + Na₂(Al,Fe)₁₂O₁₉#2 and spinel + corundum + Na₂(Al,Fe)₁₂O₁₉#1 were observed in samples NAF4-1 (Fig. 7.2(c)) and NAF5-1 (Fig. 7.2(d)), respectively. Note that the labels #1 and #2 in Na₂(Al,Fe)₁₂O₁₉ each represents an immiscible solid solution of Na₂(Al,Fe)₁₂O₁₉, which will be discussed in more details below. The three-phase assemblage HT-Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉#2 + glass was found in sample NAF8-1 (Fig. 7.2(e)). Unfortunately, the presence of intimate small dendritic HT-Na(Al,Fe)O₂ crystals and glass by EPMA. Part of the HT-Na(Al,Fe)O₂ crystals mixed with the glass in sample NAF8-1 seems to be stable crystals at this temperature. The two-phase equilibrium between spinel and Na₂(Al,Fe)₁₂O₁₉#1 was observed in sample NAF13-1 (Fig. 7.2(f)).

BSE images of samples quenched after equilibration at 1583 K in air are depicted in Fig. 7.3. The HT-Na(Al,Fe)O₂ solid solution in equilibrium with the glass was observed in samples NAF9-1 and NAF6-2. The three-phase assemblage HT-Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉#1 + Na₂(Al,Fe)₁₂O₁₉#2 was found in samples NAF10-1 (Fig. 7.3(a)) and NAF11-1. Sample NAF12-1 (Fig. 7.3(b)) contained corundum (bright white particles) and two unknown phases (labelled as phase X and phase Y) which are very similar to the phases found in sample NAF7-1.

No evidence of any ternary stoichiometric compound was found in the temperature and composition ranges investigated. In the experimental result analysis, it was very confusing whether the Na₂(Al,Fe)₁₂O₁₉#2 phase is a stoichiometric ternary phase different from the Na₂(Al,Fe)₁₂O₁₉ solution. In particular, the compositions of Na₂(Al,Fe)₁₂O₁₉#2 analyzed in samples NAF4-1 and NAF8-1 at 1698 K were almost identical, and the compositions of the same phase in samples NAF10-1 and NAF11-1 at 1583 K were also very similar to those at 1698 K (see Table 7.1). Therefore, careful XRD analyses and further experiments were carried out for this phase. As shown in Fig. 7.2(c), sample NAF4-1 equilibrated at 1698 K contained three different phases. However, the XRD pattern of this sample, illustrated in Fig. 7.4, revealed the presence of only two phases:

the Na(Al,Fe)O₂ meta-oxide and the Na₂(Al,Fe)₁₂O₁₉ Na- β "-alumina. This indicates that there are two Na₂(Al,Fe)₁₂O₁₉ phases with the same crystal structure but different compositions. The same observation was made for the XRD pattern of sample NAF10-1 equilibrated at 1583 K. The solubility limits due to the miscibility gap in the Na₂(Al,Fe)₁₂O₁₉ solid solution are Na₂(Al_{0.8},Fe_{0.2})₁₂O₁₉ and Na₂(Al_{0.3},Fe_{0.7})₁₂O₁₉ at 1698 K, and Na₂(Al_{0.6},Fe_{0.4})₁₂O₁₉ and Na₂(Al_{0.25},Fe_{0.75})₁₂O₁₉ at 1583 K. The composition of the miscibility gap, of course, changes with temperature but the gap becomes typically wider with a decrease in the temperature. However, the current experimental data show that the gap boundary at the Al-rich side becomes narrower. We believe this might be the experimental limitation. That is, the miscibility gap at 1583 K seems to be not fully developed even after 168 h due to the slow kinetics of the miscibility gap formation.

No definitive evidence about the existence of immiscibility in the Na₂(Al,Fe)₁₂O₁₉ Na- β'' -alumina solution has been reported yet. Dyson and Johnson [8] reported the formation of a solid solution with the composition Na₂(Al_{0.8},Fe_{0.2})₁₂O₁₉ but only one composition was investigated. Unfortunately, they were not specific about the temperature and merely mentioned that the solid solution was synthesized between 1373 and 1673 K. The only experimental data in the literature regarding the solubility limit of Fe in Na- β'' -alumina were reported by Roland et al. [10]. After annealing their starting materials for 2 to 18 h, they determined that the homogeneity range of Na- β'' -alumina solid solution was 12-22 Na₂O, 35-70 Al₂O₃, 16-48 Fe₂O₃ (mol %) at 1673 K in air. Considering the slow kinetics involved in the formation of the miscibility gap, the duration of their experiments seems to be too short to reach equilibrium. This will be discussed again below. In oxide crystals in general, Al³⁺ and Fe³⁺ have a tendency to form a miscibility gap. The corundum solution (Al,Fe)₂O₃, for example, has a wide miscibility gap between Al₂O₃ and Fe₂O₃, and a similar behavior can be seen in the calcium alumina-ferrite solid solution and the spinel solid solution as well.

To investigate the development of the miscibility gap in the $Na_2(Al,Fe)_{12}O_{19}$ solution, the composition NAF7 (15.0 Na₂O-52.5 Al₂O₃-32.5 Fe₂O₃ in mol %) was annealed for 5, 24, 48 and 72 h, respectively, at 1698 K in air (Fig. 7.5). Inhomogeneous composition was observed in the sample after 5 h (Fig. 7.5(a)), within 24 h, the sample was fully homogenized (Fig. 7.5(b)) and after 24 h, phase separation occurred (Figs. 7.5(c) and (d)). Crystals with a dense surface and crystals with a porous surface are observed in the samples annealed for 24 to 72 h (Figs. 7.5(b-d)).

XRD analysis confirmed that these crystals are $Na_2(Al,Fe)_{12}O_{19}$. The compositions of the phase Y and phase X analysed by EPMA showed departure from the original composition toward the Aland Fe-rich sides, respectively. Even after 72 h of annealing, the miscibility gap, discussed above, was not fully developed most probably because the NAF7 starting composition was located inside the spinodal decomposition region of the miscibility gap. With the progress of annealing at this temperature, spinel formed due to Na₂O loss in air, but this did not influence the formation of the miscibility gap.

Based on the experimental observations and analyses, the phase diagrams of the Na₂O-Fe₂O₃-Al₂O₃ system in air at 1698 K and 1583 K are presented in Fig. 7.6. The analytical errors associated to the compositions of the liquid and $Na_2(Al,Fe)_{12}O_{19}$ phases are usually very large due to compositional inhomogeneity. The composition of Na₂(Al,Fe)₁₂O₁₉ occasionally shows a deviation from the ideal line composition with a Na/(Al+Fe) molar ratio of 1/6, but it was assumed as a line solution in this study. Moreover, the solid state phase equilibria involving Na₂(Al,Fe)₁₂O₁₉ were very sluggish and thus its equilibrium phase assemblages could not be obtained within 168 h at 1583 K. In particular, the experimental compatibility triangle containing $Na_2(Al,Fe)_{12}O_{19} \#1 +$ $Na_2(Al,Fe)_{12}O_{19} #2 + Na(Al,Fe)O_2$ at 1583 K is smaller than the one at 1698 K as can be seen in Fig. 7.6. This happened most likely because the duration of the experiments was not long enough at 1583 K to reach equilibrium in the solid state. Consequently, the three-phase assemblage at 1698 K was used to draw our schematic phase diagram at 1583 K. The binary phase diagrams were also used to constrain the phase boundaries of the ternary phase diagrams. Attempts to observe experimentally the three-phase assemblage liquid + Na(A1,Fe)O₂ + Na₂(A1,Fe)₁₂O₁₉ failed; however, such phase equilibrium should occur as shown in the diagram. On the other hand, a complete Na(Al,Fe)O₂ meta-oxide solid solution between NaAlO₂ and NaFeO₂ was observed. Moreover as discussed above, Na₂(Al,Fe)₁₂O₁₉ Na-β"-alumina forms an extensive solid solution with a miscibility gap. However, no experiments were designed to determine the solubility limit of Fe in the Na(Al,Fe)₉O₁₄Na-β-alumina solution. Despite the fact that experimental data reported in the literature^{9, 23} show that the homogeneity range of the Na-β-alumina solution goes up to $Na(Al_{0.4},Fe_{0.6})_{11}O_{17}$, our current corundum + spinel + $Na_2(Al,Fe)_{12}O_{19}$ #1 compatibility triangle indicates that the solubility of Fe^{3+} in Na- β -alumina should be much smaller, most probably less than 5 mol % Fe₂O₃. For the sake of simplicity, therefore, the Na-β-alumina phase was considered

to be a stoichiometric compound, namely NaAl₉O₁₄. Clearly though, this should be further investigated in the future. Note also that no noticeable solubility of Na₂O was detected in the spinel solution and no ternary stoichiometric compound was found within the experimental temperature and composition ranges studied.

The size of equilibrium crystalline phase forming at the target temperature is much larger than that of the quench crystal. The shape of equilibrium crystal is faceted and euhedral, different from the shape of quench crystal, dendritic or acicular. Therefore, it is easy to distinguish equilibrium crystalline phases from quench crystals. As quench crystals are considered to be a part of the liquid phase, originally at the equilibrium temperature, the area mapping was performed for the liquid pool containing quench crystals to obtain the equilibrium liquid composition. Samples NAF6-1, NAf7-1, and NAf7-2 contained only the liquid phase at the equilibrium state. However, the analyzed liquid compositions (including quench crystals) using EPMA area mapping were the same as the starting compositions of samples. This confirms that the existence of quench crystals in the liquid phase.

7.4. Phase diagram study at Fe saturation

Like the phase equilibria in air, there are several solid solutions in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system at Fe saturation: Na(Al,Fe)O₂ meta-oxide, Na₂(Al,Fe)₁₂O₁₉ Na- β "-alumina, FeAl₂O₄-Fe₃O₄ spinel, and (Al,Fe)₂O₃ corundum. The homogeneity ranges of these solid solutions are expected to be much smaller at Fe saturation than those in air, but no experimental data were reported so far in this system.

7.4.1. Experimental and analytical methods

The general procedure employed to prepare the starting materials for experiments at Fe saturation is similar to the one in air. The starting powder mixtures were prepared after mixing and decarbonating reagent grade Na₂CO₃ (99.95 wt. %), Fe₂O₃ (99.998 wt. %) and Al₂O₃ (99.99 wt. %) powders from Alfa Aesar (USA). About 100 mg of Na₂O + Fe₂O₃ + Al₂O₃ mixtures were then

mechanically mixed in desired proportions with Fe powder (99.9% grade from Alfa Aesar) in an agate mortar filled with 2-propanol for 1 h. The alcohol was then evaporated from the starting materials in an oven at 373 K. Compositions of the starting materials are given in Table 7.2. The amount of Fe was carefully calculated to make sure that a small amount of Fe would remain even after reduction of Fe₂O₃ based on the reaction Fe₂O₃ + Fe \rightarrow 3FeO.

To minimize the absorption of water and the oxidation of Fe, starting materials were, immediately after preparation, tightly packed into low carbon Fe capsules (length = 15 mm, inner diameter = 3 mm, outer diameter = 6 mm). These Fe capsules were made from Fe tubing that was crimped at one end and arc welded under argon to avoid oxidation of the iron metal in air; the composition of this low carbon Fe tubing, analyzed by EPMA, is 99.4 wt. % Fe, 0.03 wt. % Mn, 0.01 wt. % Ni, 0.01 wt. % Cr, and 0.01 wt. % Si. Once filled with starting materials, capsules were quickly crimped to remove excess air as much as possible and sealed by arc welding under argon. Sealed Fe capsules were used to assure that the starting materials remained saturated with Fe. Experiments were performed in a DelTech® vertical tube furnace equipped with a dense alumina tube. Temperatures were measured using Pt₃₀Rh-Pt₆Rh (type B) thermocouples and PID-controlled within ±1 K. Argon gas was first passed at a rate of 20 ml/min through a Mg turning furnace to reduce its oxygen content from 27 x 10^{-5} to about 5 x 10^{-14} bar at 723 K and then passed through the vertical tube furnace to avoid oxidation of the Fe capsules during the entire duration of the experiments. The sealed Fe capsules, containing the starting materials, were wrapped in Ta foils, put in porous alumina boats, suspended by a Mo wire, and then placed in the hot zone of the vertical tube furnace; the Ta foil was employed to prevent reaction between the Fe capsules and the alumina boats. The vertical tube furnace was then heated up to 1473 K and kept at this temperature for 12 h. At this step, a large amount of Fe_2O_3 can be already reduced to FeO by reaction with the Fe powder. As mentioned above, an adequate amount of Fe powder was added to the starting materials to guarantee Fe saturation. After 12 h at 1473 K, samples were brought to the target temperatures (1673 or 1573 K) with a heating rate of 3 K/min, kept at equilibrium for 1 h, and quenched in water. Preliminary experiments showed that a duration of 1 h at the target temperatures was sufficient to reach equilibrium because a large quantity of liquid with a low viscosity was present in the samples.

EPMA elemental analysis and XRD phase analysis were performed on polished samples casted in
epoxy. Details of the analytical techniques employed are given in section 7.3.1.

7.4.2. Experimental results and discussion

Experimental conditions, observed phases, and phase compositions found in the samples equilibrated at Fe saturation at 1673 and 1573 K are summarized in Table 7.2. Equilibrium phases were homogeneously distributed in each sample, as shown in Fig. 7.1(b) for the representative sample NAf1-1. Run duration of 1 h at 1573 and 1673 K was enough to obtain homogenized products due to a large amount of liquid phase with high Na₂O and FeO concentrations (low viscosity).

BSE images of samples quenched after equilibration at 1673 K at Fe saturation are illustrated in Fig. 7.7. In all samples, metallic Fe droplets (white spots in the micrographs) were found which confirms that the samples were saturated with Fe. Quench crystals composed of Fe-rich phases were often observed in the glass phase due to the very low viscosity of the liquid during the experiments. Samples NAf1-1 (Fig. 7.7(a)) and NAf2-1 quenched to HT-Na(Al,Fe)O₂ + glass while samples NAf3-1 (Fig. 7.7(b)) quenched to HT-Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉ + spinel and samples NAf4-1, NAf5-1 (Fig. 7.7(c)) and NAf6-1 quenched to HT-Na(Al,Fe)O₂ + spinel + glass. Unfortunately, the glass composition of samples NAf4-1, NAf5-1 could not be analyzed because the glass pockets were too small. The only completely melted sample was NAf7-1, shown in Fig. 7.7(d); the dendritic quench crystals are seen in the entire solidified melt.

BSE images of experimental samples equilibrated at 1573 K are presented in Fig. 7.8. The twophase assemblage NaAlO₂ (with small solubility of Fe³⁺) + glass was found in sample NAf1-2, the three-phase assemblage HT-Na(Al,Fe)O₂ + spinel + glass was observed in samples NAf8-1 and NAf9-1 (Fig. 7.8(a)), and the single phase glass was seen in sample NAf7-2 (Fig. 7.8(b)).

The phase diagrams in equilibrium with metallic Fe at 1673 and 1573 K, constructed using the present experimental results, are depicted in Fig. 7.9. No ternary stoichiometric compound was found in this system in the experimental temperature and composition ranges studied. Although there is no measurement related to NaAl₉O₁₄ Na- β -alumina, this phase can be considered

stoichiometric because it has no significant Fe³⁺ solubility even in air. It should be noted that there are still noticeable solubility of Fe³⁺ in the NaAlO₂ meta-oxide and Na₂Al₁₂O₁₉ Na- β "-alumina phases even at Fe saturation. No miscibility gap in the Na₂Al₁₂O₁₉ Na- β "-alumina was observed because the solubility of Fe³⁺ in this phase at Fe saturation is lower than the immiscibility composition. The atomic ratio of Al/Fe in spinel was 1.45 ~ 1.58, which corresponds to 8 to 11 mole % of Fe₃O₄ in the FeAl₂O₄ spinel solution. No noticeable amount of Na₂O was detected in the spinel solution.

The liquidus of Na(Al,Fe)O₂ was relatively well constrained by the experimental data. In particular, the three-phase assemblage liquid + Na(Al,Fe)O₂ + spinel obtained at 1573 K clearly revealed the liquidus shape. As the composition of the liquid coexisting with Na(Al,Fe)O₂ and spinel at 1673 K could not be accurately analyzed in samples NAf4-1, NAf5-1 and NAf6-1 due to interferences with other phases, it was roughly estimated from the results obtained for sample NAf9-1 at 1573 K. It should be noted that the three-phase region liquid + Na(Al,Fe)O₂ + spinel exists at Fe saturation instead of the three-phase region liquid + Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉#2 in air. In addition, the phase assemblage Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉ + spinel at 1673 K also well constrained the general features of this system at Fe saturation. The small inconsistency observed between the tie-line of Na(Al,Fe)O₂ + spinel and the three-phase assemblage Na(Al,Fe)O₂ + Na₂(Al,Fe)₁₂O₁₉ + spinel (tie-line crossover) could be resolved by longer equilibration times. As the two-phase region between Na(Al,Fe)O₂ and spinel shrinks with increasing temperature, it is expected that Na₂Al₁₂O₁₉ Na- β "-alumina meets the liquid phase just above 1673 K even at Fe saturation.

7.5. Summary

The isothermal phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air (at 1583 and 1698 K) and in equilibrium with metallic Fe (at 1573 and 1673 K) were investigated, for the first time, using the quenching method followed by EPMA and XRD for phase analysis. General features of the phase diagrams of this system were well revealed. Several compatibility triangles of three-phase assemblages were identified. In particular, an extensive solid solution of Na₂(Al,Fe)₁₂O₁₉

 $Na-\beta''$ -alumina was observed and the existence of a miscibility gap in this solution was confirmed. In the part II of this study, the present experimental data will be used to optimize the thermodynamic properties and phase diagrams of the $Na_2O-FeO-Fe_2O_3-Al_2O_3$ system.

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Sample			-	Composition (v	Composition (mole fraction)					
Mol % ¹	Т	Duration	Phases ²	$N_{2} \cap (1-)^{3}$	A1 O (1-)	$E_{2} \cap (1_{-})$	Tatal	$N_{\rm e} O(1-)$		$E_{2} O_{1} (1 -)$
N A F	(K)	(h)		$Na_2O(1\sigma)^3$	$AI_2O_3(10)$	$Fe_2O_3(10)$	Total	$Na_2O(1\sigma)$	$AI_2O_3(10)$	$Fe_2O_3(10)$
NAF0-1	1698	1	N(A,F)	33.15 (1.08)	30.02 (5.92)	37.51 (6.27)	100.68	0.50 (0.00)	0.28 (0.05)	0.22 (0.04)
68.77 12.54 18.0	58		Glass	Not determined						
NAF1-1	1698	1	N(A,F)	32.03 (2.04)	28.09 (0.70)	41.09 (1.13)	101.21	0.49 (0.02)	0.26 (0.01)	0.25 (0.01)
57.64 14.02 28.	34		Glass	32.80 (0.67)	7.56 (1.78)	62.77 (2.01)	103.13	0.53 (0.01)	0.07 (0.02)	0.40 (0.01)
NAF2-1	1698	1	N(A,F)	33.60 (0.14)	31.04 (0.67)	37.14 (0.68)	101.78	0.50 (0.00)	0.28 (0.01)	0.22 (0.00)
50.63 23.67 25.	70		Glass	23.87 (4.75)	6.39 (3.01)	69.33 (6.81)	99.59	0.43 (0.05)	0.07 (0.03)	0.50 (0.08)
NAF3-1	1698	1	N(A,F)	35.67 (0.34)	40.31 (0.39)	26.03 (0.32)	102.01	0.51 (0.00)	0.35 (0.00)	0.14 (0.00)
44.98 24.86 30.	16		Glass	18.88 (3.78)	5.97 (1.04)	75.12 (3.79)	99.97	0.36 (0.06)	0.07 (0.01)	0.57 (0.06)
NAF4-1	1698	72	N(A,F)	34.18 (0.46)	51.97 (0.66)	9.38 (0.43)	95.53	0.49 (0.00)	0.46 (0.01)	0.05 (0.00)
36.02 43.79 20.	19		N(A,F) ₆ #1	10.39 (0.35)	62.37 (0.37)	29.01 (0.49)	101.77	0.17 (0.01)	0.64 (0.00)	0.19 (0.00)
			N(A,F) ₆ #2	6.64 (0.27)	17.60 (2.84)	73.08 (2.69)	97.32	0.15 (0.00)	0.23 (0.03)	0.62 (0.03)
NAF5-1	1698	72	Corundum	0.19 (0.32)	82.74 (1.63)	16.76 (0.61)	99.69	0.00 (0.01)	0.88 (0.01)	0.12 (0.00)
5.00 80.00 15.0	00		Spinel	0.14 (0.11)	20.20 (0.66)	79.66 (1.11)	100	0.00 (0.00)	0.28 (0.01)	0.72(0.01)
			N(A,F)6#1	13.37 (0.66)	65.43 (1.31)	21.56 (0.42)	100.36	0.22 (0.01)	0.65 (0.01)	0.13 (0.00)
NAF6-1	1698	1	Glass	19.35 (0.95)	4.55 (0.08)	75.38 (0.42)	99.28	0.38 (0.01)	0.05 (0.00)	0.57 (0.01)
38.35 5.83 55.8	82									
NAF7-1	1698	72	Spinel	0.49 (0.03)	10.12 (0.27)	90.36 (0.47)	100.97	0.01 (0.00)	0.15 (0.00)	0.84 (0.00)
15.00 52.50 32.5	50		Phase Y	7.80 (0.39)	54.54 (1.63)	38.24 (0.95)	100.58	0.14 (0.00)	0.59 (0.01)	0.27 (0.01)
			Phase X	7.45 (0.14)	49.49 (0.62)	43.83 (0.66)	100.77	0.14 (0.00)	0.55 (0.00)	0.31 (0.01)
NAF8-1	1698	1.5	N(A,F)6#2	7.22 (0.26)	18.66 (0.65)	73.63 (0.77)	99.51	0.15 (0.00)	0.24 (0.01)	0.61 (0.01)
26.83 21.95 51.2	22		N(A,F)+ Glass	26.60 (2.10)	17.90 (0.81)	57.40 (2.20)	101.9	0.44 (0.02)	0.18 (0.01)	0.38 (0.02)
NAF13-1	1698	48	Spinel	0.08 (0.02)	21.28 (0.17)	80.60 (0.42)	101.96	0.00 (0.00)	0.29 (0.00)	0.71 (0.00)
5.00 47.50 47.5	50		N(A,F) ₆ #1	11.52 (5.26)	66.77 (3.00)	22.33 (1.29)	100.62	0.19 (0.08)	0.67 (0.06)	0.14 (0.02)
NAF13-2	1698	48	Spinel	0.10 (0.02)	21.75 (0.28)	80.89 (0.32)	102.74	0.00 (.00)	0.30 (0.00)	0.70 (0.00)
5.00 47.50 47.5	50		N(A,F) ₆ #1	7.12 (1.19)	69.36 (0.64)	23.69 (0.61)	100.17	0.12 (0.02)	0.72 (0.02)	0.16 (0.01)
NAF9-1	1583	1	N(A,F)	33.51 (0.40)	31.35 (0.52)	36.88 (0.53)	101.74	0.50 (0.00)	0.28 (0.00)	0.22 (0.00)
44.40 10.80 44.8	80		Glass	16.15 (3.56)	3.85 (1.15)	77.36 (4.59)	97.36	0.33 (0.06)	0.05 (0.01)	0.62 (0.07)
NAF6-2	1583	1	N(A,F)	31.01 (1.06)	6.22 (1.97)	64.06 (2.65)	101.29	0.52 (0.01)	0.06 (0.02)	0.42 (0.02)
38.35 5.83 55.8	82		Glass	14.41 (1.04)	2.49 (0.58)	81.73 (0.95)	98.63	0.30 (0.02)	0.03 (0.01)	0.67 (0.02)
NAF10-1	1583	168	N(A,F)	33.92 (0.46)	51.21 (0.89)	13.56 (1.45)	98.69	0.48 (0.00)	0.44 (0.01)	0.08 (0.01)
36.34 41.72 21.9	94		N(A,F) ₆ #1	8.18 (0.08)	45.80 (0.64)	47.93 (0.78)	101.91	0.15 (0.00)	0.51 (0.01)	0.34 (0.01)
			N(A,F)6#2	8.09 (2.45)	14.36 (1.71)	75.48 (0.92)	97.93	0.17 (0.05)	0.19 (0.03)	0.64 (0.02)
NAF11-1	1583	168	N(A,F)	34.23 (0.44)	52.04 (1.28)	12.39 (1.21)	98.66	0.48 (0.00)	0.45 (0.01)	0.07 (0.01)
25.42 38.63 35.9	94		N(A,F) ₆ #1	8.55 (0.20)	48.81 (1.58)	44.94 (1.70)	102.3	0.15 (0.00)	0.53 (0.01)	0.32 (0.01)
			N(A,F) ₆ #2	7.80 (1.30)	16.99 (2.58)	75.54 (1.46)	100.33	0.16 (0.02)	0.22 (0.03)	0.62 (0.03)

Table 7.1: Experimental results of the Na₂O-Fe₂O₃-Al₂O₃ system in air.

NAF12-1	1583	168	Corundum	0.08 (0.23)	8.70 (0.15)	92.20 (0.58)	100.98	0.00 (0.01)	0.13 (0.00)	0.87 (0.00)
34.37 33.95 31.68			Phase Y	8.06 (0.30)	54.28 (1.84)	40.46 (1.77)	102.8	0.14 (0.00)	0.58 (0.01)	0.28 (0.01)
			Phase X	6.64 (0.17)	39.58 (1.14)	55.09 (1.32)	101.31	0.13 (0.00)	0.46 (0.01)	0.41 (0.01)

¹ Starting composition of sample: mol percent of Na₂O, Al₂O₃ and Fe₂O₃. ² N(A,F): Na(Al,Fe)O₂ and N(A,F)₆: Na₂(Al,Fe)₁₂O₁₉. ³ 1 σ : standard deviation

Sample		_	Duration (h)	Phases ²	Composition (wt. %)				Composition (mole fraction)		
Mol % ¹		T (K)									
N A	F	,			Na ₂ O (1 σ)	$Al_2O_3(1\sigma)$	$FeO(1\sigma)$	Total	Na ₂ O (1 σ)	$Al_2O_3(1\sigma)$	FeO(1o)
NAf1-1		1673	1	N(A,F)	34.67 (0.37)	54.74 (0.61)	4.02 (0.14)	93.43	0.49 (0.00)	0.47 (0.00)	0.04 (0.00)
36.26 22.04	41.70			Glass	20.59 (1.76)	1.65 (0.81)	67.39 (3.27)	89.63	0.26 (0.02)	0.01 (0.01)	0.73 (0.03)
NAf3-1		1673	1	N(A,F)	34.69 (0.83)	59.70 (0.70)	2.63 (0.56)	97.02	0.47 (0.01)	0.50 (0.01)	0.03 (0.01)
30.64 51.74	17.62			$N(A,F)_6$	10.06 (0.99)	80.60 (0.97)	10.61 (0.27)	101.27	0.15 (0.01)	0.72 (0.01)	0.13 (0.00)
				Spinel	1.54 (0.86)	52.24 (3.81)	47.30 (3.38)	101.08	0.02 (0.01)	0.43 (0.04)	0.55 (0.03)
NAf7-1		1673	1	Glass	15.00 (1.19)	5.00 (1.21)	80.00 (2.29)	100.00	0.17 (0.01)	0.03 (0.01)	0.80 (0.03)
17.23 3.49	79.28										
NAf4-1		1673	1	N(A,F)	34.91 (1.02)	60.81 (0.70)	2.69 (0.19)	98.41	0.47 (0.00)	0.50 (0.00)	0.03 (0.00)
13.58 45.41	41.01			Spinel	0.17 (0.18)	56.50 (0.82)	44.11 (0.48)	100.78	0.00(0.00)	0.47 (0.01)	0.53 (0.00)
				Glass	Too small to b						
NAf5-1		1673	1	N(A,F)	35.28 (0.85)	60.72 (0.73)	2.19 (0.05)	98.19	0.48 (0.01)	0.50 (0.01)	0.02 (0.00)
12.91 31.39	55.69			Spinel	0.10 (0.12)	56.80 (0.79)	44.93 (0.32)	101.83	0.00(0.00)	0.47 (0.00)	0.53 (0.00)
				Glass	Too small to be analyzed						
NAf6-1		1673	1	N(A,F)	36.69 (0.31)	61.14 (0.65)	3.02 (0.22)	100.85	0.48 (0.00)	0.49 (0.00)	0.03 (0.00)
16.97 35.72	47.31			Spinel	0.21 (0.15)	56.69 (0.85)	43.44 (0.29)	100.34	0.00(0.00)	0.48 (0.01)	0.52 (0.00)
				Glass	Too small to b	e analyzed					
NAf2-1		1673	1	N(A,F)	35.29 (0.16)	60.73 (0.26)	2.58 (0.17)	98.60	0.47 (0.00)	0.50 (0.00)	0.03 (0.00)
18.89 26.79	54.32			Glass	8.95 (1.11)	33.16 (0.51)	59.58 (1.03)	101.69	0.11 (0.01)	0.25 (0.00)	0.64 (0.01)
NAf1-2		1573	1	N(A,F)	37.16 (1.36)	54.48 (1.34)	6.44 (0.23)	98.08	0.49 (0.01)	0.44 (0.01)	0.07 (0.00)
36.26 22.04	41.70			Glass	25.95 (2.33)	1.70 (0.59)	70.42 (2.29)	98.07	0.30 (0.02)	0.01 (0.00)	0.69 (0.03)
NAf8-1		1573	1	N(A,F)	35.56 (0.37)	61.14 (0.56)	3.64 (0.30)	100.34	0.47 (0.00)	0.49 (0.00)	0.04 (0.00)
22.48 33.19	44.33			Spinel	0.58 (0.55)	52.14 (2.75)	47.70 (2.16)	100.42	0.01 (0.01)	0.43 (0.02)	0.56 (0.02)
				Glass	Too small to be analyzed						
NAf7-2		1573	1	Glass	15.00 (1.06)	5.00 (1.13)	80.00 (1.04)	100.00	0.17 (0.01)	0.03 (0.01)	0.80 (0.01)
17.23 3.49	79.28										
NAf9-1		1573	1	N(A,F)	35.39 (0.21)	60.47 (0.36)	2.87 (0.31)	98.73	0.47 (0.00)	0.49 (0.00)	0.04 (0.00)
9.27 18.78	71.95			Spinel	0.11 (0.13)	52.16 (0.94)	47.88 (0.61)	100.15	0.00 (0.00)	0.43 (0.01)	0.57 (0.01)
				Glass	10.00 (0.45)	14.39 (0.99)	77.68 (1.57)	102.07	0.12 (0.01)	0.10 (0.01)	0.78 (0.01)

Table 7.2: Experimental results of the Na₂O-FeO-Al₂O₃ system at metallic Fe saturation.

¹ Starting composition of sample: mol percent of Na₂O, Al₂O₃ and FeO. ² N(A,F): Na(Al,Fe)O₂ and N(A,F)₆: Na₂(Al,Fe)₁₂O₁₉.



(a)



(b)

Fig. 7.1: Backscattered electron images of samples (a) NAF3-1 at 1698 K in air and (b) NAf1-1 at 1673 K at Fe saturation.



(a)



(b)



(c)



(d)



(e)



(f)

Fig. 7.2: Backscattered electron images of experimental run products in the Na₂O-Fe₂O₃-Al₂O₃ system in air at 1698 K: (a) NAF2-1 (b) NAF6-1, (c) NAF4-1, (d) NAF5-1, (e) NAF8-1 and (f) NAF13-1. N(A,F) and N(A,F)₆ represent HT-Na(Al,Fe)O₂ and Na₂(Al,Fe)₁₂O₁₉, respectively.



(b)

Fig. 7.3: Backscattered electron images of experimental run products in the Na₂O-Fe₂O₃-Al₂O₃ system in air at 1583 K: (a) NAF10-1 and (b) NAF12-1.



Fig. 7.4: XRD pattern of quenched sample NAF4-1 equilibrated in air at 1698 K (the background was removed) confirming a miscibility gap of Na₂(Al,Fe)₁₂O₁₉.



(a)



(b)



Fig. 7.5: Microstructural evolutions of samples NAF7 equilibrated at 1698 K for (a) 5, (b) 24, (c) 48 and (d) 72 h in air for investigating the miscibility gap of Na₂(Al,Fe)₁₂O₁₉. The white particles in (c) and (d) are spinel solution.

(d)

10 µm



Fig. 7.6: Phase diagrams of the Na₂O-Fe₂O₃-Al₂O₃ system in air at (a) 1698 K and (b) 1583 K. The dashed-dotted lines are key experimental tie lines and three-phase assemblages. Thick solid lines, thin solid lines and dashed lines represent the estimated homogeneity ranges of different solid solution phases, the phase boundaries and the tie-lines, respectively. L, N(A,F), N(A,F)₆, Spl and Crn represent liquid, Na(Al,Fe)O₂, Na₂(Al,Fe)₁₂O₁₉, spinel and corundum, respectively.



(a)



(b)



Fig. 7.7: Backscattered electron images of experimental run products in the Na₂O-FeO-Al₂O₃ system (at Fe saturation) at 1673 K, (a) NAf1-1, (b) NAf3-1, (c) NAf5-1, and (d) NAf7-1.



Fig. 7.8: Backscattered electron images of experimental run products in the Na₂O-FeO-Al₂O₃ system (at Fe saturation) at 1573 K: (a) NAf9-1 and (b) NAf7-2.



Fig. 7.9: Phase diagrams of the Na₂O-FeO-Al₂O₃ system at Fe saturation at 1673 K and (b) 1573 K. The dashed-dotted lines are key experimental tie lines and three-phase assemblages. Thick solid lines, thin solid lines and dashed lines represent the estimated homogeneity ranges of different solid solution phases, the phase boundaries and the tie-lines, respectively.

Chapter 8

PAPER 4: COUPLED EXPERIMENTAL AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃-AI₂O₃ SYSTEM: PART 2. THERMODYNAMIC OPTIMIZATION

Elmira Moosavi-Khoonsari and In-Ho Jung, *Journal of the American Ceramic Society*, 2015 (accepted).

8.1. Abstract

A complete thermodynamic description of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system was conducted based on the critical evaluation and optimization of available thermodynamic properties and phase diagram data. The thermodynamic behavior of the liquid solution was described using the Modified Quasichemical Model, and the solid solutions Na(Al,Fe)O₂ meta-oxides and Na₂(Al,Fe)₁₂O₁₉ Na- β "-alumina were modeled using the Compound Energy Formalism considering their sublattice structures. Most experimental phase diagram data at reducing and oxidizing conditions were reproduced within 3 mol % of compositional error ranges. Many unexplored phase diagrams of this system under different oxygen partial pressures were predicted within the estimated accuracy of ± 5 mol % in composition and ± 50 K in temperature from the present thermodynamic models with optimized parameters.

8.2. Introduction

In the first part [1] of this series, the phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air and at metallic Fe saturation were experimentally investigated. In order to obtain the maximum amount of phase diagram information using the minimum amount of experiments, key experimental compositions were selected from phase diagrams predicted using the preliminary thermodynamic database of binary and ternary subsystems. In particular, key phase diagram compositions were designed to obtain three-phase or two-phase assemblages.

In the current study, the thermodynamic optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system was conducted based on the present experimental results and literature data. As very few experimental phase diagram studies are available, thermodynamic models with optimized model parameters were used to predict many unexplored phase diagrams at different oxygen partial pressures. This work is part of a large thermodynamic database development for the Na₂O-FeO-Fe₂O₃-Al₂O₃-Al₂O₃-SiO₂-CaO-MgO system.

8.3. Phases and thermodynamic models for the Na₂O-FeO-Fe₂O₃-Al₂O₃ system

Figure 8.1 is the schematic presentation of stoichiometric compounds and solid solutions reported in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system at 1 atm total pressure. There are total 11 stoichiometric phases, six solid solutions (FeO wüstite, FeAl₂O₄-Fe₃O₄ spinel, Fe₂O₃-Al₂O₃ corundum, two kinds of NaFeO₂-NaAlO₂ meta-oxides, and Na₂Al₁₂O₁₉ Na- β "-alumina), and the liquid solution in this system. Thermodynamic models applied to describe the solid and liquid solutions are summarized below.

8.3.1. Solid oxide phases

8.3.1.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{8-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{8-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(8-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given compound from pure elements at 298 K (ΔH_{298K}^{o} of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy at 298 K, and C_{p} is the heat capacity of a compound.

Gibbs energies of solid Na₂O, FeO, Fe₂O₃, Al₂O₃, all stoichiometric compounds and end-members of all solid and liquid solutions were described using these thermodynamic equations. Gibbs energies of stoichiometric compounds were optimized in the previous studies [2-4], and taken in this work without any further modification.

8.3.1.2. Meta-oxide solid solutions

There are two kinds of NaAlO₂-NaFeO₂ meta-oxide solid solutions, which were modeled within the framework of the Compound Energy Formalism (CEF). The high- and intermediate-temperature meta-oxide solid solutions can be structurally formulated as Na^{Na}[Al, Fe]^MO₂ and (NaAl, NaFe)O₂, respectively, considering the structural information [5-6]. Both phases are complete solid solutions. The intermediate-temperature meta-oxide has a tendency to form a miscibility gap. This will be discussed later.

As the effective mixing in both meta-oxide solutions occurs only on one sublattice, both solutions can be described using one-sublattice CEF:

$$G_{soln} = y_i G_i^o + y_j G_j^o + RT(y_i \ln y_i + y_j \ln y_j) + \sum_n {}^n L_{ij} y_i y_j (y_j - y_i)^n$$
(8-4)

where G_i^o is the Gibbs energy of the end-member *i* of the solution, and y_i is the site fraction of the species *i*. *R* and *T* are gas constant and temperature in kelvin, and ${}^nL_{ij}$ are the excess interaction parameters.

The Gibbs energies of both solutions' end-members can be taken from stoichiometric NaAlO₂ and NaFeO₂. It should be noted that NaAlO₂ has two polymorphs, α (low-temperature) and β (high-temperature), while NaFeO₂ has three polymorphs, α (low-temperature), β (intermediate-temperature) and γ (high-temperature). β -NaAlO₂ and γ -NaFeO₂, having the tetragonal crystal structure, form a complete solid solution between each other. This solution is designated as high-temperature meta-oxide in this study. The solid solution between α -NaAlO₂ and β -NaFeO₂, having orthorhombic crystal structure, is called intermediate-temperature meta-oxide. α -NaFeO₂ is treated as a stoichiometric compound in the current study.

8.3.1.3. Na- β "-alumina solid solution

As experimentally reported in the first part¹ of this series, a large solubility of Fe³⁺ was observed in Na₂Al₁₂O₁₉ Na- β "-alumina by replacing Al³⁺. This solution can be structurally written as Na₂[Al,Fe]₁₂O₁₉. Therefore, one-sublattice model described in Eq. (8.4) was applied to treat this solution. The Gibbs energy of the Na₂Al₁₂O₁₉ end-member was directly taken from the Gibbs energy of Na- β "-alumina. As the end-member Na₂Fe₁₂O₁₉ is unstable in the Na₂O-Fe₂O₃ system in air, its Gibbs energy is one of main model parameters determining the solubility of Fe³⁺ in this solution. The Gibbs energy of the Na₂Fe₁₂O₁₉ end-member was determined as $G_{Na_2Fe_{12}O_{19}}^o = 2G_{NaFeO_2}^o + 5G_{Fe_2O_3}^o + G_{add}$, where G_{add} is the model parameter.

8.3.1.4. Other solid solutions

In the Na₂O-FeO-Fe₂O₃-Al₂O₃ system, there are also spinel [2], corundum [2], and wüstite (monoxide) [4] solutions. The Gibbs energies of these solutions were already optimized in the previous studies and prior descriptions were adopted in the present study without any further modification.

8.3.2. Liquid oxide phase

The Gibbs energy of liquid solution was described using the Modified Quasichemical Model (MQM) [7]. The sub-binary Na₂O-Al₂O₃ [3] and sub-ternary Na₂O-FeO-Fe₂O₃ [4] and Al₂O₃-FeO-Fe₂O₃ [2] liquid solutions were previously optimized using the MQM. The so-called charge compensation effect was reported in the Na₂O-Al₂O₃-SiO₂ and Na₂O-Fe₂O₃-SiO₂ melts [8,9]. That is, when both Na⁺ and Al³⁺ (or Fe³⁺) coexist in SiO₂-rich melts, NaAl⁴⁺ (or NaFe⁴⁺) can replace Si⁴⁺ to enhance the polymerization of silicate melts. Therefore, NaAl⁴⁺ and NaFe⁴⁺ associates were also taken into account for the description of the Na₂O-Al₂O₃³ and Na₂O-Fe₂O₃⁴ binary liquid solutions, respectively.

In the MQM, the following quasichemical reaction in the oxide melt can be considered:

$$(A - A) + (B - B) = 2(A - B)$$
: Δg_{AB} (8-5)

where A and B are cationic species in the solution, and (A - B) represents a second-nearestneighbour A-B pair containing oxygen anion in-between. The Gibbs energy of the above reaction Δg_{AB} is the model parameter which can be expanded as an empirical function of composition. Therefore, the Gibbs energy of the solution is given by:

$$G_{soln} = \left(n_A g_A^{\ o} + n_B g_B^{\ o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right) \Delta g_{AB}$$
(8-6)

where n_i and g_i^o are the number of moles and molar Gibbs energies of liquid oxide components and n_{AB} is the number of moles of (A – B) bonds at equilibrium. ΔS^{config} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation, and Δg_{AB} can be expressed by the pair fraction, X_{ij} :

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge I} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge I} g^{0j}_{AB} X^{j}_{BB}$$
(8-7)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature. Details of the MQM can be found elsewhere.⁷

Cationic species (A and B in Eq. (8.5)) considered in the Na₂O-FeO-Fe₂O₃-Al₂O₃ solution are Na⁺, Fe^{2+} , Fe^{3+} , Al^{3+} , $NaAl^{4+}$ and $NaFe^{4+}$. Gibbs energies of liquid $NaO_{0.5}$ (1/2 Na_2O), FeO, FeO_{1.5} (1/2 Fe₂O₃) and AlO_{1.5} (1/2Al₂O₃) were taken from the FACT pure substance database [10]. Gibbs energies of NaAlO₂ [3] and NaFeO₂ [4] liquid associates were adopted from the previous optimizations. Fifteen possible quasichemical reactions were considered. The previously optimized Na⁺-Al³⁺ [3], Al³⁺-NaAl⁴⁺ [3], Fe²⁺-Fe³⁺ [11], Fe²⁺-Al³⁺ [2], Fe³⁺-Al³⁺ [2], Na⁺-Fe²⁺ [4], and Na⁺-Fe³⁺ [4] quasichemical reactions for the respective binary solutions were taken into account in the present optimization. The rest of binary reactions were considered ideal solutions where $\Delta g_{AB} = 0$. There are twenty ternary liquid systems within the NaO_{0.5}-FeO-FeO_{1.5}-AlO_{1.5}-NaAlO₂-NaFeO₂ solution. The Gibbs energies of the liquid solutions NaO_{0.5}-FeO_{1.5}-AlO_{1.5} and FeO_{1.5}-NaAlO₂-NaFeO₂ (in terms of components: NaO_{0.5}, FeO_{1.5}, AlO_{1.5}, NaAlO₂ and NaFeO₂) were calculated from binary and ternary model parameters using a geometric model [12]. The model parameters of the liquid solutions NaO_{0.5}-FeO-FeO_{1.5} and NaO_{0.5}-FeO-NaFeO₂ (in terms of components: NaO_{0.5}, FeO, FeO_{1.5} and NaFeO₂) were taken from the previous study [4]. The rest of ternary reactions were considered ideal solutions. The NaO_{0.5}-FeO-FeO_{1.5} [4] and NaO_{0.5}-NaAlO₂-NaFeO₂ systems were treated using 'Toop' type approximation with NaO_{0.5} as the 'asymmetric component'. The NaO_{0.5}-FeO-NaAlO₂ and AlO_{1.5}-FeO-NaAlO₂ systems were treated using 'Toop' type model with NaAlO₂ as the 'asymmetric component'. The AlO_{1.5}-NaAlO₂-NaFeO₂ and FeO_{1.5}-NaAlO₂-NaFeO₂ systems were treated using 'Toop' type approximation with AlO_{1.5} and FeO_{1.5} as the 'asymmetric components', respectively. The rest of ternary systems were treated using the symmetric 'Kohler' type model. Details of ternary geometric models can be found elsewhere [12].

8.4. Metallic and gas phases

In order to calculate phase equilibria at metallic saturation, metallic solid and liquid phases of Fe and Na were taken from FACT pure substance database [10]. Gibbs energies of gas species were also taken from FACT pure substance database.

8.5. Critical evaluation and optimization

All experimental data in the literature and our new experimental results presented in the first part [1] of this series under oxygen partial pressures ranging from metallic saturation to air were critically evaluated. As a result, one set of optimized thermodynamic model parameters were obtained to reproduce all reliable thermodynamic properties and experimental phase diagram data within the experimental error limits. The optimized model parameters are listed in Table 8.1. Strictly speaking, there are certain amounts of Fe³⁺-containing oxides (up to about 15 % of total Fe oxides) in molten state even at metallic Fe saturation and also Fe²⁺-containing oxides (up to about 15 % of total Fe oxides) in air. However, for the sake of simplicity, the notations of the Na₂O-Fe₂O₃-Al₂O₃ and Na₂O-FeO-Al₂O₃ systems were used below to represent oxidizing and reducing conditions, respectively.

8.5.1. The Na₂O-Fe₂O₃-Al₂O₃ system in air

Mazel and Astanovitzkaia [13] studied chemical reactions between Na₂O, Fe₂O₃ and Al₂O₃, and reported the formation of homogeneous crystals on the NaFeO₂-NaAlO₂ join. Following their finding, Toropov and Shishacow [14] investigated this system using the quenching method followed by optical microscopy and XRD phase analysis, and observed the NaAlO₂-NaFeO₂ solid solution. Arakelyan [15] also reported the presence of complete NaFeO₂-NaAlO₂ solid solution on the NaFeO₂-NaAlO₂ section using thermal analysis and XRD phase analysis. Arakelyan [16] further investigated the NaAlO₂-Fe₂O₃ and NaFeO₂-Al₂O₃ joins at 1523 K using the same techniques and found a non-stoichiometric hexagonal structured phase at low Na₂O region (7.3-7.4 Na₂O, 18.1-51.4 Al₂O₃, and 74.5-41.2 Fe₂O₃ in mol%). From the similarity of the XRD pattern of the new phase to that of Na- β -alumina NaAl₁₁O₁₇, he reported that this new phase would be the mixture of Na- β -alumina and hypothetical Na- β -ferrite NaFe₁₁O₁₇. Later, Arakelyan [17] concluded the reversible polymorphic phase transition of the NaFeO₂-NaAlO₂ and the NaAl₁₁O₁₇-NaFe₁₁O₁₇ solid solutions. He also mentioned that there is a large miscibility gap in the latter solution, similar to that of the Al₂O₃-Fe₂O₃ corundum solution. Using dilatometry technique, Thery et al. [18] studied the sub-solidus phase diagram of the NaAlO₂-NaFeO₂ system. They also reported continuous series of solid solutions with reversible polymorphic transformation along the entire composition range. Nurmagambetov et al. [19] found the complete NaFeO₂-NaAlO₂ solid solution using thermal analysis and XRD. Kennedy and Sammells [20] implied the existence of Na- β -alumina solid solution at 1373 K in the compositional range 8.3 Na₂O, 36.7-50.4 Al₂O₃, 55.0-41.3 Fe₂O₃ in mol %, but the equilibration was conducted only for 1 to 24 h. Kennedy and Stuber [21] reconfirmed the formation of Na- β -alumina, but also reported that the amount of Na- β "-alumina increased with increasing Fe level in starting materials. Using the quenching method and XRD phase analysis, Roland et al. [22] also investigated phase equilibria of the Na₂O-Fe₂O₃-Al₂O₃ system in air from 1473 to 1873 K for a wide range of compositions, Na₂O·y(Al_{1-x}Fe_x)₂O₃, where y = 2.5-9.0 and x = 0.05-0.6. Partial melting of the system was observed for compositions with x > 0.33 and y > 4.7 at 1873 K and x > 0.5 and y > 4 at 1773 K. The Na- β "-alumina and Na- β -alumina solutions, and Fe₂O₃ (or Fe₃O₄) were also reported above 1573 K. However, in general, it is doubted whether Roland et al. [22] reached equilibrium because samples were annealed only for 2 to 18 h, and XRD phase analyses were carried out on non-equilibrium samples.

The present experimental phase diagram data at 1698 and 1583 K showed that there is a large miscibility gap in the Na-\beta"-alumina Na2(Al,Fe)12O19 solid solution [1]. The three-phase equilibria meta-oxide + Na- β "-alumina#1 + Na- β "-alumina#2, several tie lines for two-phase assemblages, and liquidus compositions were identified. The homogeneity range of Na-B-alumina Na(Al,Fe)₉O₁₄ solid solution was not well investigated, but if this phase existed, only less than 10 mol % of Al³⁺ would be replaced by Fe³⁺ at about 1573 to 1698 K based on the experimental phase relation at high Al₂O₃ region. A large homogeneity range of the high temperature meta-oxide solution HT-Na(Al,Fe)O2 was also observed. Moreover, no ternary compounds were found in the Na₂O-Fe₂O₃-Al₂O₃ system in air in the compositional and temperature ranges studied. The present equilibration experiments were carried out up to 168 h to attain solid state equilibria even at higher temperatures than those of most previous studies, and all samples were analyzed by means of XRD and EPMA. Therefore, the current experimental results are considered to be more reliable, especially for the Na-β-alumina and Na-β"-alumina solutions. That is, the large solid solution of Na-β-alumina reported in the previous studies [20-22] would result from the wrong interpretation of Na- β "-alumina solution or metastability of the system due to relatively short equilibration duration.

In the current thermodynamic optimization, the complete meta-oxide solid solutions Na(Al,Fe)O₂, the Na- β "-alumina Na₂(Al,Fe)₁₂O₁₉ solid solution with a large miscibility gap, the stoichiometric Na- β -alumina NaAl₉O₁₄ and the liquid solution were considered along with all other phases existing in the binary and ternary subsystems. The present experimental phase diagram data were mainly employed to optimize the liquid phase and Na- β "-alumina solid solution. Unfortunately, no experimental thermodynamic data for the Na₂O-Fe₂O₃-Al₂O₃ system in air are available.

Figure 8.2 shows the calculated phase diagrams of the NaAlO₂-NaFeO₂ (meta-oxide) and the Na₂Al₁₂O₁₉-Na₂Fe₁₂O₁₉ (Na- β "-alumino-ferrite) sections. The phase transition between intermediate and high-temperature meta-oxides measured by Arakelyan [15], Thery [18] and Nurmagambetov et al. [19] reveals nearly a linear behavior from NaAlO₂ to NaFeO₂, as seen in Fig. 8.2(a). The optimized phase diagram is in good agreement with the experimental data on the phase transition of meta-oxide solutions. It should be noted that α -NaFeO₂ with rhombohedral crystal structure is considered to be a stoichiometric phase [23]. In the thermodynamic optimization of the meta-oxides, an asymmetric positive parameter was intentionally introduced for each solution to take into account the interaction between Fe³⁺ and Al³⁺, similar to the Al₂O₃-Fe₂O₃ corundum and Na- β "-alumina solutions. No direct liquidus information is available on the NaAlO₂-NaFeO₂ join. However, based on our experimental phase diagram data, we could roughly estimate the solidus and liquidus at 1698 K, which were reasonably reproduced in the calculated phase diagram (Fig. 8.2(a)).

There is very few phase diagram information on the Na₂Al₁₂O₁₉-Na₂Fe₁₂O₁₉ join. The present experimental results at 1698 and 1583 K are the only reasonable data available in this system. The current experimental investigation revealed that the Na- β "-alumina solid solution has a large immiscibility [1], and the formation of the misciblity gap is kinetically very slow. The only reliable result we could obtain to define the gap size in the Na- β "-alumina solid solution was the threephase assemblage meta-oxide + Na- β "-alumina#1 + Na- β "-alumina#2 at 1698 K. Typically, the full development of the miscibility gap is inhibited by low thermodynamic driving force, and the phase separation ends up at the spinodal composition. Even after annealing for 168 h at 1583 K, the miscibility gap was not fully developed, as discussed in the first part [1] of this series. The gap size determined from several two- and three-phase assemblages at 1698 K was more reliable. The calculated Na₂Al₁₂O₁₉-Na₂Fe₁₂O₁₉ phase diagram, illustrated in Fig. 8.2(b), reasonably describes the miscibility gap which was experimentally measured. The liquidus and peritectic temperatures of the Na₂Fe₁₂O₁₉-rich β "-alumina solution are pure estimation from the present thermodynamic optimization The calculated diagram would be accurate within the error range of ± 5 mol % in composition and ± 50 K in temperature.

The calculated phase diagrams of the Na₂O-Fe₂O₃-Al₂O₃ system in air at 1698 and 1583 K are illustrated in Fig. 8.3 along with the present experimental data. Overall, the experimental data were well reproduced at both temperatures, with the exception of the meta-oxide composition in the three-phase assemblage meta-oxide + Na- β "-alumina#1 + Na- β "-alumina#2. Lower amounts of NaFeO₂ are expected than the current optimization results. In order to reproduce the experimental data, more positive interaction parameters in the meta-oxide solutions were required, which induced the miscibility gap in meta-oxide solution to appear in phase transition of meta-oxides. Furthermore, the three-phase equilibrium meta-oxide + Na- β "-alumina + spinel at Fe saturation was well described with the current optimized parameters. Therefore, we did not introduce more positive interaction parameters for the meta-oxide solutions. The composition of spinel solution in the three-phase assemblage Na- β "-alumina#1 + corundum + spinel at 1698 K was about 2.5 to 5 mol % off from the experimental data; this originated from the discrepancy about the compositional homogeneity range of the spinel solution in the Al₂O₃-Fe₂O₃ binary system. Most tie-lines of two-phase equilibria and the liquidus compositions were well represented by the calculations.

The thermodynamic description of Na₂Fe₁₂O₁₉-rich β "-alumina with a large miscibility gap was the most difficult part of this study. Na₂Fe₁₂O₁₉ is one of the solution end-members, which is unstable in the Na₂O-Fe₂O₃ binary system in air. Hence, its Gibbs energy was estimated slightly higher Gibbs energy of stable than the the phase assemblage 'NaFeO₂ + Fe₂O₃' ($_{2G_{NaFeO_2}(\gamma)}^{o}$ + $5G_{Fe_2O_3}^{o}$). The miscibility gap in the solution was reasonably determined only at 1698 K; its temperature dependence could not be well constrained, unfortunately. In order to describe the extent of immiscibility in the Na-β"-alumina solid solution, two temperature-independent interaction parameters were required. There is certainly room to

improve the description of the Na- β "-alumina solid solution with more experimental data. One small ternary model parameter for each Fe₂O₃-NaFeO₂-NaAlO₂ and Na₂O-Fe₂O₃-Al₂O₃ liquid solution was introduced to reproduce the liquidus of the present system.

Using the present thermodynamic models with optimized parameters, the predicted isothermal phase diagrams at 1873 and 1773 K, and the liquidus projection of the Na₂O-Fe₂O₃-Al₂O₃ system in air are depicted in Fig. 8.4. As seen in Figs. 8.4(a and b), Na₂Fe₁₂O₁₉-rich β "-alumina noticeably destabilizes with temperature increment so that it completely disappears at 1873 K while it is still in equilibrium with the liquid solution at 1773 K. The estimated liquidus projection shows the wide primary crystallization fields of meta-oxide and Na- β "-alumina solutions. Although no experimental data are available to validate the calculations, it is expected from our experience that the predicted phase diagrams would be accurate within the error range of ± 5 mol % in composition and ± 50 K in temperature.

8.5.2. The Na₂O-FeO-Al₂O₃ system at Fe saturation

Less experimental results than those reported in air are available in the Na₂O-FeO-Al₂O₃ system at Fe saturation. No thermodynamic property or phase diagram data related to this system were reported in the literature, with the exception of those from Grigoreva et al. [24]. Grigoreva et al. investigated the phase diagram of the NaAlO₂-FeO section in equilibrium with Fe at 1723 K using the quenching method and XRD phase analysis. They reported that this system is a simple eutectic. However, their experimental results are doubtable because they observed the solid wüstite (FeO) in XRD patterns of quenched samples. It is well known that wüstite melts at 1642 K at Fe saturation. This means that their samples were improperly quenched, and quenched crystals were not appropriately distinguished from stable crystals to obtain accurate phase equilibria at 1723 K. Furthermore, final compositions of samples could be different from initial compositions since the evaporation of Na₂O could be significant in this system, as witnessed in our experimental studies. Therefore, the results of Grigoreva et al. [24] were not taken into account in the present optimization. The thermodynamic optimization of the Na₂O-FeO-Al₂O₃ system at Fe saturation was carried out based on our new experimental phase diagram data at 1673 and 1573 K¹.

The calculated phase diagrams of the Na₂O-FeO-Al₂O₃ system at Fe saturation at 1673 and 1573 K are presented in Fig. 8.5 along with the experimental data obtained in this study. The measured solubility limit of NaFeO2 in NaAlO2 meta-oxide and that of Na2Fe12O19 in Na2Al12O19 Na-B"alumina are about 2.5 and 12 mol %, respectively, which were well reproduced in the present optimization. In comparison with the experimental results in air, the Fe³⁺ solubility in both solid solutions is much smaller in equilibrium with Fe. In particular, the Na₂Fe₁₂O₁₉-rich β "-alumina solution is not stable at Fe saturation. The three-phase equilibria meta-oxide + spinel + liquid and meta-oxide + spinel + Na- β "-alumina were well reproduced at both 1673 and 1573 K. The calculated phase diagram at 1673 K (Fig. 8.5(a)) reveals a very narrow two-phase region metaoxide + spinel, which is in agreement with the experimental data. According to the calculations, this two-phase region disappears at 1675 K and the two-phase field Na- β "-alumina + liquid appears above 1675 K. The liquidus compositions of meta-oxide experimentally measured in the current study were also well represented. Since thermodynamic model parameters for both meta-oxide and Na-B"-alumina solid solutions were already determined in the optimization of the Na₂O-Fe₂O₃-Al₂O₃ system in air, the only solution optimized at metallic Fe saturation was the liquid phase. A small positive quasichemical reaction energy term between FeO and NaAlO₂ and a small positive ternary parameter for the Na₂O-FeO-Al₂O₃ liquid were introduced to reproduce the liquidus of this system. All liquidus compositions were reproduced within $\pm 3 \mod \%$.

Figure 8.6 illustrates the predicted phase diagrams of the NaAlO₂-FeO and NaAlO₂-Na₂FeO₂ systems at Fe saturation. The calculated NaAlO₂-FeO phase diagram (Fig. 8.6(a)) shows rather complex sub-solidus phase equilibria. However, a eutectic type melting behavior is observed, which qualitatively agrees with the report from Grigoreva et al. [24] in spite of their questionable results in terms of temperature and composition. The NaAlO₂-Na₂FeO₂ phase diagram presents the formation of liquid phase even at about 910 K (Fig. 8.6(b)).

The calculated phase diagrams of the Na₂O-FeO-Al₂O₃ system at Fe saturation, illustrated in Fig. 8.7, reveal wider liquid regions than those in air at equal temperatures. It should be also noted that the Na- β -alumina NaAl₉O₁₄ phase rather than the Na- β "-alumina solution is in equilibrium with the liquid solution at 1873 K (Fig. 8.7(a)). The predicted liquidus projection (Fig. 8.7(c)) shows a large primary crystallization region of Na- β -alumina and a very small field of Na- β "-alumina. The

estimated primary crystallization region of meta-oxide at Fe saturation is even wider than that in air. Similar to the calculations in air, the calculated diagrams would be accurate within the error range of \pm 5 mol % in composition and \pm 50 K in temperature.

8.6. Discussions

The current thermodynamic optimization was based on well-defined descriptions of sub-binary and sub-ternary systems, and limited phase diagram data available in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system around 1573 and 1673 K. As the Gibbs energies of all phases present in sub-binary and sub-ternary systems were well optimized based on a large amount of experimental phase diagram and thermodynamic property data [1-3], the calculations in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system would be still quite reliable even with a few amounts of phase diagram data in this quaternary system. Moreover, the present thermodynamic description was already tested in the higher order system Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂, and accurate predictions of phase diagram data [25-29], especially in air.

However, there is certainly room to improve the thermodynamic description of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system. For example, further phase diagram experiments regarding the miscibility gap in the Na- β "-alumina solid solution are necessary to better constrain the Gibbs energy of the Na- β "-alumina phase, which is considered to be a potential candidate for solid solution electrodes in electrochemical cells [20, 22, 30]. The inhomogeneity range of Na- β -alumina phase should be also further investigated. The liquidus above 1673 K has not been studied yet.

A coupled experimental phase diagram study and thermodynamic modeling approach can be an efficient way to investigate phase diagrams and thermodynamic properties of multicomponent systems with minimum experimental efforts. Of course, to select key experimental compositions and temperatures, preliminary thermodynamic descriptions of binary and ternary subsystems are necessary. In this study, about 20 well-designed key experimental phase diagram data were employed to optimize the thermodynamic model parameters, which allow reasonably accurate

predictions of complex phase equilibria in a broad range of temperatures, compositions and oxygen partial pressures. One of great advantages of this approach is the development of a consistent thermodynamic database which can describe all thermodynamic properties and phase diagrams in the entire composition and temperature ranges from unary to multicomponent systems.

8.7. Summary

The thermodynamic optimization of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system was conducted based on the critical evaluation of the literature data and the key phase diagram results obtained in the present study. All reliable phase diagram data in this system under oxidizing (in air) and reducing (at Fe saturation) conditions were well described using the thermodynamic models with optimized parameters. Experimentally unexplored phase diagrams and liquidus projections under both oxidizing and reducing conditions were predicted within the accuracy of \pm 5 mol % in composition and \pm 50 K in temperature. In particular, it was shown that a coupled key phase diagram experiments and thermodynamic modeling can be an efficient methodology to obtain a full description of phase equilibria in multicomponent systems with minimum amount of experiments. However, further experimental studies may improve the accuracy of phase equilibria in this system.

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Table 8.1: Optimized model parameters of solutions in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system (J/mol and J/mol-K).

Liquid solution (NaO0.5-FeO-FeO1.5-NaFeO2-NaAlO2-AlO1.5)*

$$\begin{split} & Z_{Na \ Na}^{Na} = 0.68872 \ , \ Z_{Fe(II)}^{Fe(II)} = 1.37744 \ , \ Z_{Fe(III)}^{Fe(III)} = 2.06617 \ , \ Z_{NaFe \ NaFe}^{NaFe} = 2.75489 \ , \\ & Z_{NaAl \ NaAl}^{NaAl} = 2.75489 \ , \ Z_{AlAl}^{Al} = 2.06617 \\ & G_{NaAlO_2}^o = 1/2 (G_{Al_2O_3(1)}^o + G_{Na_2O(1)}^o) - 101218.03096 + 17.93262T \\ & q_{Fe(III),NaFe;NaAl}^{001} = 20920 \\ & q_{Na,Fe(III);Al}^{001} = 16736 \\ & \Delta g_{Fe(II),NaAl} = 14644 \\ & q_{Al,Na;Fe(II)}^{001} = 14644 \\ \\ & \mathbf{Meta-oxide\ solid\ solutions} \\ \\ & \text{High-temperature\ Na^{Na}[A1, Fe]^{M}O_2: \ {}^{I}L_{Al,Fe} = 12552 \\ \\ & \text{Intermediate-temperature\ (NaAl, NaFe)O_2: \ {}^{I}L_{NaAl,NaFe} = 12552 \end{split}$$

Na-β"-alumina solid solution

 ${}^{l}L_{Al,Fe;Na} = -251040, \; {}^{2}L_{Al,Fe;Na} = -669440$

* Gibbs energies of other pure stoichiometric species and model parameters were taken from the previous optimizations. ^{2-4, 10, 11}



Fig. 8.1: Schematic presentation of solid phases in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system.



Fig. 8.2: Phase diagrams of the (a) NaAlO₂-NaFeO₂ and (b) Na₂Al₁₂O₁₉-Na₂Fe₁₂O₁₉ joins calculated from optimized model parameters in comparison with the experimental data [1, 15, 18, 19]. The arrow indicates the possible equilibrium direction of immisibility composition. L, HT-N(A,F), IT-N(A,F), NF(α), NA₉, N(A,F)₆, Crn and N₃F₅ represent liquid, high-temperature Na(Al,Fe)O₂, intermediate-temperature Na(Al,Fe)O₂, NaFeO₂(α), NaAl₉O₁₄, Na₂(Al,Fe)₁₂O₁₉, corundum and Na₃Fe₅O₉, respectively.



Fig. 8.3: Optimized isothermal phase diagrams of the Na₂O-Fe₂O₃-Al₂O₃ system calculated in air at (a) 1698 K and (b) 1583K along with the experimental data [1]. Spl represents spinel.



(a)



(b)



Fig. 8.4: Predicted isothermal phase diagrams at (a) 1873 K and (b) 1773 K, and (c) the liquidus projection of the Na₂O-Fe₂O₃-Al₂O₃ system in air.



Fig. 8.5: Optimized isothermal phase diagrams of the Na₂O-FeO-Al₂O₃ system at metallic Fe saturation along with the experimental data [1] at (a) 1673 K and (b) 1573 K. Wüs represents wüstite.



Fig. 8.6: Predicted (a) NaAlO₂-FeO and (b) NaAlO₂-Na₂FeO₂ isopleths of the Na₂O-FeO-Al₂O₃ system at Fe saturation. N₂F, NF, N₃F represent Na₄FeO₃, Na₂FeO₂ and Na₃FeO₃, respectively.





Fig. 8.7: Predicted isothermal phase diagrams at (a) 1873 K and (b) 1773 K, and (c) the liquidus projection of the Na₂O-FeO-Al₂O₃ system at metallic Fe saturation.

Chapter 9 PAPER 5: CRITICAL EVALUATION AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ SYSTEM

Elmira Moosavi-Khoonsari and In-Ho Jung, Submitted to *Journal of the European Ceramic* Society, 2015.

9.1. Abstract

A comprehensive literature review, critical assessment and thermodynamic optimization of phase diagrams and thermodynamic properties of the entire Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system were carried out at 1 atm total pressure. A set of optimized model parameters obtained for all phases present in this system reproduces available and reliable thermodynamic property and phase equilibrium data within experimental error limits from 298 K to above liquidus temperatures for all compositions and oxygen partial pressures from metallic Fe saturation to 1 atm. The Gibbs energy of liquid solution was described based on the Modified Quasichemical Model considering the possible formation of NaAlO₂ and NaFeO₂ associates in the liquid state. The solid solutions wüstite, spinel, nepheline, carnegieite, mullite, corundum, clino-pyroxene, meta-oxides and Na- β "-alumina were treated within the framework of Compound Energy Formalism considering their crystal structures. Complicated phase relations in this system were elucidated and discrepancies among experimental data were resolved. The database of model parameters can be used to calculate any thermodynamic property and phase diagram section of the present system.

9.2. Introduction

The Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system either in whole or in part is of significant interest in both industrial processes and natural phenomena. For example, the Na₂O-FeO-Fe₂O₃ system was studied for the cooling system of fast breeder reactors [1-6]. The Na₂O-FeO-Fe₂O₃-SiO₂ system is important for the desulfurization [7-10] and dephosphorization [7-9] of hot metal and liquid steel, the production of bioactive glasses [11-13] and coal-combustion slags [9, 14, 15]. The Na₂O-FeO-Fe₂O₃-Al₂O₃ system is directly related to the reduction process of bauxite with soda for the production of Al₂O₃[16], and the production of solid-state electrodes for electrochemical cells [17-19]. The Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system possesses many well-known minerals such as wüstite, spinel, corundum, aegirine, nepheline, carnegieite, albite, jadeite, fayalite and silica (quartz, tridymite cristobalite) of importance in geology. However, phase equilibria of this system are indeed very complex due to the change of Fe oxidation state with oxygen partial pressure and the substitution of Fe³⁺ by Al³⁺ in solid solutions. Moreover, the high vapor pressure of sodium, hygroscopicity, high viscosity of SiO₂-rich melts, and the high fluidity of Na₂O- and FeO-rich melts make the experimental study of this system quite challenging.

The purpose of the present study was to critically evaluate and optimize thermodynamic properties and phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system, which was not previously attempted. In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the evaluation of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back-calculated. Using this approach, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from low order to high order systems can be applied to industrial processes.

Many lower order systems of Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ were already critically evaluated and optimized. For example, the Na₂O-Al₂O₃-SiO₂ [20], Na₂O-FeO-Fe₂O₃ [21], Na₂O-FeO-Fe₂O₃-

SiO₂ [22], Na₂O-FeO-Fe₂O₃-Al₂O₃ [23, 24] and FeO-Fe₂O₃-Al₂O₃-SiO₂ [25] systems were previously studied. In particular, as very few experimental phase diagram data were available in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system, a coupled key phase diagram experiments and thermodynamic optimization was conducted in this system to properly constrain Gibbs energies of all phases (solids and liquid) under reducing (in equilibrium with metallic Fe) and oxidizing (in air) conditions [23, 24].

To describe the entire Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system at oxygen partial pressures ranging from metallic saturation to 1 atm, a set of consistent thermodynamic models and optimized parameters for all existing phases are necessary. Therefore, all previous thermodynamic models and optimized parameters of the sub-systems were integrated together using proper extrapolation techniques, especially for the liquid solution, and modeling of the clino-pyroxene solid solution was newly performed to develop a thermodynamic database for this system. Many unexplored phase diagrams were predicted from the database.

9.3. Phases and thermodynamic models

Figure 9.1 shows the solid phases, considered for the current optimization, in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system at 1 atm total pressure. There are many stoichiometric phases and extensive solid solutions. The solution phases present in this system are as follows:

1) Liquid solution: NaO_{0.5}-FeO-FeO_{1.5}-AlO_{1.5}-SiO₂, containing NaAlO₂ and NaFeO₂ associates,

2) Wüstite: FeO solid solution with limited solubility of Fe₂O₃, Al₂O₃ and Na₂O,

3) Spinel: solid solution between magnetite Fe₃O₄ and hercynite FeAl₂O₄ with excess solubility of γ -Fe₂O₃ and γ -Al₂O₃, structurally formulated as (Fe²⁺, Fe³⁺, Al³⁺)^T[Fe²⁺, Fe³⁺, Al³⁺, Va]₂^OO₄,

4) Corundum: solid solution between Al_2O_3 and Fe_2O_3 with a large sub-solidus miscibility gap, structurally formulated as $(Al^{3+}, Fe^{3+})_2O_3$,

5) Nepheline: low-temperature NaAlSiO₄ solid solution with excess solubility of SiO₂,

6) Carnegieite: high-temperature NaAlSiO₄ solid solution with excess solubility of SiO₂,

7) Mullite: Al₆Si₂O₁₃ with excess solubility of both Al₂O₃ and SiO₂, structurally formulated as $(Al^{3+})_2^{O}[Al^{3+}, Si^{4+}]^T \{O^{2-}, Va\}_5^V$,

8) High-temperature meta-oxide: a complete solid solution between γ -NaFeO₂ and β -NaAlO₂ with limited solubility of SiO₂, belonging to the tetragonal crystal system, and structurally formulated as (Na⁺,Va)[Fe³⁺, Al³⁺, Si⁴⁺]O₂,

9) Intermediate-temperature meta-oxide: a complete solid solution between β -NaFeO₂ and α -NaAlO₂ with limited solubility of SiO₂, belonging to the orthorhombic crystal system, and structurally formulated as (NaFe⁴⁺, NaAl⁴⁺, Si⁴⁺)O₂,

10) β "-alumina: Na- β "-alumina Na₂Al₁₂O₁₉ extending to about 90 mol % of hypothetical Na₂Fe₁₂O₁₉ with a large miscibility gap in the middle, and structurally formulated as (Na⁺)₂[Al³⁺, Fe³⁺]₁₂O₁₉,

11) Clino-pyroxene: a complete solid solution between NaFeSi₂O₆ (aegirine) and metastable NaAlSi₂O₆ (jadeite) at 1 atm, structurally formulated as $(Na^+)^{M2}[Fe^{3+}, Al^{3+}]^{M1}{Al^{3+}, Fe^{3+}, Si^{4+}}^BSiO_6$.

In the above descriptions, cations shown within a set of brackets occupy the same sublattice, and Va represents vacancy.

9.3.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound (species) is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{9-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{9-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(9-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given stoichiometric compound from pure elements at 298 K (ΔH_{298K}^{o} of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy at 298 K, and C_{p} is the heat capacity.

Nineteen binary and nine ternary stoichiometric phases were considered in the entire Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system under 1 atm total pressure, Na₁₀SiO₇, Na₄SiO₄, Na₆Si₂O₇, Na₂SiO₃, Na₂Si₂O₅, Na₆Si₈O₁₉, FeSiO₃ (metastable), Fe₂SiO₄, NaAlO₂, Na₂Al₁₂O₁₉, NaAl₉O₁₄, Al₂Fe₂O₆, Al₂Si₂O₇ (metastable), Na₂FeO₂, Na₄FeO₃, Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, Na₈Fe₂O₇, NaAlSi₂O₆ (jadeite, metastable), NaAlSi₃O₈ (albite), Fe₂Al₄Si₅O₁₈, Fe₃Al₂Si₃O₁₂, NaFe₂O₃, Na₂FeSiO₄, Na₈Fe₆Si₁₅O₄₀, NaFeSi₂O₆ (aegirine, formerly named as acmite), and Na₅FeSi₄O₁₂. Gibbs energies of all these stoichiometric compounds, presented in Fig. 9.1, were previously optimized [20-22, 25-29]. Some of these phases are end-members of ternary and quaternary solid solutions.

9.3.2. Solid solutions

As listed above, ten solid solutions were considered in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system. The solid solutions wüstite monoxide [21], cubic spinel [28], corundum [28], nepheline [20], carnegieite [20], mullite [29] and β "-alumina solution [24] were taken from the previous optimizations without any further modification.

9.3.2.1. Clino-pyroxene solution

NaFeSi₂O₆ (aegirine) and NaAlSi₂O₆ (jadeite) both crystallize in the *C2/c* space group of the monoclinic structure, and form the clino-pyroxene solid solution. The most well-known clino-pyroxene is CaMgSi₂O₆ (diopside) which has the $(Ca,Mg)^{M2}[Mg]^{M1}{Si}^BSiO_6$ structure. Trivalent

cations such as Fe^{3+} and Al^{3+} substitute for divalent cations and Si^{4+} . This is known as a coupled substitution in the pyroxene solution:

$$[X^{3+}]^{M1} + \{X^{3+}\}^{B} = [M^{2+}]^{M1} + \{Si^{4+}\}^{B}$$
(9-4)

where M and X represent divalent and trivalent cations, respectively. Therefore, for the clinopyroxene solid solution in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system, the following sublattice structure can be considered:

$$(Na^{+})^{M2}[Fe^{3+}, Al^{3+}]^{M1}\{Fe^{3+}, Al^{3+}, Si^{4+}\}^{B}SiO_{6}$$
(9-5)

The Fe^{2+} species can also enter the M2 and M1 sites. However, it was not taken into account in the present study because $Fe_2Si_2O_6$ is metastable, and the solubility of $Fe_2Si_2O_6$ in the clino-pyroxene is very limited in this system even under reducing oxygen partial pressures.

Schairer and Yoder [30] investigated the NaFeSi₂O₆-NaAlSi₂O₆ join in air using the quenching method and XRD for phase analysis. They reported the presence of NaFeSi₂O₆ (aegirine) or its solid solution (clino-pyroxene) as the secondary solid phase after the primary hematite solid solution phase for melt compositions containing 0 to 55 mol % NaAlSi₂O₆. Yoder [31] reinvestigated the NaFeSi₂O₆-NaAlSi₂O₆ phase diagram, and reported the formation of pyroxene solid solution rich in aegirine but, Al solubility was not specified. Gilbert [32] studied single phase pyroxene samples of NaAlSi₂O₆ containing 0 to 53 mol % NaFeSi₂O₆ at high pressure. The samples were prepared under 40 kbar at 1673 K. XRD analysis revealed a linear change in lattice parameters of prepared pyroxene samples, meaning NaFeSi₂O₆ and NaAlSi₂O₆ form an ideal substitutional solution where Fe³⁺ (ionic radius = 0.64 Å) replaces Al³⁺ (ionic radius = 0.51Å). It should be noted that NaAlSi₂O₆ is not stable at atmospheric pressure, but its Gibbs energy at 1 atm was relatively well determined from the extrapolation of its stability data at high pressures.

The Gibbs energy of clino-pyroxene solid solution was described using the Compound Energy Formalism (CEF) [33] considering the site occupancy of cations in Eq. (9-5). As M2 site is occupied only by Na⁺, the solution can be modeled considering the cation distribution only on M1 and B sites. The Gibbs energy of the solution per formula unit in the framework of CEF is then expressed as follows:

$$G = \sum_{i} \sum_{j} Y_{i}^{M I} Y_{j}^{B} G_{ij} - TS_{C} + G^{Ex}$$
(9-6)

where Y_i^{M1} and Y_j^B represent the site fractions of cations *i* and *j* in the M1 and B sublattices, G_{ij} is the Gibbs energy of an "end member" Na^{M2}[*i*]^{M1}{*j*}^BSiO₆ in which the M1 and B sublattices are occupied only by *i* and *j* cations, respectively, and G^{Ex} is the excess Gibbs energy. S_c is the configurational entropy, assuming random mixing of cations in the M1 and B sublattices, and is given by:

$$S_C = -R\left(\sum_i Y_i^{M1} \ln Y_i^{M1} + \sum_j Y_j^B \ln Y_j^B\right)$$
(9-7)

 G^{Ex} is expressed using the Redlich-Kister power series considering interaction energies between cations *i* and *j* on one sublattice when the other sublattice is occupied by *k*:

$$G^{Ex} = \sum_{i} \sum_{j} Y_{i}^{MI} Y_{j}^{MI} Y_{k}^{B} \sum_{m} {}^{m} L_{ij;k} (Y_{j}^{MI} - Y_{i}^{MI})^{m} + \sum_{i} \sum_{j} Y_{k}^{MI} Y_{i}^{B} Y_{j}^{B} \sum_{m} {}^{m} L_{k;ij} (Y_{j}^{B} - Y_{i}^{B})^{m}$$
(9-8)

Figure 9.2 is the schematic presentation of composition lines between the end-members of the clino-pyroxene solid solution according to the present model. As seen, two of the end-members are charge-neutral, and four of them have (-1) charge. Therefore, neutral compositional line resides between the NaFeSi₂O₆ and NaAlSi₂O₆ end-members. In the CEF, the most important model parameters are Gibbs energies of end-members. Among six end-members in the present solution (see Fig. 9.2), the Gibbs energies of the charge-neutral end-members NaFeSiSiO₆ and NaAlSiSiO₆ are identical to the Gibbs energies of NaFeSi₂O₆ and NaAlSi₂O₆ compounds, respectively. The Gibbs energies of the NaFeAlSiO₆ (-1) and NaAlFeSiO₆ (-1) end-members can be determined by the combination of Eqs. (9) and (10) as following:

$$I_{FeAl} = G_{FeAl} - G_{AlFe} \tag{9-9}$$

$$\Delta_{FeAl} = (G_{FeAl} + G_{AlFe}) - (G_{FeFe} + G_{AlAl})$$
(9-
10)

where G_{FeAl} , G_{AlFe} , G_{FeFe} and G_{AlAl} are the Gibbs energies of NaFeAlSiO₆ (-1), NaAlFeSiO₆ (-1), NaFeFeSiO₆ (-1) and NaAlAlSiO₆ (-1) end-members, respectively. The parameter I_{FeAl} determines the preference of Fe³⁺ and Al³⁺ for either the M1 or B sites. In this study, both I_{FeAl} and Δ_{FeAl} were set as zero to obtain an ideal distribution of Fe³⁺ and Al³⁺ between the M1 and B sites. No G^{Ex} parameters were used for the NaFeSi₂O₆-NaAlSi₂O₆ solution, and it was treated as an ideal solution. It should be noted that all charged end-members have (-1) negative charge, and thus, their Gibbs energies do not influence the solution with neutral-charged compositions in this study. That is, the Gibbs energies of NaFeSi₂O₆ and NaAlSi₂O₆ are the most important model parameters for the clino-pyroxene solid solution.

9.3.2.2. Meta-oxide solutions

There are two meta-oxide solid solutions; high-temperature meta-oxide, belonging to the tetragonal crystal system, is a complete solid solution between γ -NaFeO₂ and β -NaAlO₂ [23, 24], and the intermediate-temperature meta-oxide, belonging to the orthorhombic crystal system, is a complete solid solution between β -NaFeO₂ and α -NaAlO₂ [23, 24]. The high-temperature and intermediate-temperature meta-oxide solutions have also noticeable excess solubility of SiO₂ up to about 20 and 10 mol %, respectively [22].

Dissolution mechanisms of SiO₂ in high- and intermediate-temperature meta-oxides are different in terms of crystal structure. Grey et al. [34] investigated the dissolution of SiO₂ in the β - and γ' -NaFeO₂ phases using XRD Rietveld refinement. They revealed that Si replaces Fe in β -NaFeO₂ (intermediate-temperature meta-oxide), and this is charge-compensated by the loss of Na from a proximate tetrahedron. From the viewpoint of configurational entropy, this can be mimicked as the replacement of NaFe pair by Si. Hence, the sublattice structure of intermediate-temperature meta-oxide can be written as following:

$$(NaFe^{4+}, NaAl^{4+}, Si^{4+})O_2$$
 (9-11)

According to Grey et al. [34], in the γ' -NaFeO₂ solution (which is considered to be a part of the γ -NaFeO₂ high-temperature meta-oxide) with a collapsed high cristobalite structure, Si replaces Fe

in the tetrahedral framework (M site). This is charge-balanced by taking away Na from the cavity framework (Na site). On the contrary to the β -NaFeO₂ solution, where Fe and neighboring Na are replaced by Si and Va, such a neighbor pair restriction was not observed in the γ' -NaFeO₂ solution, and a more random replacement of cationic pairs was reported. Therefore, high-temperature meta-oxide solid solution can be structurally formulated as:

$$(Na^+, Va)^{Na}[Al^{3+}, Fe^{3+}, Si^{4+}]^MO_2$$
 (9-12)

where Va forms in the Na sublattice with the replacement of Fe by Si on the M site.

These sublattice structures were already successfully implemented in the form of CEF to describe the phase diagrams of NaAlO₂-SiO₂ [35], NaFeO₂-SiO₂ [22] and NaFeO₂-NaAlO₂ [24] solid solutions, present in the Na₂O-Al₂O₃-SiO₂, Na₂O-Fe₂O₃-SiO₂ and Na₂O-Fe₂O₃-Al₂O₃ systems, respectively. In the current study, all previously optimized Gibbs energies of end-members and interaction parameters for each binary solution were combined together to predict the Gibbs energy of the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ quaternary meta-oxide solution. No additional parameters were used in ternary sub-systems.

9.3.2.3. Other solid solutions

Bailey and Schairer [36] reported that there is a solubility limit for Fe in NaAlSiO₄ (nepheline) and NaAlSi₃O₈ (albite) however, exact solubility limits were not determined. Even if they exist, the solubility of Fe in these phases is expected to be very small at 1 atm pressure because both NaFeSiO₄ and NaFeSi₃O₈ are unstable in the Na₂O-Fe₂O₃-SiO₂ system in air. Therefore, no Fe solubility was considered in these phases for the current optimization.

9.3.3. Liquid oxide phase

In the current study, the molten oxide phase was described using the Modified Quasichemical Model (MQM) [37]. Short range ordering (SRO) in the molten oxide solution is taken into account

by considering second-nearest-neighbor (SNN) pair exchange reactions of cationic species, and oxygen is a common anion. Therefore, the liquid components in the MQM were NaO_{0.5}, FeO, FeO_{1.5}, AlO_{1.5} and SiO₂. Moreover, the NaFeO₂ (associate of Na₂O and Fe₂O₃) and NaAlO₂ (associate of Na₂O and Al₂O₃) components were taken into account in the liquid phase. These associates were considered to explain the so-called charge compensation effect which was reported in the Na₂O-Al₂O₃-SiO₂ and Na₂O-Fe₂O₃-SiO₂ melts [38, 39]. That is, when both Na⁺ and Al³⁺ (or Fe³⁺) coexist in SiO₂-rich melts, NaAl⁴⁺ (or NaFe⁴⁺) can replace Si⁴⁺ to enhance the polymerization of silicate melts. Hence, the NaAl⁴⁺ and NaFe⁴⁺ associates were considered for the optimization of the Na₂O-Al₂O₃-SiO₂ [20] and Na₂O-Fe₂O₃-SiO₂ [22] liquid solutions, respectively, and consequently in the present liquid phase.

Detailed descriptions of the MQM for binary and multicomponent systems can be found elsewhere [37, 40]. In the MQM, the following quasichemical reaction in the binary oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B);$$
 Δg_{AB} (9-13)

where A and B are cationic species in the solution, and (A - B) represents a second-nearestneighbour A-B pair containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{o} + n_{B}g_{B}^{o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$

$$(9-14)$$

where n_i and g_i^o are the number of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{config} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{config} = -R \left(n_A \ln X_A + n_B \ln X_B \right) - R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right]$$
(9-15)

 Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge I} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge I} g^{0j}_{AB} X^{j}_{BB}$$
(9-16)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature.

In the present study, cationic species (A or B in Eq. (9-13)) are Na⁺, Fe²⁺, Fe³⁺, Al³⁺, Si⁴⁺, NaFe⁴⁺ and NaAl⁴⁺. Gibbs energies of the liquid NaO_{0.5} (1/2 Na₂O), FeO, FeO_{1.5} (1/2 Fe₂O₃), AlO_{1.5} (1/2 Al₂O₃) and SiO₂ were taken from the FACT pure substance database [41]. Gibbs energies of the liquid NaFeO₂ and NaAlO₂ are the model parameters, previously determined for the optimization of the Na₂O-Fe₂O₃ [21] and Na₂O-Al₂O₃ [20] systems, respectively. To respect the consistency of the database, coordination numbers of all species were kept the same as those in the previous studies [21, 22, 24]. Among twenty-one possible binary quasichemical reactions, Gibbs energy parameters (Δg_{AB}) of Na⁺-Si⁴⁺ [26], Fe²⁺-Fe³⁺ [25], Fe²⁺-Si⁴⁺ [27], Fe³⁺-Si⁴⁺ [27], Na⁺-Al³⁺ [20], Fe²⁺-Al³⁺ [28], Fe³⁺-Al³⁺ [28], NaAl⁴⁺-Si⁴⁺ [20], NaFe⁴⁺-Si⁴⁺ [22], Na⁺-Fe²⁺ [21] and Na⁺-Fe³⁺ [21] were taken from previous optimizations without any modification. The rest of binary solutions were considered to be ideal where $\Delta g_{AB} = 0$.

There are thirty-five ternary solutions within the NaO_{0.5}-FeO-FeO_{1.5}-AlO_{1.5}-SiO₂-NaFeO₂-NaAlO₂ system. Gibbs energies of ternary solutions were first predicted from binary model parameters using a specific geometric model and if it was necessary, ternary model parameters were introduced to improve Gibbs energy descriptions of ternary solutions. Gibbs energies of quaternary and higher order systems were then predicted without any additional model parameter. Gibbs energies of the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂ [21], NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-SiO₂ [22] and NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-AlO_{1.5}-NaAlO₂ [24] solutions were already optimized by the present authors and were adopted for the present optimization. Gibbs energy descriptions of the FeO-FeO_{1.5}-SiO₂ [27], NaO_{0.5}-NaAlO₂-SiO₂ [20], NaAlO₂-AlO_{1.5}-SiO₂ [20], FeO-AlO_{1.5}-SiO₂ [25] and FeO_{1.5}-AlO_{1.5}-SiO₂ [25] solutions were taken from previous optimizations. In the current study, a few ternary model parameters were newly introduced into the NaAlO₂-SiO₂-FeO solution for a more accurate description of the NaO_{0.5}-FeO-FeO_{1.5}-AlO_{1.5}-SiO₂-NaFeO₂-NaAlO₂ system. No parameters were added in other ternary solutions.

Regarding geometric extrapolation techniques, the NaO_{0.5}-FeO-FeO_{1.5}, NaO_{0.5}-FeO_{1.5}-AlO_{1.5}, NaO_{0.5}-SiO₂-AlO_{1.5}, and NaO_{0.5}-NaAlO₂-NaFeO₂ systems were treated using the 'Toop-type'

model with NaO_{0.5} as the 'asymmetric component'. The ternary systems FeO-FeO_{1.5}-SiO₂, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-FeO-SiO₂, NaO_{0.5}-SiO₂-NaAlO₂, FeO-SiO₂-AlO_{1.5}, FeO-SiO₂-AlO_{1.5}, FeO-SiO₂-AlO_{1.5}-SiO₂-AlO_{1.5}, FeO_{1.5}-SiO₂-NaAlO₂, SiO₂-AlO_{1.5}-NaFeO₂, and SiO₂-NaAlO₂-NaFeO₂ were modeled using the 'Toop-type' approximation with SiO₂ as the 'asymmetric component'. The NaO_{0.5}-FeO-AlO_{1.5} and AlO_{1.5}-NaAlO₂-NaFeO₂ systems were treated using the 'Toop-type' model with AlO_{1.5} as the 'asymmetric component' because AlO_{1.5} can behave differently from the other two components in each ternary solution. Due to the similar reason, the 'Toop-type' approximation was used for the NaO_{0.5}-FeO-NaAlO₂ and FeO-AlO_{1.5}-NaAlO₂ systems with NaAlO₂ as the 'asymmetric component'. The rest of ternary solution. Due to deled using the symmetric 'Kohler-type' approximation. Details of ternary systems were modeled using the symmetric component'. The rest of ternary systems were modeled using the symmetric 'Kohler-type' approximation. Details of ternary systems were modeled using the symmetric 'Kohler-type' approximation.

9.3.4. Metallic and gas phases

For calculations at metallic saturation, Gibbs energies of liquid metallic components were taken from FACT pure substance database [41]. Gibbs energies of gas species were also taken from FACT pure substance database [41], which is mostly based on the JANAF thermodynamic compilation table [43].

9.4. Review of literature data and thermodynamic optimization

All experimental data in the literature were reviewed, and one set of optimized thermodynamic model parameters were obtained to reproduce all reliable experimental phase diagram data as much as possible within experimental error limits. Optimized model parameters are listed in Table 9.1. Phase diagrams were determined either at Fe saturation or in air. Strictly speaking, there are certain amounts of Fe^{3+} -containing oxides at metallic Fe saturation, and also Fe^{2+} -containing oxides in air. However, for the sake of convenience, the notations Na₂O-Fe₂O₃-Al₂O₃-SiO₂ and Na₂O-FeO-Al₂O₃-SiO₂ are used to represent oxidizing and reducing conditions, respectively.

9.4.1. The Na₂O-FeO-Al₂O₃-SiO₂ system at metallic Fe saturation

Experimental phase diagram data available at Fe saturation are limited to the NaAlSiO₄-FeO-SiO₂ system. Bowen and Schairer [44] investigated the NaAlSi₃O₈-Fe₂SiO₄ phase diagram at metallic Fe saturation using the quenching method and petrographic microscopy for phase analysis. Experiments were performed in N₂ atmosphere using pure Fe crucibles. Bowen [45] studied phase equilibria of the NaAlSiO₄-FeO-SiO₂ system using the same methods.

The liquidus projection of the NaAlSiO₄-FeO-SiO₂ system, calculated in equilibrium with metallic Fe from the present thermodynamic optimization, is illustrated in Fig. 9.3, and the pseudo-binary section NaAlSi₃ O_8 (albite) - Fe₂SiO₄ (fayalite) is also depicted in Fig. 9.4. All calculated invariant reactions are listed in Table 9.2. The calculated phase diagrams are in good agreement with experimental data within the maximum deviation of ± 20 K except for the primary crystallization region of spinel solution. In particular, the very flat liquidus of the NaAlSi₃O₈-Fe₂SiO₄ join was well represented. Without any ternary parameter, general features of the calculated and experimental phase diagrams were similar and the NaAlSi₃O₈ - Fe₂SiO₄ join was well predicted. However, the primary phase field of SiO₂ in the NaAlSiO₄-FeO-SiO₂ system was calculated much larger than that experimentally measured. Therefore, to better reproduce the NaAlSiO₄-FeO-SiO₂ phase diagram, four temperature-independent ternary parameters were added into the NaAlO₂-FeO-SiO₂ liquid solution. From our experience, rather large number of parameters is not common. These ternary parameters are only effective in the Na₂O-FeO-Al₂O₃-SiO₂ quaternary solution without influencing ternary sub-systems. However, even with these parameters, the primary phase region of spinel could not be reproduced, and the wüstite solid solution was calculated to be stable instead. Further phase diagram experiments are necessary to resolve the spinel and wüstite phase boundary in this system.

From the thermodynamic models with optimized parameters, liquidus projections of two quaternary sections (Fig. 9.5), important in pyro-metallurgical applications, especially refining processes were predicted. The accuracy of the calculated diagrams would be about maximum \pm 50 K in temperature and \pm 5 wt.% in composition from our experience in oxide systems, where calculation results cannot be validated due to the very limited number of experimental data.

The predicted liquidus projection of the FeO-Al₂O₃-SiO₂ section with 40 wt.% Na₂O at Fe saturation (Fig. 9.5(a)) shows wide primary phase fields of meta-oxide solid solution and Na₂SiO₃. In particular, the liquid phase is stable up to 20 wt.% Al₂O₃ at 1773 K. The predicted Na₂O-FeO-SiO₂ section with 20 wt.% Al₂O₃ at Fe saturation (Fig. 9.5(b)) illustrates wide primary phase regions of meta-oxide, spinel, nepheline and wüstite. According to the calculations, the liquid phase is stable in a large composition area at 1773 K. This indicates that the Na₂O-FeO-SiO₂ flux with maximum ~20 wt.% Al₂O₃ can be used as a liquid agent for the desulfurization or dephosphorization of steel. Of course, the sulfur removal capacity of the flux is expected to be better at higher Na₂O and FeO regions but once solid phases form, the desulfurization capacity drastically decreases. Therefore, the proper adjustment of composition can be calculated from the phase diagram information. The dephosphorization reaction is more complex since it occurs at a higher oxygen potential. Hence, a good balance of Na₂O and FeO is required to maximize the dephosphorization capacity.

9.4.2. The Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system in air

Schairer and Yoder [30] studied phase equilibria of the NaAlSi₂O₆-NaFeSi₂O₆ system in air using the quenching method followed by XRD phase analysis. Primary crystalline phase fields of corundum and nepheline were observed for 0-82 and 82-100 mol % NaAlSi₂O₆, respectively. The secondary phase regions of NaFeSi₂O₆ (clino-pyroxene), nepheline and corundum were reported for 0-55, 55-82 and 82-100 mol % NaAlSi₂O₆, respectively. However, no further details about results were provided. Later, Yoder [31] investigated the phase diagram of this join using the same methods.

Schairer and Thwaite [46] studied several sections of the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system in air using the quenching method and XRD for phase analysis. In the NaAlSiO₄-NaFeSi₂O₆-Na₂Si₂O₅ section, three invariant reactions were determined: liquid (L) + carnegieite (Cg) + nepheline (Nph) + corundum (Crn), L + Nph + NaFeSi₂O₆ + Crn and L + Nph + NaFeSi₂O₆ + Na₂Si₂O₅. Nepheline was the NaAlSiO₄ phase with excess solubility of SiO₂. In the NaAlSi₃O₈-NaFeSi₂O₆-Na₂Si₂O₅ section, two invariant reactions were defined: L + albite (Ab) + Crn + NaFeSi₂O₆ and L + Ab + NaFeSi₂O₆ + Na₂Si₂O₅. In the NaAlSiO₄-NaFeSi₂O₆-Na₅FeSi₄O₁₂ section, three quaternary invariant reactions were determined: L + Cg + Nph + Crn, $L + Nph + NaFeSi_2O_6 + Crn$ and $L + Nph + Na_5FeSi_4O_{12} + NaFeSi_2O_6$. However, unfortunately, experimental phase diagram data were not provided. Although they reported the possible solubility of Fe³⁺ in nepheline and albite, no details in terms of crystal structures and solubility limits were reported. Later, Bailey and Schairer [36] further investigated different sections of the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system in air using the quenching method followed by petrographic microscopy and XRD for phase analysis. Yagi [47] measured the NaAlSiO₄-NaFeSi₂O₆ phase diagram in air using the quenching method and XRD for phase identification, and found the primary crystallization of corundum and carnegieite. Newton and Smith [48] studied the NaAlSi₃O₈-NaFeSi₃O₈ join at 873 K and high pressure using a hydrothermal method and reported the formation of pyroxene solid solution.

It should be noted that no ternary parameters were newly added into the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ liquid solution in air, and the clino-pyroxene solid solution was treated as an ideal solution with no interaction parameters as discussed in section 9.3.2.1. That is, phase diagrams of this system in air are purely prediction from the ternary sub-systems.

The predicted phase diagrams of the NaFeSi₂O₆-NaAlSiO₄ and NaFeSi₂O₆-NaAlSi₂O₆ joins in air are illustrated in Fig. 9.6 along with available experimental data. As seen, the experimental data from Yagi [47] and Yoder [31] were very well represented by the prediction. According to the calculation, the solubility of NaAlSi₂O₆ in NaFeSi₂O₆ clino-pyroxene is less than 0.5 mol %, which is consistent with the observation by Bailey and Schairer [36] who reported that NaFeSi₂O₆ (aegirine) is nearly a stoichiometric compound. However, according to Gilbert [32], there is a complete solid solution between NaFeSi₂O₆ and NaAlSi₂O₆ at 40 kbar because NaAlSi₂O₆ is stable at high pressure. Based on the calculations, the corundum solid solution mostly consists of Fe₂O₃ with small amounts of Al₂O₃, and nepheline and carnegeiete solutions contain several moles of excess SiO₂.

Predicted liquidus projections of seven ternary isopleths in the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system in air are shown in Fig. 9.7 along with experimental data. Bailey and Schairer [36] investigated primary crystallization regions in various ternary sections containing more than 50 mol % SiO₂: (a) Na₂Fe₂Si₄O₁₂-Na₂Al₂Si₄O₁₂-Na₂Si₄O₉, (b) Na₂Fe₂Si₄O₁₂-Na₂Al₂Si₂O₈-SiO₂, (c) Na₂Fe₂Si₄O₁₂- $Na_2Al_2Si_2O_8-Na_2Si_2O_5$, (d) $Na_2Fe_2Si_4O_{12}-Na_2Si_2O_5-Na_2Al_2Si_6O_{16}$, (e) $Na_2Fe_2Si_4O_{12}-Na_{10}Fe_2Si_8O_{24}-Na_2Al_2Si_2O_8$, (f) $Na_2Fe_2Si_4O_{12}-Na_2Al_2Si_2O_8-Na_2Si_4O_9$, and (g) $Na_2Fe_2Si_4O_{12}-Na_2SiO_3-Na_2Al_2Si_2O_8$. All calculated invariant reactions are listed in Table 9.3. In general, the predicted phase diagrams agree well with experimental data in most of the ternary isopleths within maximum errors of \pm 5 mol % in composition and \pm 30 K in temperature. In the $Na_2Fe_2Si_4O_{12}-Na_2Al_2Si_2O_8-Na_2Si_2O_5$ system (Fig. 9.7(c)), Bailey and Schairer [36] observed five primary phases $NaFeSi_2O_6$, Crn, Nph, Cg and $Na_2Si_2O_5$. According to the present prediction, the primary phase fields of Na_2SiO_3 and $Na_5FeSi_4O_{12}$ are also present at high $Na_2Si_2O_5$ region.

The thermodynamic models with optimized parameters can be used to predict phase diagrams in oxidizing condition. The predicted liquidus projections of the Na₂Fe₂Si₄O₁₂-Na₂Al₂Si₂O₈-Na₄SiO₄, Na₂Fe₂O₄-Na₂Al₂O₄-XO and Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-XO (XO = SiO₂, Na₂SiO₃ and Na₄SiO₄) systems in air are illustrated in Figs. 9.8 to 9.10, respectively.

Comparison of the Na₂Fe₂Si₄O₁₂-Na₂Al₂Si₂O₈-Na₄SiO₄ system (Fig. 9.8) with the ternary sections $Na_2Fe_2Si_4O_{12}-Na_2Al_2Si_2O_8-SiO_2$ (Fig. 9.7(b)) and $Na_2Fe_2Si_4O_{12}-Na_2Al_2Si_2O_8-Na_2SiO_3$ (Fig. 9.7(g)) reveals that the primary crystalline field of corundum shrinks and those of the pyroxene and meta-oxide solid solutions appear with increasing the Na₂O/SiO₂ ratio. Figure 9.9 shows the predicted liquidus projections of the Na₂Fe₂O₄-Na₂Al₂O₄-SiO₂, Na₂Fe₂O₄-Na₂Al₂O₄-Na₂SiO₃ and Na₂Fe₂O₄-Na₂Al₂O₄-Na₄SiO₄ systems in air. The primary phase regions of high-temperature metaoxide solid solution, Na₂SiO₃ and Na₄SiO₄ occupy a broad composition range in the two latter sections. On the other hand, the liquidus projection of the former system is complex due to the interplay of Na-alumino-silicate, corundum and β'' -alumina solid solutions. The predicted liquidus projections Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-SiO₂, Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-Na₂SiO₃ and Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-Na₄SiO₄ in air are presented in Fig. 9.10. At low basicity (SiO₂-rich) region (Fig. 9.10(a)), β'' -alumina, corundum and spinel are widely present as primary solid phases. With increasing the basicity (Na₂O/SiO₂ ratio), the primary crystalline areas of corundum and spinel become smaller but that of meta-oxide becomes larger. Although no experimental data are available in these sections, the predicted liquidus projections would be accurate within maximum errors of \pm 5 mol % in composition and \pm 30 K in temperature.

9.5. Summary

A critical assessment/thermodynamic optimization of phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system were carried out at 1 atm total pressure. While a couple of ternary liquid parameters were optimized to reproduce phase equilibria at Fe saturation, complex phase relations in air were well predicted from the thermodynamic models with optimized model parameters of binary and ternary sub-systems without any additional parameter. As a result of thermodynamic optimization for all phases, unexplored phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system important for various industrial processes were predicted within the error ranges of \pm 5 mol % in composition and \pm 50 K in temperature.

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Table 9.1: Optimized model parameters of solutions in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system (J/mol and J/mol-K).

Liquid solution (NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-AlO_{1.5}-NaAlO₂-SiO₂)* $q_{NaAl, Si, Fe(II)}^{021} = -8368$ $q_{Fe(II), NaAl, Si}^{001} = -117152$ $q_{Si, Fe(II), NaAl}^{001} = 29288$ $q_{NaAl, Si, Fe(II)}^{011} = -25104$

* All other model parameters can be found in previous work [20-22, 24-28]. The formalism of the ternary excess parameters can be found elsewhere [40].

Meta-oxide solid solutions					
High-temperature: (Na ⁺ ,Va) ^{Na} [Al ³⁺ , Fe ³⁺ , Si ⁴⁺] ^M O ₂					
$G_{NaAlO_2} = G^o_{NaAlO_2(\beta)}$					
$G^{o}_{NaAlO}(\beta)$	$\varDelta H_{298K} = -1131893 , \ S_{298K} = 72.15270$				
$NaAlO_2(p)$	$C_P = 89.14849 + 0.01529T - 1793262.4T^{-2}$				
$G_{NaFeO_2} = G^o_{NaFeO_2(\gamma)}$					
$G^{o}_{NaFaO_{1}(\gamma)}$	$\varDelta H_{298K} = -695132.47999 , \ S_{298K} = 90.10223$				
Nure0 ₂ (7)	$C_P = 110.95000 + 0.00769T - 2552200.0T^{-2}$				
$G_{VaSiO_2} = G_{SiO_2(high cristobalite)}^o + G_1^{add}; \ G_l^{add} = 5999.99826$					
$G_{NaSiO_2} = 0.5G_{NaAlO_2} + 0.5G_{VaSiO_2} + G_2^{add}; \ G_2^{add} = 41840$					
$G_{VaAlO_2} = 0.5G_{NaAlO_2} + 0.5G_{VaSiO_2} - G_2^{add}$					
$G_{VaFeO_2} = -0.5G_{NaAlO_2} + G_{NaFeO_2} + 0.5G_{VaSiO_2} - G_2^{add}$					
${}^{0}L_{NaVa;Si} = -29288$					
${}^{0}L_{NaVa;Al} = -161084$					
$^{l}L_{NaVa;Fe} = -118624.768 + 2$	20.89010T				
${}^{l}L_{Al,Fe} = 12552$					

Intermediate-temperature: (NaFe⁴⁺, NaAl⁴⁺, Si⁴⁺)O₂

$$\begin{split} G_{NaAlO_2} &= G^o_{NaAlO_2(\alpha)} \\ G^o_{NaAlO_2(\alpha)} & \Delta H_{298K} = -1133190, \ S_{298K} = 70.40000, \\ C_P &= 89.14849 + 0.01529T - 1793262.4T^{-2} \end{split}$$

 $G_{NaFeO_2} = G^o_{NaFeO_2(\beta)}$

$$\Delta H_{298K} = -697308.16$$
, $S_{298K} = 88.3891$

$$G^{o}_{NaFeO_2(\beta)}$$

$$\begin{split} G_{VaSiO_2} &= G^o_{SiO_2(highcristobalite)} + G^{add}_3; \ G^{add}_3 = 4999.99715 \\ {}^{1}L_{NaFe \ VaSi} &= 20920 \\ {}^{4}L_{NaFe \ VaSi} &= -205016 \\ {}^{1}L_{NaAl \ NaFe} &= 12552 \\ {}^{0}L_{NaAl \ VaSi} &= -115060 \\ {}^{1}L_{NaAl \ VaSi} &= 83680 \end{split}$$

Clino-pyroxene solid solution (Na⁺)^{M2}[Fe³⁺, Al³⁺]^{M1}{Al³⁺, Fe³⁺, Si⁴⁺}^BSiO₆

 $\begin{array}{ll} G_{NaAlSi_2O_6} = G_{NaAlSi_2O_6}^o \\ & \Delta H_{298K} = -3025118.23 \,,\, S_{298\,K} = 133.57394 \\ G_{NaAlSi_2O_6}^o & \Delta H_{298K} = -3025118.23 \,,\, S_{298\,K} = 133.57394 \\ C_P = 311.29297 - 5350264.05920T^{-2} - 2005.10100T^{-0.5} \\ + 662566901.36000T^{-3} \\ \end{array} \\ G_{NaFeSi_2O_6} = G_{NaFeSi_2O_6}^o \\ & \Delta H_{298K} = -2590525.0 \,,\, S_{298\,K} = 171.0 \\ G_{NaFeSi_2O_6}^o & 298 - 1263 \, \mathrm{K} \quad C_P = 171.44948 + 0.14880T - 3611152.58200T^{-2} - 5.96E - 5T^2 \\ 1263 - 5000 \, \mathrm{K} \quad C_P = 261.98380 \\ I_{FeAl} = G_{FeAl} - G_{AlFe} \,,\, \Delta_{FeAl} = \left(G_{FeAl} + G_{AlFe}\right) - \left(G_{FeFe} + G_{AlAl}\right) \\ G_{AlAl} \, \mathrm{and} \, G_{FeFe} \, \mathrm{were} \, \mathrm{taken} \, \mathrm{from previous} \, \mathrm{work} \, [49]. \\ G_{FeAl}, \, G_{AlFe}, \, G_{FeFe} \, \mathrm{and} \, G_{AlAl} \, \mathrm{represent} \, G_{NaFeAlSiO_6} \,,\, G_{NaAlFelSiO_6} \,,\, G_{NaFeFeSiO_6} \,,\, G_{NaAlAlSiO_6} \,, \\ \mathrm{respectively}. \end{array}$

No. ¹⁾	T (K)			Composition (mol %)						
			Invariant reactions ³⁾	SiO ₂		NaAlSiO ₄		FeO		
	Exp.	Calc.		Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	
1	ND ²⁾	1528	L+Cg→Nph+Spl	ND	7.5	ND	58.4	ND	34.1	
2	ND	1390	L+Spl→Wüs+Nph	ND	18.2	ND	38.2	ND	43.6	
3	ND	1329	L+Wüs→Fa+Nph	ND	26.6	ND	34.7	ND	38.7	
4	1253	1278	$L \rightarrow Fa + Ab(s_2) + Trd$	~77.6	74.3	~18.1	18.3	~4.3	7.4	
5	1263	1268	$L \rightarrow Fa + Ab(s_2) + Nph$	~47.9	47.1	~40.2	38.0	~11.9	14.9	

Table 9.2: Calculated invariant reactions involving the liquid phase of the NaAlSiO₄-FeO-SiO₂ system at Fe saturation in comparison with experimental data from Bowen [45].

¹⁾ Reaction number corresponds to the composition of the invariant reaction indicated in Fig. 9.3.

²⁾ ND: Not Determined.

³⁾ Cg: carnegieite, Nph: nepheline, Spl: spinel, Wüs: wüstite, Fa: Fayalite, Ab: Albite, Trd: Tridymite.

No. ¹⁾	T (K)		Invariant reactions ³⁾	Composition (mole fraction)					
				Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
	Exp.	Calc.		$Na_2Fe_2Si_4O_{12}$		$Na_2Al_2Si_4O_{12}$		Na ₂ Si ₄ O ₉	
1	1271±5	1285	L+Nph→Ab+Crn	22.7	15.8	65.5	76.8	11.8	7.4
2	1216±5	1194	L+Crn→Ab+CPx	44.8	37.4	36.0	42.4	19.2	20.2
3	1044±5	1048	L→Ab+CPx+Qz-h	13.0	20.0	13.7	13.5	73.3	66.4
				Na ₂ Fe ₂ Si ₄ O ₁₂		$Na_2Al_2Si_2O_8$		SiO ₂	
4	1521±5	1537	L+Cg→Nph+Crn	15.9	11.2	62.2	57.0	21.8	31.8
5	1333±5	1336	L→Nph+Ab+Crn	2.5	1.7	28.2	29.2	69.4	69.1
6	1328±5	1322	$L \rightarrow Ab+Crn+Trd$	0.5	0.8	11.0	10.6	88.5	88.6
				Na ₂ Fe ₂ Si ₄ O ₁₂		Na ₂ Al ₂ Si ₂ O ₈		Na ₂ Si ₂ O ₅	
7	1521±5	1533	$L+Cg\rightarrow Crn+Nph$	27.3	23.2	68.0	71.6	4.7	5.2
8	1181±5	1148	L+Crn→CPx+Nph	36.3	37.7	30.9	37.7	27.7	26.0
9	-	1030	$L+CPx \rightarrow Nph+N_5FS_8$	-	13.9	-	21.1	-	65.0
10	-	1003	L→Disil+Metasil+ N5FS8	-	4.6	-	18.9	-	76.6
11	-	1003	$L \rightarrow N_5 FS_8 + Metasil + Nph$	-	4.5	-	19.9	-	75.6
				Na ₂ Fe ₂ Si ₄ O ₁₂		Na ₂ Si ₂ O ₅		Na ₂ Al ₂ Si ₆ O ₁₆	
12	1223±5	1200	L+Crn→Ab+CPx	47.8	39.8	17.2	20.1	34.9	40.0
13	1018±5	991	$L \rightarrow CPx+Ab+Disil$	7.2	10.9	77.2	76.4	15.7	12.7
				$Na_2Fe_2Si_4O_{12}$ $Na_{10}Fe_2$		$_2Si_8O_{24}$	$Na_2Al_2Si_2O_8$		
14	1511±5	1533	$L+Crn+Cg \rightarrow Nph$	29.1	24.0	1.5	1.5	69.4	74.5
15	1166±5	1129	L+Crn→CPx+Nph	53.1	43.2	12.3	10.8	34.5	46.0
16	1051±5	1056	$L \rightarrow CPx + Nph + N_5FS_8$	25.3	30.0	38.3	26.7	36.4	43.4
				$Na_2Fe_2Si_4O_{12}$ $Na_2Al_2Si_2O_8$		Na ₂ Si ₄ O ₉			
17	ND ²⁾	1534	$L+Cg\rightarrow Crn+Nph$	ND	22.0	ND	73.6	ND	4.4
18	1181±5	1161	L+Crn→Nph+CPx	37.7	33.4	38.2	44.7	24.1	21.8
19	1131±5	1123	$L \rightarrow CPx+Nph+Ab$	23.1	22.6	41.5	42.1	35.4	35.2
20	1019±5	1028	L→CPx+Ab+Qz-h	9.0	17.8	12.3	11.6	78.6	70.5
				Na ₂ Fe ₂ Si ₄ O ₁₂		Na ₂ SiO ₃		Na ₂ Al ₂ Si ₂ O ₈	
214)	ND	1532	$L+Cg\rightarrow Crn+Nph$	28.5	24.0	6.2	5.7	65.3	70.3
22	ND	1129	L+Crn→CPx+Nph	43.5	37.7	33.6	30.1	22.8	32.1
23	1066±5	1079	L+Metasil→Nph+ N ₅ FS ₈	16.5	16.2	69.1	64.7	14.4	19.2
24	ND	1056	$L \rightarrow CPx+Nph+N_5FS_8$	25.1	27.4	61.3	51.7	13.6	21.0

Table 9.3: Calculated invariant reactions involving the liquid phase of the Na₂O-Fe₂O₃-Al₂O₃-SiO₂ system in air in comparison with experimental data from Bailey and Schairer [36].

¹⁾ Reaction number corresponds to the composition of the invariant reaction indicated in Fig. 9.7.

²⁾ ND: Not Determined.

³⁾ Crn: corundum, CPx: clino-pyroxene, Qz: quartz, N_5 FeS₈: $5Na_2O \cdot Fe_2O_3 \cdot 8SiO_2$, Disil: sodium disilicate, Metasil: sodium metasilicate. For the rest of abbreviations see Table 9.2.

⁴⁾ The join Aeg-Nph-Metasil was not experimentally measured. The liquidus projection was merely approximated by Bailey and Schairer [36].



Fig. 9.1: Schematic diagram of the solid phases in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system. N₄F³⁺: Na₈Fe₂O₇, N₃F³⁺: Na₃FeO₃, NF³⁺: NaFeO₂, N₃F³⁺5: Na₃Fe₅O₉, N₂F²⁺: Na₄FeO₃, NF²⁺: Na₂FeO₂, NA: NaAlO₂, NA₆: Na₂Al₁₂O₁₉, NA₉: NaAl₉O₁₄, N₅S: Na₁₀SiO₇, N₂S: Na₄SiO₄, N₃S₂: Na₆Si₂O₇, NS: Na₂SiO₃, NS₂: Na₂Si₂O₅, N₃S₈: Na₆Si₈O₁₁, AF³⁺: AlFeO₃, AF²⁺: FeAl₂O₄, F²⁺F³⁺: Fe₃O₄, F²⁺S: FeSiO₃, F²⁺₂S: Fe₂SiO₄ (Fa), A₃S₂: Al₆Si₂O₁₃, AS₂: Al₂Si₂O₇, N₅F³⁺S₈: Na₅FeSi₄O₁₂, N₄F²⁺₆S₁₅: Na₈Fe₆Si₁₅O₄₀, NF²⁺S: Na₂FeSiO₄, NF²⁺₂F³⁺: NaFe₂O₃, NAS₂: NaAlSiO₄, F²⁺₃AS₃: Fe₃Al₂Si₃O₁₂, F²⁺₂A₂S₅: Fe₂Al₄Si₅O₁₈, NF³⁺S₄: NaFeSi₂O₆ (Aeg), NAS₄: NaAlSi₂O₆ (Jd), NAS₆: NaAlSi₃O₈ (Ab), Wüs: wüstite, Spl: spinel, Crn: corundum, Mul: mullite, Nph: nepheline, Cg: carnegieite, Ab: albite, Aeg: aegirine, Jd: jadeite, Fa: fayalite, MOx: meta-oxide, CPx: clino-pyroxene, β": β"-alumina. Phases marked with '*' are metastable.



Fig. 9.2: Schematic diagram for the end-members of clino-pyroxene solid solution in the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system.


Fig. 9.3: Calculated optimized liquidus projection and primary phase regions of the NaAlSiO₄-FeO- SiO₂ system in equilibrium with metallic Fe. Trd and Crs represent tridymite and cristobalite, respectively (for the rest of abbreviations see Fig. 9.1). The invariant reactions indicated by numbers are listed in Table 9.2.



Fig. 9.4: Calculated optimized phase diagram of the NaAlSi₃O₈-Fe₂SiO₄ system in equilibrium with metallic Fe along with experimental data from Bowen and Schairer [44].



Fig. 9.5: Liquidus projections of the (a) FeO-Al₂O₃-SiO₂- 40 wt.% Na₂O and (b) Na₂O-FeO-SiO₂- 20 wt.% Al₂O₃ systems at Fe saturation, predicted from the present study. For abbreviations see Fig. 9.1.



Fig. 9.6: Calculated optimized phase diagrams of the (a) NaFeSi₂O₆-NaAlSiO₄ and (b) NaFeSi₂O₆-NaAlSi₂O₆ systems in air along with experimental data [31, 36, 47, 50]. For abbreviations see Fig. 9.1.







(b)



(c)



(d)



(e)



(f)







Fig. 9.8: Liquidus projection of the Na₂Fe₂Si₄O₁₂-Na₂Al₂Si₂O₈-Na₄SiO₄ ternary isopleth in air, predicted from the present study. For the abbreviations see Fig. 9.1.



(a)



Fig. 9.9: Liquidus projections of the (a) Na₂Fe₂O₄-Na₂Al₂O₄-SiO₂, (b) Na₂Fe₂O₄-Na₂Al₂O₄-Na₂SiO₃ and (c) Na₂Fe₂O₄-Na₂Al₂O₄-Na₄SiO₄ ternary isopleths in air, predicted from the present study. For the abbreviations see Fig. 9.1.



(a)



(b)



Fig. 9.10: Liquidus projections of the (a) Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-SiO₂, (b) Na₂Fe₁₂O₁₉-Na₂Al₁₂O₁₉-Na

Chapter 10

CRITICAL EVALUATION AND THERMODYNAMIC OPTIMIZATION OF THE Na₂O-FeO-Fe₂O₃-X (X = CaO and MgO) SYSTEMS

10.1. Abstract

No complete and systematic experimental investigations were performed in the Na₂O-FeO-Fe₂O₃-X (X = CaO and MgO) systems either in air or at Fe saturation. Only a couple of studies focused on phase relations between Na₂Fe₂O₄, Na₂Al₂O₄, and Ca_xFe_yO_z compounds in air. Based on available experimental data, the thermodynamic optimization of the Na₂O-Fe₂O₃-CaO system in air was carried out. At the moment, critical evaluation/optimization of the systems is not possible. In the present research, thermodynamic properties of ternary and quaternary liquid solutions were estimated from binary model parameters. No ternary interaction parameters were newly introduced into the liquid solution, and it was also assumed that no ternary stoichiometric compounds are stable.

10.2. Phases and Thermodynamic models

10.2.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound is expressed by:

$$G_T^o = H_T^o - TS_T^o \tag{10-1}$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^T C_P \, dT \tag{10-2}$$

$$S_T^o = S_{298K}^o + \int_{298K}^T \binom{C_P}{T} dT$$
(10-3)

where ΔH_{298K}^{o} is the standard enthalpy of formation of a given compound from pure elements at 298 K (ΔH_{298K}^{o} of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^{o} is the standard entropy of formation at 298 K, and C_{p} is the heat capacity.

In the Na₂O-FeO-Fe₂O₃ system, six binary compounds, Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, Na₈Fe₂O₇, Na₂FeO₂ and Na₄FeO₃, and one ternary stoichiometric phase, NaFe₂O₃, are considered at 1 atm total pressure. There are three binary stoichiometric compounds, Ca₂Fe₂O₅, CaFe₂O₄ and CaFe₄O₇, in the FeO-Fe₂O₃-CaO system. There are several other stoichiometric phases reported in the Na₂O-FeO-Fe₂O₃ system, but due to the lack of experimental data regarding their stability ranges and thermodynamic properties, they were not taken into account in the previous optimization (see *Chapter 5*) and the present study.

10.2.2. Solid solutions

Two solid solutions including CaO-MgO-FeO-FeO_{1.5}-NaO_{0.5} wüstite and Fe₃O₄-MgFe₂O₄ spinel exist in the Na₂O-FeO-Fe₂O₃-CaO-MgO system. The previous description of spinel [1] solid solution was taken in the current study without any further modification. The extension of wüstite in the FeO-Fe₂O₃-CaO-MgO system [2] to the Na₂O side was modeled in *Chapter 5*.

10.2.3. Liquid oxide phase

In this work, the molten oxide phase was described using the Modified Quasichemical Model (MQM) [3]. Short range ordering (SRO) in the molten oxide solution is taken into account by considering Second-Nearest-Neighbor (SNN) pair exchange reactions of cationic species in the

molten oxide, and oxygen is a common anionic species. In the MQM, the following quasichemical reaction in the oxide melt can be written:

$$(A - A) + (B - B) = 2(A - B);$$
 Δg_{AB} (10-4)

where A and B are cationic species in the solution and (A - B) represents a SNN A-B pair, containing an oxygen anion in-between. The Gibbs energy of the above reaction, Δg_{AB} , is the model parameter which can be expanded as an empirical function of composition. Therefore, the Gibbs energy of the solution is given by:

$$G^{m} = \left(n_{A}g_{A}^{o} + n_{B}g_{B}^{o}\right) - T\Delta S^{config} + \left(\frac{n_{AB}}{2}\right)\Delta g_{AB}$$
(10-5)

where n_i and g_i^o are the number of moles and molar Gibbs energies of the pure components, n_{AB} is the number of moles of (A – B) bonds at equilibrium, and ΔS^{config} is the configurational entropy for the random distribution of the (A – A), (B – B) and (A – B) pairs in the one dimensional Ising approximation:

$$\Delta S^{config} = -R \left(n_A \ln X_A + n_B \ln X_B \right) - R \left[n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2} \right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2} \right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B} \right) \right]$$
(10-6)

 Δg_{AB} is expanded in terms of the pair fractions:

$$\Delta g_{AB} = \Delta g^{o}_{AB} + \sum_{i \ge l} g^{i0}_{AB} X^{i}_{AA} + \sum_{j \ge l} g^{0j}_{AB} X^{j}_{BB}$$
(10-7)

where Δg^{o}_{AB} , g^{i0}_{AB} and g^{0j}_{AB} are the model parameters which may be functions of temperature.

10.2.3.1. The Na₂O-FeO-Fe₂O₃-CaO system

For the present research, the liquid components of the Na₂O-FeO-Fe₂O₃-CaO system in the MQM were NaO_{0.5}, FeO, FeO_{1.5}, NaFeO₂, and CaO. Gibbs energies of the liquid NaO_{0.5} (1/2 Na₂O), FeO, FeO_{1.5} (1/2 Fe₂O₃), and CaO were taken from the FACT pure substance database [4]. The Gibbs energy of the liquid NaFeO₂ was previously determined for the thermodynamic optimization of

the Na₂O-Fe₂O₃ system in air (see *Chapter 5*). To respect the consistency of the databases, coordination numbers of all species were kept the same as those in the previous studies (for coordination numbers see *Chapter 5* and reference [5]). Among six possible binary quasichemical reactions, Gibbs energy parameters (Δg_{AB}) of Fe²⁺-Fe³⁺ [2], Fe²⁺-Ca²⁺ [6], and Ca²⁺-Fe³⁺ [6] were taken from the previous optimizations without any further modification. Those of Na⁺-Fe²⁺ and Na⁺-Fe³⁺ were optimized in this work (see *Chapter 5*). The Na₂O-CaO binary solution was considered to be ideal where $\Delta g_{AB} = 0$.

There are ten ternary solutions within the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-CaO system. Gibbs energies of ternary solutions were first predicted from binary model parameters using a specific geometric model and if it was necessary, ternary model parameters were introduced to improve Gibbs energy descriptions of the solutions. Gibbs energies of quaternary and higher order systems were then predicted without any additional model parameter. The Gibbs energy description of the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂ solution was optimized in *Chapter* 5, and that of the FeO-FeO_{1.5}-CaO solution was taken from the previous optimization [6]. In the current study, no ternary model parameters were newly added. Regarding geometric extrapolation techniques for ternary systems, the NaO_{0.5}-FeO-FeO_{1.5} system was treated using 'Toop-type' model with NaO_{0.5} as the 'asymmetric component' (see *Chapter* 5). The NaO_{0.5}-FeO_{1.5}-CaO and NaO_{0.5}-FeO-CaO ternary systems were treated using 'Toop-type' approximation with FeO_{1.5} and CaO as the 'asymmetric components', respectively. The rest of ternary systems were treated using the symmetric 'Kohlertype' model. Details of ternary geometric models can be found elsewhere [7].

10.2.3.2. The Na₂O-FeO-Fe₂O₃-MgO system

For the present research, the liquid components of the Na₂O-FeO-Fe₂O₃-MgO system in the MQM were NaO_{0.5}, FeO, FeO_{1.5}, NaFeO₂, and MgO. Gibbs energies of the liquid NaO_{0.5} (1/2 Na₂O), FeO, FeO_{1.5} (1/2 Fe₂O₃), and MgO were taken from the FACT pure substance database [4]. The Gibbs energy of the liquid NaFeO₂ was previously determined for the thermodynamic optimization of the Na₂O-Fe₂O₃ system in air (see *Chapter 5*). To respect the consistency of the databases, coordination numbers of all species were kept the same as those in the previous studies (for

coordination numbers see *Chapter 5* and reference [5]). Among six possible binary quasichemical reactions, Gibbs energy parameters (Δg_{AB}) of Fe²⁺-Fe³⁺[2], Fe²⁺-Mg²⁺[1], and Mg²⁺-Fe³⁺[1] were taken from the previous optimizations without any further modification. Those of Na⁺-Fe²⁺ and Na⁺-Fe³⁺ were optimized in this work (see *Chapter 5*). The Na₂O-MgO binary solution was considered to be ideal where $\Delta g_{AB} = 0$.

There are ten ternary solutions within the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂-MgO system. Gibbs energies of ternary solutions were first predicted from binary model parameters using a specific geometric model and if it was necessary, ternary model parameters were introduced to improve Gibbs energy descriptions of the solutions. Gibbs energies of quaternary and higher order systems were then predicted without any additional model parameter. The Gibbs energy description of the NaO_{0.5}-FeO-FeO_{1.5}-NaFeO₂ solution was optimized in *Chapter* 5. No ternary parameters were required in the FeO-FeO_{1.5}-MgO solution [1]. In the current study, no ternary model parameters were newly added. Regarding geometric interpolation techniques for ternary systems, the NaO_{0.5}-FeO-FeO_{1.5} system was treated using 'Toop-type' model with NaO_{0.5}-FeO-MgO ternary systems were treated using 'Toop-type' approximation with MgO as the 'asymmetric components'. The rest of ternary systems were treated using the symmetric 'Kohler-type' model. Details of ternary geometric models can be found elsewhere [7].

10.2.4. Metallic and gas phases

To calculate the metallic saturation condition, solid and liquid Fe from FACT pure substance database [4] were considered. The Gibbs energies of gas species were also taken from FACT pure substance database [4].

10.3. Critical evaluation and optimization

Unfortunately, no experimental thermodynamic property and phase equilibrium data are available for the Na₂O-FeO-Fe₂O₃-MgO and Na₂O-FeO-CaO (in equilibrium with metallic Fe) systems in the literature. For the moment, thermodynamic properties of the liquid solutions may be predicted from optimized binary model parameters using extrapolation techniques suggested in section 10.2.3. However, to appropriately describe Gibbs energies of solid and liquid phases present in these systems, their thermodynamic data should be investigated.

10.3.1. The Na₂O-Fe₂O₃-CaO system in air

Toropov and Arakelyan [8] studied phase equilibrium relations on the Na₂Fe₂O₄-Ca₂Fe₂O₅, Na₂Fe₂O₄-CaFe₂O₄, and Na₂Fe₂O₄-CaFe₄O₇ joins using polarizing microscopy, thermal analysis, and XRD. All three phase diagrams are simple eutectic systems. The crystal-optical analysis showed the presence of two phases in the Na₂Fe₂O₄-Ca₂Fe₂O₅ system, Na₂Fe₂O₄ and Ca₂Fe₂O₅. The results were verified by XRD. Using thermal analysis, a clear thermal break was observed at the eutectic temperature. The eutectic occurred at 1468 ± 10 K and 53 mol% Na₂Fe₂O₄ in the Na₂Fe₂O₄-Ca₂Fe₂O₅ system. They also reported the occurrence of the eutectic at 1373 K and 50-60 mol% Na₂Fe₂O₄ on the Na₂Fe₂O₄-CaFe₂O₄ join. No information was revealed about the eutectic temperature and composition along the Na₂Fe₂O₄-CaFe₄O₇ join. Mazel and Arakelyan [9] reported that the Na₂Fe₂O₄-Ca₂Fe₂O₅ is a simple eutectic system, occurring at 50 mol% Na₂Fe₂O4 close to 1473 K. No evidence regarding the formation of new phases was observed. Krasnenko et al. [10] studied phase equilibria at sub-solidus regions in the Na₂O-Fe₂O₃-CaO system in air using thermal analysis and XRD. The formation of no ternary compound was reported in this system.

The calculated sub-solidus region in the Na₂O-Fe₂O₃-CaO system at 1273 K (slightly below the solidus temperature) in air is illustrated in Fig. 10.1. No ternary compounds were newly added in this system which is in agreement with the literature [8-10]. The calculated Na₂Fe₂O₄-CaFe₂O₄ and Na₂Fe₂O₄-Ca₂Fe₂O₅ joins in air are depicted in Fig. 10.2 along with experimental data. There is a discrepancy regarding the eutectic composition between the two sets of experiments. However, the eutectic temperatures in both systems were well reproduced by our model without the addition

of any ternary interaction model parameter, and merely sing a proper extrapolation technique for the liquid solution.

The liquidus projection of the Na₂O-Fe₂O₃-CaO system in air, predicted from binary model parameters, is presented in Fig. 10.3. Liquidus of different phases were calculated to be stable in the system however, primary crystallization regions of wüstite, NaFeO₂ (γ) and Ca₂Fe₂O₅ occupy a broad composition range.

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Fig 10.1: Calculated sub-solidus region in the Na₂O-Fe₂O₃-CaO system at 1273 K in air. Wüs represents wüstite.





Fig 10.2: Calculated (a) Na₂Fe₂O₄-CaFe₂O₄ and (b) Na₂Fe₂O₄-Ca₂Fe₂O₅ joins in air along with experimental data [8,9].



Fig 10.3: Calculated liquidus projection of the Na₂O-Fe₂O₃-CaO system in air, predicted from the present optimization.

Chapter 11

PAPER 6: THERMODYNAMIC MODELING OF SULFIDE CAPACITIES OF Na₂O-CONTAINING OXIDE MELTS

Elmira Moosavi-Khoonsari and In-Ho Jung, submitted to *Metallurgical and Materials Transactions B*, 2015.

11.1. Abstract

Thermodynamic modeling of the sulfide dissolution in the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ multicomponent slags was performed to investigate the desulfurization of hot metal using Na₂O-containing fluxes. The dissolution behavior of sulfur in the melts was modeled using the Modified Quasichemical Model in the quadruplet approximation. This model can take into account the short range ordering and the reciprocal exchange reaction of cations and anions in oxy-sulfide slags. Experimental sulfide capacity data were well predicted from the model with only three model parameters.

11.2. Introduction

The sulfur solubility in oxide melts at high temperatures is important for ironmaking, steelmaking, combustion, glassmaking, and geochemistry. Particularly, there is currently a strong demand for the production of high quality steels with very low levels of impurities for line pipes, electrical tools, and advanced automotive applications. The desulfurization process of hot metal is often carried out prior to decarburization in the basic oxygen furnace, and further desulfurization of steel can be conducted in the ladle furnace in the secondary steelmaking process. As a result, the sulfide segregation and inclusions of steel are reduced, and the surface quality is improved, which decreases the need for subsequent surface treatments [1].

Various desulfurizers such as mixtures of CaO (lime), CaC₂ (calcium carbide), Na₂CO₃ (soda ash), metallic Mg, etc. have been widely used in hot metal pretreatment. Lime is a strong desulfurization agent often used in the Kanbara Refining (KR) station. In order to accelerate the desulfurization kinetics, a small amount of CaF₂ is mixed. However, the CaF₂ consumption has raised serious concern regarding the corrosion of refractories, health, and environment [2, 3]. The desulfurization operation using CaC₂ and Mg is rather costly, and cares must be given to the storage and transport due to possible explosion [4]. Therefore, Na₂O-containing fluxes from Na₂CO₃ have regained interest as desulfurization agents in ironmaking and steelmaking. However, to optimize the sulfur removal efficiency, accurate knowledge of sulfide capacities of the fluxes is essential.

Sulfide capacities of Na₂O-containing silicate melts [5-13] and the sulfur partition ratio between the slag and liquid Fe [10-12, 14-22] were experimentally studied. However, experimental data are inconsistent and limited to specific composition and temperature ranges. This is attributed to difficulties in performing experiments involving Na₂O-containing slags: (i) the high vapor pressure of Na in slags and subsequent loss of Na, especially those slags with high Na₂O contents [10, 11, 13, 17], (ii) very hygroscopic nature of slags, and (iii) the absorption of CO₂ and other gaseous species from the atmosphere by slags [13, 16].

The main objective of the present study is to develop a thermodynamic database to predict sulfide capacities of slags, especially those of Na₂O-containing slags. In the past, the Modified Quasichemical Model (MQM) was used to explain the dissolution of gaseous species in slags ²³⁻²⁶⁾. For example, the dissolution of H (H₂O and hydroxyl ion), N (various nitrides), and C (carbonates and carbides) in steelmaking slags was described using the MQM and simplified Blander-Reddy capacity model [25, 26]. Recently, the MQM in the quadruplet approximation [27] has successfully modeled the dissolution behavior of sulfur in the form of sulfide in various molten slags [28]. That is, thermodynamics of oxy-sulfide melts was well described using the MQM. This work is the extension of the MQM description to Na₂O-containing oxy-sulfide melts.

11.3. Sulfide capacity

Fincham and Richardson [29] investigated the sulfur solubility in the CaO-Al₂O₃-SiO₂ melt using the slag/gas equilibration at 1623 and 1923 K. They reported that sulfur dissolved in the form of sulfate ($SO_4^{2^-}$) at log $p_{O_2} > -3.0$ atm, while it dissolved as sulfide (S^{2^-}) at log $p_{O_2} < -5.0$ atm. The same results were reported later by Pierre and Chipman [30], and Turkdogan and Darken [31]. Nagashima and Katsura [6] who studied the sulfur solubility in the Na₂O-SiO₂ melt also demonstrated that sulfur dissolved mostly as sulfide at log $p_{O_2} < -9.0$ atm, while sulfate was the dominant form of S at log $p_{O_2} > -6.8$ atm. Under ironmaking and steelmaking conditions where the liquid Fe exists, therefore, sulfur is considered to be in the form of sulfide in oxide melts.

11.3.1. Definition of sulfide capacity

The sulfide capacity is "the potential capacity of a melt to hold sulfur as sulfide", and was simplified by Fincham and Richardson [29] to the following equation:

$$C_{S} = (wt.\% S) \left(\frac{p_{O_{2}}}{p_{S_{2}}}\right)^{1/2}$$
(11-1)

where C_S stands for the sulfide capacity, and (wt.% S), p_{O_2} , and p_{S_2} represents the weight percent of sulfur in the oxide (strictly speaking, oxy-sulfide) melt, and the partial pressures of oxygen and sulfur in the gas phase in equilibrium with the slag, respectively.

Fincham and Richardson [29] reported that the sulfide capacity of the oxide melt depends only on the melt composition and temperature. They showed that sulfide capacities of silicate melts decreased as SiO₂ content increased, related to the reduced activity of the metal oxide. They found a close relation between the sulfide capacity and the activity of basic metal oxide in the aluminosilicate melt. Sulfide capacities of slags can be determined using either the slag/gas equilibrium or the slag/metal equilibrium. According to the latter method, the equilibrium distribution of sulfur between the slag and metal called "sulfur partition ratio (%S)_{slag}/[%S]_{metal}" is measured. The sulfide capacity is then calculated from the sulfur partition results.

11.3.1.1. Slag/gas equilibrium

Let us consider the slag/gas reaction as follows:

$$(O^{2-}) + \frac{1}{2} S_2(g) = (S^{2-}) + \frac{1}{2} O_2(g)$$
(11-2)

$$K_{2} = \frac{a_{S^{2-}}}{a_{O^{2-}}} \sqrt{\frac{p_{O_{2}}}{p_{S_{2}}}} = \frac{(wt.\%S)f_{S^{2-}}}{a_{O^{2-}}} \sqrt{\frac{p_{O_{2}}}{p_{S_{2}}}}$$
(11-3)

where p_{O_2} and p_{S_2} are the partial pressures of O_2 and S_2 in the gas phase in equilibrium with the oxy-sulfide melt, and $a_{O^{2-}}$ and $a_{S^{2-}}$ are the activities of oxygen and sulfide anions, respectively. $f_{S^{2-}}$ is the activity coefficient of S^{2-} in the infinitely dilute region in the weight percent standard state. Since $a_{O^{2-}}$ and $f_{S^{2-}}$ cannot be measured in ionic melts, Fincham and Richardson [29] proposed a definition for the sulfide capacity as following:

$$C_{S} = (wt.\%S) \left(\frac{p_{O_{2}}}{p_{S_{2}}}\right)^{1/2} = \frac{a_{O^{2-}}K_{2}}{f_{S^{2-}}}$$
(11-4)

When the sulfur concentration is very small in the slag (about 1 wt.% or lower), Henry's law may be assumed. That is, $f_{s^{2-}}$ becomes dependent on the slag composition and temperature. Hence, C_s is only influenced by the slag composition and temperature regardless of p_{O_2} and p_{S_2} . As a result, a unique value of C_s could be assigned to a given slag composition.

11.3.1.2. Metal/slag equilibrium

The sulfide capacity can be also defined based on the slag/metal equilibrium reaction:

$$[S] + (O^{2-}) = (S^{2-}) + [O]; \quad K_5 = \frac{a_O a_{S^{2-}}}{a_S a_{O^{2-}}}$$
(11-5)

where [] and () represent components in the molten metal and slag, respectively, a_0 and a_s are the activities of O and S in the metal, and $a_{0^{2-}}$ and $a_{s^{2-}}$ are the activities of O²⁻ and S²⁻ in the oxysulfide melt. K_2 and K_5 are related via the following metal/gas exchange reaction:

$$\frac{1}{2} S_2(g) + [O] = [S] + \frac{1}{2} O_2(g); \quad K_6 = \frac{a_S}{a_O} \left(\frac{p_{O_2}}{p_{S_2}}\right)^{1/2}$$
 (11-6)

By rearranging Eqs. (4) and (6), a relation between the sulfur partition ratio and sulfide capacity is obtained:

$$\log C_{S} = \log \frac{(wt\%S)}{[wt\%S]} + \log a_{O} + \log K_{6} - \log f_{S}$$
(11-7)

The activity of oxygen in the metal, a_0 , is proportional to the oxygen partial pressure at the metal/slag interface, and f_s is the activity coefficient of sulfur in the metal.

11.3.2. Limitation of sulfide capacity concept for Na₂O-containing melts

The sulfide capacity concept cannot be applied as a unique slag property to Na₂O-containing melts because the dissolved amount of sulfide (Na₂S) is very significant in many cases, and thus, the fundamental assumption of this concept is not valid anymore. This also happens when the slag contains large amounts of CaO, MgO, MnO, FeO, and K₂O. The limitation of sulfide capacity idea introduced by Fincham and Richardson [29] occurs when the activity of a strong network modifier in the slag approaches unity. Details will be explained below.

The sulfide capacity concept was developed to objectively define the sulfur dissolution capacity of the slag regardless of the sulfur and oxygen partial pressures (of course under reducing conditions where the sulfide is the dominant form of sulfur in the slag). That is, the sulfide capacity is a unique value for a given slag composition, only depending on the temperature. However, this is merely valid when the solubility of sulfur in the slag is dilute enough to maintain $f_{s^{2-}}$ and $a_{o^{2-}}$ constant. In reality, this is not true anymore, especially for slags containing high amounts of Na₂O.

Figure 11.1 illustrates the calculated sulfide capacities of three different binary silicate melts containing CaO, FeO, and Na₂O, under different oxygen and sulfur partial pressures. Modeling of the sulfide solubility in both CaO-SiO₂ and FeO-SiO₂ systems was performed, previously, by Kang and Pelton [28], and that of the Na₂O-SiO₂ system was conducted in the present study, which will be elaborated later. The solid lines in the figures represent the sulfide capacities where the liquid phase is stable, and the dotted lines represent the predicted sulfide capacities of the metastable liquid phase where all solid phases were suppressed in the calculations.

In the case of the CaO-SiO₂ melt at 1873 K (Fig. 11.1(a)), the sulfide capacities of the liquid, stable between about 34 and 58 mol % CaO, are slightly different depending on p_{O_2} and p_{S_2} . As it is seen, the difference among the calculated sulfide capacities under various partial pressures of oxygen and sulfur is nearly zero at low CaO region, but it becomes very noticeable at high CaO contents (above the orthosilicate composition). Since the difference in the sulfide capacities of the stable liquid (between 34 and 58 mol % CaO) is relatively small, experimental studies could hardly reveal such a slight variation in the sulfide capacity of the CaO-SiO₂ slag depending on p_{O_2} and

 p_{S_2} . The change in the slag composition under different oxygen and sulfur partial pressures is also plotted in the CaO-CaS-SiO₂ diagram (Fig. 11.1(b)). It is clear that the calculated compositional trajectories almost lie on the CaO-SiO₂ binary system at CaO concentrations less than 40 mol %. The compositional trajectories, then, largely deviate from the binary system depending on p_{O_2} and p_{S_2} . This results from the high activity of CaO (that is, O²⁻) and consequently, the high concentration of CaS (that is, S²⁻) in the slag. As $f_{S^{2-}}$ and $f_{O^{2-}}$ change with composition at high CaO and CaS regions, the compositional trajectory varies with p_{O_2} and p_{S_2} . However, such a large difference can be only observed at compositions rich in CaO, where the CaO-SiO₂ liquid phase is unstable at common steelmaking temperatures. So far, no experimental study has revealed the possible variation of sulfide capacity with p_{O_2} and p_{S_2} .

In the case of the FeO-SiO₂ melt at 1773 K (Fig. 11.1(c)), the liquid region further extends toward high FeO contents since the melting temperature of FeO at Fe saturation is 1667 K. The sulfide capacity of the FeO-rich melt changes depending on p_{O_2} and p_{S_2} , but the difference is within 0.25 in logarithmic scale which is still difficult to be detected in experimental studies. However, the difference in the compositional trajectories in the FeO-FeS-SiO₂ diagram is very large (Fig. 11.1(d)), due to the same reason explained above for the CaO-SiO₂ melt.

As shown in Fig. 11.1(e), disagreement in the sulfide capacities of the Na₂O-SiO₂ melt at 1773 K under different gas atmospheres is very significant even at low Na₂O concentrations. This originates from the large solubility of Na₂S in the melt, even under low p_{S_2} (Fig. 11.1(f)). Therefore, if sulfide capacity experiments were carried out under slightly different gas compositions, significant differences in the sulfide capacity results could be expected. This might be one of reasons explaining large discrepancies among sulfide capacity data in the Na₂O-SiO₂ melt.

The standard Gibbs energy of reaction between a pure metal oxide (network modifier), MO (CaO, MgO, MnO, FeO, and BaO) and N₂O (Na₂O and K₂O), and its sulfide is plotted in Fig. 11.2:

$$MO(l) + \frac{1}{2} S_2(g) = MS(l) + \frac{1}{2} O_2(g)$$
(11-8)

$$N_2O(l) + \frac{1}{2}S_2(g) = N_2S(l) + \frac{1}{2}O_2(g)$$
(11-9)

All the calculations were performed using either FactSage – FACTPS database [32] or SGTE pure substance database [33]. As expected, the standard Gibbs energies of exchange reactions between alkali oxides such as K_2O and Na_2O and their correspondent sulfides are much more negative than those between alkaline earth or transition metal oxides and their related sulfides. However, interestingly, the Gibbs energy of MgO/MgS reaction is much higher than the others. This means that, the tendency toward the formation of MgS in the liquid is much lower than that of other

sulfides when the activities of oxides (in the liquid standard state) in the slag are all the same. Moreover, the Gibbs energy diagram reveals that a similar behavior to that shown in Fig. 11.1 is also observed for the oxides such as K₂O, MnO, and BaO.

However, to calculate sulfide capacities of real silicate and aluminate slags, it is the activity of metal oxide in the slag which must be taken into account. Therefore, the standard Gibbs energy of reaction, illustrated in Fig. 11.2, and the activity of the oxide component in the slag must be considered, simultaneously, to evaluate the potential of the slag to form sulfide.

Furthermore, it is hard to compare between experimental data in the literature because in many cases, authors did not specify how they measured Na₂O, SiO₂, and S contents of melts. There would be two possible definitions for the mole fraction of Na₂O: (i) $x_{Na_2O} = 0.5n_{Na}/(0.5n_{Na} + n_{Si})$ considering all Na are associated to oxygen, and (ii) $x_{Na_2O} = (0.5n_{Na} - n_S)/(0.5n_{Na} - n_S + n_{Si})$ excluding Na associated to sulfur (Na₂S). If the sulfide concentration is very low, both definitions will give nearly the same results. However, when large amounts of sulfide exist in the melt, two definitions give completely different results for the base composition of oxide melt. In the present study (including Fig. 11.1), the first definition was exclusively used to normalize the slag composition, which was also typically employed in experimental studies.

11.4. Thermodynamic model

Liquid solutions showing a Short Range Ordering (SRO) tendency can be modeled using the Modified Quasichemical Model (MQM) [34]. This model well reproduces experimentally measured binary phase diagrams and thermodynamic properties, and accurately predicts thermodynamic properties of ternary and higher order liquid phases based on optimized binary model parameters. If necessary, small ternary parameters can be added into the model to reproduce available experimental data. The MQM is superior to the conventional random-mixing Bragg-Williams Model (BWM) in the prediction of thermodynamic behaviors of binary liquid solutions, especially those with a strong SRO tendency like molten silicates. Details of the model can be found elsewhere [34]. The MQM is also very strong in the prediction of sulfide capacities of slags

with almost no empirical model parameters. The model is not limited to dilute regions and nonacidic slags. The concept of the model in the quadruplet approximation for oxy-sulfide solutions is briefly explained below (details can be found elsewhere [28]).

11.4.1. The MQM in the quadruplet approximation

To describe the dissolution behavior of sulfur in Na₂O-MO-SiO₂ melts, the following reactions are important:

(i) The reciprocal exchange reactions among pure components of the melt:

$$2Na_2O(l) + SiS_2(l) = 2Na_2S(l) + SiO_2(l); \Delta g_{NaSi/OS}^{exchange}$$
(11-10)

$$MO(l) + SiS_2(l) = MS(l) + SiO_2(l); \quad \Delta g_{MSi/OS}^{exchange}$$
(11-11)

where M is Fe, Ca, Mg, Mn, and Al in the present study. These equilibria explain the formation of cation-anion First-Nearest-Neighbor (FNN) pairs mainly including (Na-S), (M-S), and (Si-S) in oxide slags.

(ii) The Second-Nearest-Neighbor (SNN) pair exchange reactions between cations of the molten slag:

$$(Na-O-Na) + (Si-O-Si) = 2(Na-O-Si); \Delta g_{NaSi/OO}$$
(11-12)

$$(M-O-M) + (Si-O-Si) = 2(M-O-Si); \Delta g_{MSi/OO}$$
 (11-13)

The above equations determine a very strong SRO tendency in the molten slag. To consider the FNN SRO and SNN SRO, simultaneously, cationic (Na⁺, Fe²⁺, Fe³⁺, Ca²⁺, Mg²⁺, Mn²⁺, Al³⁺, Si⁴⁺) and anionic [O²⁻, S²⁻] sublattices are assumed in the slag. To better understand the structure of oxy-sulfide slags, consider the Na₂O-SiO₂ binary system in which sulfur dissolved. Figure 11.3 illustrates the reciprocal ionic system, (Na⁺, Si⁴⁺)[O²⁻, S²⁻], in the form of a composition square.

The Gibbs energy of an oxy-sulfide liquid solution is obtained from:

$$G = \sum_{i,j,k,l} n_{ij/kl} g_{ij/kl} - T\Delta S^{config}$$
(11-14)

where *i* and *j* are cationic species, Na⁺ and Si⁴⁺, and *k* and *l* are anionic species, O²⁻ and S²⁻, and $n_{ij/kl}$ is the number of moles of *ij/kl* quadruplet species. $g_{NaNa/OO}$ and $g_{SiSi/OO}$ are the partial molar Gibbs energies of pure oxides, and $g_{NaNa/SS}$ and $g_{SiSi/SS}$ are the partial molar Gibbs energies of pure sulfides. $g_{NaSi/OO}$ and $g_{NaSi/SS}$ are the partial molar Gibbs energies of binary quadruplets on the edges of the square, $g_{NaNa/OS}$ and $g_{SiSi/OS}$ are the partial molar Gibbs energies of oxy-sulfides, and $g_{NaSi/OS}$ is the average of $g_{NaSi/OO}$, $g_{NaSi/SS}$, $g_{NaNa/OS}$, and $g_{SiSi/OS}$. ΔS^{config} is the configurational entropy, obtained by the random distribution of the quadruplets on the quadruplet sites, and is calculated based on an Ising-type approximation:

$$-\frac{\Delta S^{config}}{R} = \sum_{i} n_{i} \ln X_{i} + \sum_{k} n_{k} \ln X_{k} + \sum_{i,k} n_{i/k} \ln\left(\frac{X_{i/k}}{Y_{i}Y_{k}}\right)$$

$$+ \sum_{i,j,k,l} n_{ij/kl} \ln\left(\frac{X_{ij/kl}}{(2 - \delta_{ij})(2 - \delta_{kl})X_{i/k}X_{i/l}X_{j/K}X_{j/l}}\right)$$
(11-15)

where $n_{i,i}$, X_i , and Y_i are the number of moles, mole fraction and equivalent fraction of *i*, respectively, $X_{i/j}$ and $X_{ij/kl}$ are mole fraction of the *i*-*j* pairs and *ij/kl* quadruplets, respectively, and δ_{ij} is Kröneker delta.

To study slags containing sulfur, the coordination number of each ion is fixed as a constant value and does not vary with composition. It is assumed that coordination numbers of cations in oxysulfide solutions are the same as those in oxide solutions, and the coordination number of S^{2-} is the same as that of O^{2-} . It is also assumed that all FNN coordination numbers are equal to two times the corresponding SNN coordination numbers. In Eq. (11-14), the Gibbs energies of unary quadruplets (Na₂O₂, Si₂O₂, Na₂S₂, and Si₂S₂) at the four corners of the square (Fig. 11.3) are taken from the Gibbs energies of pure liquid oxides and sulfides:

$$g_{NaNa/OO} = \left(\frac{2}{Z_{Na}}\right) g_{Na_2O}^o \tag{11-16}$$

where Z_{Na} is the SNN coordination number of Na^+ , and $g^o_{Na_2O}$ is the standard molar Gibbs energy of pure liquid Na₂O per charge equivalent. The Gibbs energies of the binary quadruplets ($g_{NaSi/OO}$, ...) are derived from the Gibbs energies of the SNN pair exchange reactions, e.g. in the Na₂O-SiO₂ system:

$$(NaNa/OO) + (SiSi/OO) = 2(NaSi/OO); \Delta g_{NaSi/OO}$$
(11-17)

$$2g_{NaSi/OO} = \Delta g_{NaSi/OO} + g_{SiSi/OO} + g_{NaNa/OO}$$
(11-18)

where $\Delta g_{NaSi/OO}$ is an adjustable model parameter which was previously obtained based on the assessment/optimization of available thermodynamic property and phase diagram data in the Na₂O-SiO₂ system [35]. This parameter can be a function of temperature and composition. Zero or non-zero parameters may be assigned to other reaction energies, $\Delta g_{NaSi/SS}$, $\Delta g_{NaNa/OS}$, and $\Delta g_{SiSi/OS}$, to reproduce experimental sulfide capacity data. Equilibrium concentrations of quadruplets ($n_{ij/kl}$) for a specific composition are calculated so that the total Gibbs energy (Eq. (11-14)) of the system is minimized.

Kang and Pelton [28] showed that sulfide capacities of oxide melts containing small amounts of sulfur in the form of sulfide can be well predicted from the MQM in the quadruplet approximation. That is, without any model parameter, an accurate prediction is obtained for sulfide capacities of slags. However, in the case of concentrated sulfide-containing melts such as CaO-Al₂O₃-CaS [36] and MnO-SiO₂-MnS [37], a small ternary parameter was introduced in each system to improve the sulfide capacity predictions and simultaneously reproduce the phase diagrams of the ternary systems (strictly speaking, these are reciprocal systems):

$$q_{CaAl/O(S)}^{001} = 6276 \text{ J/mol}$$
(11-19)

$$q_{MnSi/O(S)}^{002} = 10460 \text{ J/mol}$$
(11-20)

where $q_{AB/O(S)}^{ijk}$ are ternary empirical coefficients that describe the effect of the presence of S²⁻ anion on the energy of formation of AB/OO quadruplets.

Due to the similar reason, to reproduce all experimental sulfide capacity data as accurate as possible, a small temperature independent parameter was assigned to $\Delta g_{NaNa/OS}$ for the binary Na₂O-Na₂S system:

$$\Delta g_{NaNa/OS} = -37656 \text{ J/mol}$$
 (11-21)

In fact, this parameter can also roughly reproduce the Na₂O-Na₂S binary phase diagram.

11.5. Sulfide capacity of Na₂O-containing silicate melts

In the present study, thermodynamic modeling of the sulfide capacities of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ multicomponent slags was carried out. The thermodynamic optimization of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ system is a prerequisite to describe its sulfide capacity. In the thermodynamic optimization of a system, all available experimental phase diagram and thermodynamic property data relevant to the given system are simultaneously taken into account to obtain a set of optimized model parameters which can reproduce all reliable experimental data within experimental error limits. The thermodynamic optimization of the binary, ternary, and higher order sub-systems of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ slag was already carried out, and detailed descriptions are available elsewhere [35, 38-45]. In particular, the MQM is exclusively used to treat the liquid phase. In this research, previous thermodynamic descriptions of liquid solutions were used without any further modification. Gibbs energies of sulfides such as FeS, Fe₂S₃, CaS, MgS, MnS, Al₂S₃, and SiS₂ were presented in the earlier work by Kang and Pelton [28]. All these Gibbs energies were adopted in the current modeling without any adjustment to keep the consistency of the database. The Gibbs energy of Na₂S was taken from the FACTPS database [32], originally constructed based on the JANAF thermodynamic table [46]. All the thermodynamic calculations were carried out using the FactSage software [32], which uses the powerful Gibbs energy minimization routine.

Table 11.1 summarizes all experimental studies of sulfide capacities of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ multicomponent slags. Experimental conditions such as temperature and partial pressures of oxygen and sulfur are listed in the table. Many of experimental studies on the sulfide capacity of the same slag system were conducted under quite different partial pressures of oxygen and sulfur, and measurements are often very scattered. This may be originated from experimental difficulties, the possible evaporation of Na [10, 11, 13, 17] and the noticeable absorption of water or CO_2 from the atmosphere [13, 16] during experiments. However, to date, no study discussed that such inconsistencies would stem from the limitation of sulfide capacity concept in sulfide-rich melts.

As mentioned earlier in section 11.3.2, sulfide capacities of slags, especially those of Na₂Ocontaining melts could largely depend on partial pressures of oxygen and sulfur. Therefore, we tried to calculate the sulfide capacity using reported experimental conditions to accurately compare the computation results with experimental data. Equilibrium p_{O_2} and p_{S_2} were calculated from experimental inlet gas compositions, and if compositions of gas mixtures were not reported [9-12], those values of p_{O_2} and p_{S_2} provided by the authors were taken as reported. The slag/metal equilibration results were also used to calculate the sulfide capacities of the slags. All sulfur partition data excluding those investigated by Chen et al. [18], and Inoue and Suito [16] were measured by equilibrating the C saturated liquid Fe and the slags in graphite crucibles. Chen et al. equilibrated the C saturated liquid Fe with the slags in MgO crucibles, and Inoue and Suito [16] did not use C saturated metal for equilibration. Therefore, in the present study, the oxygen partial pressure at the slag/metal interface for the experiments was calculated from the C/CO equilibrium. In the case of slag/metal equilibration, a small amount of FeO dissolved in the liquid [10-12, 15, 16, 18], but the influence of FeO content on the sulfide capacity was assumed to be negligible.

Experimental studies of sulfide capacities in the literature were sometimes carried out at solid + liquid two-phase regions because phase diagrams of many Na₂O-containing systems were not well known. In the present work, the sulfide capacity was predicted only for the liquid single-phase region. As mentioned earlier, when a large amount of sulfide dissolves in the melt, it is hard to define the nominal composition of oxide slag. In the current research, the cationic species in the slag were used to determine the slag composition. For example, for the Na₂O-Na₂S-SiO₂ slag,

 $n_{Na}/2 = n_{Na_2O}$ and $n_{Si} = n_{SiO_2}$ were assumed to normalize the base composition of oxide slag regardless of whether Na is associated to oxygen or sulfur. This method has been typically used in the literature to define the base composition of oxide slag.

Calculated sulfide capacities with all available experimental data for binaries, ternaries and multicomponent slags in the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ system are illustrated in Figs. 11.4 to 11.11. In general, the calculations and literature data are in fair agreement within experimental error limits. Details for each slag system are discussed below.

11.5.1. The Na₂O-SiO₂ system

The calculated sulfide capacities of the Na₂O-SiO₂ melt from 1473 to 1773 K were investigated by many researchers, as shown in Fig. 11.4. At 1473 K, the calculated sulfide capacities and the experimental data from Körber and Oelson [15], and Chan and Fruehan [10] are in fair correspondence; the calculated sulfide capacity line touches the bottom of experimental error limits. At 1523 K, the prediction is in accordance with the experimental data from Nagashima and Katsura [6], and Denier [5] (internal report cited by Inoue and Suito [16])). It should be noted that the slag studied by Inoue and Suito [16] contained up to 1 mol % Al₂O₃. At 1573 K, the experimental results by Körber and Oelson [15] and Chen et al. [18] were performed under quite different p_{S_2} thus, it is impossible to be directly compared. The calculated sulfide capacity agrees well with the experimental results from Körber and Oelson [15]. However, the calculations lie below the measurements from Chen et al. [18], especially at low Na₂O region. As Chen et al. [18] used MgO crucibles for slag/metal equilibration experiments, there is a possibility that MgO dissolved in the slag; Inoue and Suito [16] reported that the MgO dissolution from crucibles in the Na₂O-SiO₂ melt reached up to 17 wt.% at 1473 K. With this consideration, the calculated results would better match with the experimental data. There are numerous experimental studies at 1623 K. The calculated sulfide capacity line is slightly lower than the experimental data [5, 7, 16, 18, 19], but the sulfide capacity trend is very well reproduced within the experimental uncertainty. At 1673 and 1773 K, agreement with measurements [11, 13, 15] is excellent within the experimental error ranges.

It should be noted that the present model can properly predict the S shape of the sulfide capacity (for example, see the results at 1523 and 1623 K); the steep increment in the sulfide capacity at about 40 mol % Na₂O was well reproduced. Although the sharp increase with the S shape is well expected, its composition (basicity) is rather unexpected. The activity of Na₂O, proportional to $a_{0^{2^{-}}}$, is directly related to the sulfide capacity as shown in Eq. (11-4). Therefore, a significant change in the sulfide capacity would be anticipated near the orthosilicate composition ($X_{SiO_2} = 0.33$), where the Na₂O activity largely varies in the Na₂O-SiO₂ binary melt. However, the sulfide capacity results deviate from the expectation.

The calculated sulfide capacities and corresponding components of the Na₂O-SiO₂ melt under a controlled sulfur gas atmosphere are presented in Fig. 11.5. The partial pressures of oxygen and sulfur used in the calculations are 10^{-17} and 10^{-8} atm, respectively, which are the average partial pressures of gaseous species employed in most experiemental studies. As it is seen in Fig. 11.5(a), the sulfide capacities at various temperatures are largely different at low Na₂O contents; however, a significant change in the sulfide capacity occurs near 40 mol % Na₂O, and it becomes almost constant at high concentrations of Na₂O regardless of the temperature. It should be noted that the mole fraction of Na₂O in the x-axis was calculated based on the cation fraction, $x_{Na_2O} = 0.5n_{Na^+}/(0.5n_{Na^+} + n_{Si^{4+}})$, as mentioned before. The variation of calculated slag components with composition is depicted in Fig. 11.5(b). According to the calculated results, most Na cations are present in the form of Na₂O in the slag with low basicity. However, Na₂S becomes dominant with increasing Na₂O content of the original slag. The acutal amount of Na₂S in the melt is mostly controlled by the Na₂O-Na₂S equibrium. As pointed out by Reddy et al. [47], and Reddy and Zhao [48], the amount of sulfide becomes nearly constant at low Na₂O region regardless of temperature while it significantly changes with temperature for low concentrations of Na₂O. Figure 11.5(c) shows the calculated activities of the slag constituents.

The large variation in the sulfide capacity at around 40 to 50 mol% Na₂O instead of at the orthosilicate composition is pertinent to the formation of a significant amount of Na₂S in the liquid, changing the activity behavior of Na₂O. In equilibrium conditions, the ratio of Na₂O and Na₂S activities should be constant at a given temperature, and also that of given oxygen and sulfur partial pressures regardless of Na₂O content. This ratio is only governed by the equilibrium constants of
reactions (11.8) and (11.9). That is, the equilibrium constants can determine the ratio of Na₂O and Na₂S activities from the following relations:

$$K_{reaction\,(8)} = \frac{a_{MS(l)}}{a_{MO(l)}} \sqrt{\frac{p_{O_2}}{p_{S_2}}}$$
(11-22)

$$K_{reaction(9)} = \frac{a_{M_2S(l)}}{a_{M_2O(l)}} \sqrt{\frac{p_{O_2}}{p_{S_2}}}$$
(11-23)

At low Na₂O region (the left side of the x-axis in Fig. 11.5), where SiO₂ and Na₂O are the major constituents of the slag, the Na₂S concentration is mainly determined by the activity of Na₂O from the Na₂O/Na₂S exchange reaction. On the other hand, at high Na₂O region (the right side of the x-axis in Fig. 11.5), where Na₂S and SiO₂ are the main constituents of the slag, the Na₂S content may be defined by the Na₂S/SiO₂ interaction, and it can, in return, determine the concentration of Na₂O.

In the case of other binary systems like CaO-SiO₂ and FeO-SiO₂, the sharp change in the S shape of the sulfide capacity would occur close to the orthosilicate composition (see Figs. 11.1(a) and (c)) as concentrations of sulfides, CaS and FeS, are generally much lower than the Na₂S content in Na₂O-containing slags (this is also understood from the standard Gibbs enegies of exchange reactions in Fig. 11.2). Therefore, it could be concluded that the sulfide capacities of FeO, CaO, MgO, and MnO silicate slags are directly influenced by the activities of corresponding metal oxides while those of Na₂O and K₂O silicate slags are determined in a more complex manner.

11.5.2. Na₂O-containing ternary systems

Predicted iso-sulfide capacity lines for several ternary slags at different temperatures are presented in Figs. 11.6 to 11.9. All experimental data and calculated lines are plotted as $-logC_S$ for the convenience. The iso-thermal diagrams were plotted only considering oxide components without the S dissolution.

11.5.2.1. The Na₂O-Fe_tO-SiO₂ system

The predicted iso-sulfide capacity ($-logC_S$) lines of the Na₂O-Fe₁O-SiO₂ melt at 1373 K (Fig. 11.6) show an interesting trend. At low SiO₂ region, the predicted sulfide capacity at a constant SiO₂ content reveals a minimum near the Na₂O/FeO molar ratio equal to 1.0. In the liquid, the stable sulfide could alter from Na₂S to FeS with increasing FeO content at constant mole fraction of SiO₂. The minimum sulfide capacity happens because of a strong negative interaction between Na₂O and FeO [38]. That is, the activities of Na₂O and FeO in the Na₂O-FeO binary melt show a large negative deviation from the ideal solution behavior. As a result of such a strong ordering in the melt, the effect of Na₂O and FeO activities on the sulfide formation becomes the least in the middle composition range. It should be also noted that, for more acidic region, the sulfide capacity of FeO is still not negligible in the slag with low basicity, opposite to that of Na₂O. Hence, the sulfide capacity at low basicity region increases with increasing FeO content of the melt at constant mole fraction of SiO₂.

The sulfide capacities of the Na₂O-Fe_tO-SiO₂ slags measured by DeYoung [8] at 1373 K are somewhat questionable. For example, for the FeO-containing system, the final slag compositions are far from the original ones even at high SiO₂ contents. Significant loss of FeO and Na₂O was reported, which is not well understood. Agreement with the measurements at two compositions is very good. However, the other two experimental data are much higher than our predictions.

11.5.2.2. The Na₂O-MO-SiO₂ systems (M = Ca, Mg, and Mn)

The predicted sulfide capacities of the Na₂O-CaO-SiO₂, Na₂O-MgO-SiO₂, and Na₂O-MnO-SiO₂ systems in comparison with available experimental data are illustrated in Figs. 11.7, 11.8(a), and

8(b), respectively. The predicted iso-sulfide capacity lines show a decreasing trend with replacement of Na₂O by CaO or MgO at a constant SiO₂ concentration. This is due to a lower tendency of CaO and MgO, in comparison with Na₂O, to form sulfides, as shown in Fig. 11.2. Of course, a steeper reduction in the sulfide capacity is observed with MgO than CaO since the tendency toward the formation of MgS is less than that of CaS.

In the case of the Na₂O-CaO-SiO₂ slag, several experimental studies were carried out at different temperatures. The experimental data from Inoue and Suito [16] at 1523 K, and Kunisada and Iwai [13] at 1773K were well predicted at relatively high Na₂O contents. However, the predictions lie below the measurements at low Na₂O region. The experimental data obtained by Niekerk and Dippenaar [20] at 1623 K at relatively high SiO₂ concentrations well agree with the calculations. The results from Chan and Fruehan [12] at low mole fraction of Na₂O are somewhat scattered, but they were reasonably well reproduced. That is, there is inconsistency between two groups of data at low Na₂O contents: one group includes data collected by Inoue and Suito [16], and Kunisada and Iwai [13], and the other group includes results from Niekerk and Dippenaar [20], and Chan and Fruehan [12]. According to our model, the latter would be thermodynamically more consistent with the binary system. Some of the data obtained by Chan and Fruehan [12] using the slag/gas equilibration technique locate inside the liquid + CaSiO₃ two-phase region, as shown in Fig. 11.7(c). For the Na₂O-MgO-SiO₂ system, the experimental data from Kunisada and Iwai [13] at 1773 K were fairly reproduced in the present study, depicted in Fig. 11.8(a).

Based on the calculations for the Na₂O-MnO-SiO₂ melt (Fig. 11.8(b)), the iso-sulfide capacity lines do not significantly vary with the replacement of Na₂O by MnO at constant SiO₂ contents. Although the capacity of MnO to form MnS is less than that of Na₂O (see Fig. 11.2), the relative activity of MnO in silicate melts is higher than that of Na₂O at the same SiO₂ concentration, because the Na₂O-SiO₂ interaction is much more negative than that of MnO-SiO₂. This may explain the formation of a high amount of MnS, which is almost equivalent to the concentration of Na₂S, in the Na₂O-MnO-SiO₂ melt. The experimental results from Kunisada and Iwai [13] at 1773 K are in reasonable correspondent with the calculations from the present model.

11.5.2.3. The Na₂O-Al₂O₃-SiO₂ system

The predicted iso-sulfide capacity lines of the Na₂O-Al₂O₃-SiO₂ melt is illustrated in Fig. 11.9 along with the experimental data obtained by DeYoung [8] at 1373 K, and Kunisada and Iwai [13] at 1773 K. Although the two experimental compositions from DeYoung [8] are quite different in terms of basicity, their sulfide capacities are nearly the same, which is less likely. The present model could reasonably well predict the results from the two sets of investigations [8, 13] at quite different temperatures. The predicted sulfide capacity rapidly decreases with the replacement of Na₂O by Al₂O₃ at a constant SiO₂ content in the Na₂O-Al₂O₃-SiO₂ melt. The iso-sulfide capacity lines are to a certain extent directly related to the iso-activity lines of Na₂O.

11.5.3. Quaternary and higher order systems

The sulfide capacities of the Na₂O-CaO-Al₂O₃-SiO₂ and Na₂O-CaO-MgO-Al₂O₃-SiO₂ systems, calculated from the present model, are shown in Figs. 11.10 and 11.11, respectively, along with experimental data. Choi et al. [21], and Chan and Fruehan [12] using the slag/metal equilibration technique, and Kärsrud [9] employing the slag/gas equilibration method investigated the variation of sulfide capacity with Na₂O and Al₂O₃ contents of the melts. In general, the predictions reasonably agree with the experimental data, as illustrated in Fig. 11.10. The predicted sulfide capacities of the Na₂O-CaO-MgO-Al₂O₃-SiO₂ melts are compared with the experimental data from Kärsrud [9] in Fig. 11.11. There is a discrepancy between the experimental data and the prediction by about 0.6 in logarithmic scale. This is a relatively large deviation even considering experimental difficulties in Na₂O-containing systems. However, the difference originates from the CaO-MgO-Al₂O₃-SiO₂ melt sare and Pelton [28], the predicted sulfide capacity of the CaO-MgO-Al₂O₃-SiO₂ melt is very accurate in comparison with numerous experimental data (see reference by Kang and Pelton). Therefore, the accuracy of the measurements from Kärsrud [9] in the Na₂O-CaO-MgO-Al₂O₃-SiO₂ slag is rather questionable.

The overall accuracy of the present model for the sulfide capacities of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ multicomponent slags are plotted in Fig. 11.12. The experimental data varies,

widely, from -5.0 to -2.0 in logarithmic scale. All experimental data were reproduced within maximum ± 1.0 error in logarithmic scale.

11.6. Summary

Sulfide capacities of many sub-systems of the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ slag were modeled and predicted using the Modified Quasichemical Model (MQM) in the quadruplet approximation. In addition to two previously optimized sulfide model parameters for the MnO-SiO₂-MnS and CaO-Al₂O₃-CaS systems, one model parameter for the Na₂O-Na₂S binary liquid was newly introduced in the MQM to reproduce experimental data for Na₂O-containing slags. All experimental data in the current systems were relatively well predicted from the model with optimized parameters within experimental uncertainty.

It was discussed that the sulfide capacity concept do not give a unique sulfide capacity value for a given slag composition containing a noticeable amount of Na₂O. Since the solubility of sulfide in Na₂O-containing slags is very significant, Henrian activity coefficient of sulfide cannot be satisfied. That is, the sulfide capacity of slag varies depending on partial pressures of oxygen and sulfur.

The MQM with optimized parameters may be used along with other thermodynamic databases in the FactSage system to predict the sulfur distribution between the metal and Na₂O-containing fluxes.

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Reference	T (K)	p_{O_2} (atm)	p_{S_2} (atm)	^e Sulfide (mol %)			
Na ₂ O-SiO ₂							
	1473	8.4×10^{-18}	5.1 × 10 ⁻⁸	3 – 8			
a. d [15]	1573	2.7×10^{-17}	2.3×10^{-7}	3 – 9			
^{a, a} [15]	1673	7.7×10^{-17}	8.4×10^{-7}	7 – 13			
	1773	1.8×10^{-16}	$2.8 imes 10^{-6}$	9 - 15			
^b [5]	1523	-	-	-			
	1623	-	-	-			
^{b, c} [6]	1523	2.4×10^{-10}	5.3×10^{-5}	0 - 1			
[7]	1623	-	-	-			
L'J	1523	1.4×10^{-17}	$2.2 \times 10^{-10} - 2.0 \times 10^{-7}$	0 - 6			
^{a, d} [16]	1623	4.4×10^{-17}	$4.6 \times 10^{-10} - 1.4 \times 10^{-7}$	0 - 6			
	^{a, d} 1473	7.6×10^{-18}	$9.8 \times 10^{-13} - 4.0 \times 10^{-8}$	1 - 3			
[10]	^{b, c} 1473	2.7×10^{-11}	$1.7 imes 10^{-2}$	1 - 4			
[10]	^{a, d} 1603	3.5×10^{-17}	4.7×10^{-10}	1 - 2			
[11]	^{a, d} 1673	7.3×10^{-17}	$9.7 \times 10^{-9} - 9.0 \times 10^{-7}$	1 - 3			
	^{b, c} 1673	1.0×10^{-10}	1.6×10^{-3}	0			
[17]	1873	-	-	-			
د L	1573	2.5×10^{-17}	$4.4 \times 10^{-13} - 6.1 \times 10^{-11}$	0 - 1			
^{a, u} [18]	1623	4.4×10^{-17}	$4.2 \times 10^{-12} - 2.0 \times 10^{-10}$	1 - 4			
^{a, d} [19]	1623	4.4×10^{-17}	$5.7 \times 10^{-10} - 3.6 \times 10^{-7}$	2 - 3			
^{b, c} [13]	1773	1.1×10^{-8}	1.7×10^{-3}	0 - 2			
		Na ₂ O-F	etO-SiO2				
^{b, c} [8]	1373	$\sim 7.0 \times 10^{-14}$	$\sim 5.6 imes 10^{-4}$	-			
		Na ₂ O-Fe _t O	D-MgO-SiO ₂				
^{a, d} [17]	1873	-	-	-			
Na ₂ O-Fe _t O-CaO-MgO-SiO ₂							
^{a, d} [17]	1873	-	_	-			
Na ₂ O-CaO-SiO ₂							
^{a, d} [16]	1523	1.42×10^{-17}	$4.7 \times 10^{-12} - 5.3 \times 10^{-10}$	4 - 8			
[12]	1673	^{b, c} 1.0×10^{-11}	$4.0 imes 10^{-3}$	0 - 1			
	1075	^{a, d} 7.3×10^{-17}	$\sim 2.0 imes 10^{-7}$	-			
^{a, d} [17]	1873	-	-	-			
^{b, c} [13]	1773	$1.1 imes 10^{-8}$	1.7×10^{-3}	-			
^{a, d} [20]	1623	4.38×10^{-17}	$4.6 \times 10^{-10} - 1.2 \times 10^{-8}$	-			
Na ₂ O-Al ₂ O ₃ -SiO ₂							
^{b, c} [8]	1373	$7.0 imes 10^{-14}$	5.6×10^{-4}	-			
^{b, c} [13]	1773	1.1 × 10 ⁻⁸	1.7×10^{-3}	-			
Na ₂ O-MgO-SiO ₂							
^{b, c} [13]	1773	1.1 × 10 ⁻⁸	1.7 × 10 ⁻³	-			
Na ₂ O-MnO-SiO ₂							
^{b, c} [13]	1773	1.1×10^{-8}	1.7×10^{-3}	-			
Na ₂ O-CaO-Al ₂ O ₃ -SiO ₂							
^{a, d} [12]	1673	$7.3 imes 10^{-17}$	3.2×10^{-11}	-			
^{a, d} [21]	1623	4.4×10^{-17}	$5.5 \times 10^{-10} - 1.2 \times 10^{-10}$	-			

Table 11.1: Summary of experimental data on sulfide capacities of Na₂O-containing slags.

Na ₂ O-CaO-MgO-Al ₂ O ₃ -SiO ₂							
^{b, c} [9]	1773	$3.4 imes 10^{-8}$	2.7×10^{-3}	-			
Na ₂ O-Fe ₂ O ₃ -CaO-SiO ₂ -CaF ₂							
[22]	1573		ambiguous				

^a slag-metal equilibration.

^b slag-gas equilibration. ^c Equilibrium P_{O_2} and P_{S_2} were calculated using FactSage from known experimental input gas compositions.

^d Equilibrium P_{O_2} was calculated using FactSage from C/CO equilibrium assuming C

saturation was met during the course of experiments, and P_{S_2} was calculated using FactSage

from final compositions of the liquid Fe.

^e Total Fe of the slag was counted as FeO.



Fig. 11.1: Calculated sulfide capacities and composition profiles in ternary diagrams: (a) and (b) for the CaO-SiO₂ melt at 1873 K, (c) and (d) for the FeO-SiO₂ melt at 1773K, and (e) and (f) for the Na₂O-SiO₂ melt at 1773 K. The solid lines and dotted lines represent the stable liquid single-phase and subliquidus regions, respectively. All solid phases were suppressed for the calculations.



Fig. 11.2: Calculated standard Gibbs energies of oxide-sulfide exchange reactions for various basic oxides: $MO(l) + \frac{1}{2}S_2(g) = MS(l) + \frac{1}{2}O_2(g)$ and $N_2O(l) + \frac{1}{2}S_2(g) = N_2S(l) + \frac{1}{2}O_2(g)$.



Fig. 11.3: The schematic representation of the present model: nine quadruplets in the Na₂O-SiO₂-Na₂S-SiS₂ melt.



Fig. 11.4: Calculated sulfide capacities of the Na₂O-SiO₂ melt from the present model at (a) 1473, (b) 1523, (c) 1573, (d) 1623, (e) 1673, and (f) 1773 K along with the experimental data [5-7, 10, 11, 13, 15, 16, 18, 19]. [S]_i and (S)_i indicate that sulfur was initially added to the metal and slag, respectively.



Fig. 11.5: Variation of (a) sulfide capacity, (b) dissolved sepcies, and (c) activity of slag constituent as functions of compositiona and temperature in the Na₂O-SiO₂ melt. The calculations were performed for $p_{O_2} = 10^{-17}$ and $p_{S_2} = 10^{-8}$ atm.



Fig. 11.6: Calculated iso-sulfide capacity (- $log C_s$) lines in the Na₂O-Fe_tO-SiO₂ melt along with the experimental data [8]. The calculations were performed for $P_{O_2} = 2 \times 10^{-12} - 2 \times 10^{-8}$ and

 $P_{S_2} = 5.6 \times 10^{-4}$ atm. L: liquid, Wüs: wüstite, Crs: cristobalite.





Fig. 11.7: Calculated iso-sulfide capacity (- *log C_s*) lines in the Na₂O-CaO-SiO₂ melt along with the experimental data [12, 13, 16, 20] at (a) 1523, (b) 1623, (c) 1673, and (d) 1773 K. L: liquid, Wüs: wüstite, Trd: tridymite, Crs: cristobalite



Fig. 11.8: Calculated iso-sulfide capacity (- *log C_s*) lines in the (a) Na₂O-MgO-SiO₂ melt and (b) Na₂O-MnO-SiO₂ melts along with the experimental data [13]. L: liquid, Wüs: wüstite, Crs: cristobalite



Fig. 11.9: Calculated iso-sulfide capacity (- *log C_s*) lines in the Na₂O-Al₂O₃-SiO₂ melt along with the experimental data [13] at (a) 1373 and (b) 1773 K. L: liquid, Trd: tridymite, Crs: cristobalite, Mul: mullite, Nph: nepheline, Cg: carnegieite, M-Ox h: high temperature meta-oxide.



Fig. 11.10: Variation of sulfide capacity of the Na₂O-CaO-Al₂O₃-SiO₂ melt with mole fraction of (a) Na₂O and (b) Al₂O₃, along with the experimental data [9, 12, 21].



Fig. 11.11: Calculated sulfide capacity of the Na₂O-CaO-MgO-Al₂O₃-SiO₂ melt along with the experimental data [9].



Fig. 11.12: Comparison of experimental data [6, 8-13, 15, 16, 18-21] and calculated sulfide capacities of Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ slags. Calculations were carried out for oxygen and sulfur partial pressures corresponding to the experimental conditions listed in Table 11.1.

Chapter 12

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

12.1 Conclusions

The present research was conducted to develop a comprehensive and consistent thermodynamic database for the Na₂O-FeO-Fe₂O₃-CaO-MgO-Al₂O₃-SiO₂ system. A complete literature review, critical evaluation, and thermodynamic optimization of phase diagrams and thermodynamic properties of 2 binary, 6 ternary, and multicomponent sub-systems (including all solid and liquid phases) were performed at 1 atm total pressure. A coherent database including a set of optimized model parameters was obtained for Gibbs energies of all phases reproducing available and reliable thermodynamic properties and phase equilibria within experimental error limits from 298 K to above liquidus temperatures for all compositions and oxygen partial pressures from metallic Fe saturation to 1 atm. In this way, all data were rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data were often resolved, and interpolations and extrapolations were made in a thermodynamically correct manner. The optimized thermodynamic database which was self-consistently built from low order to high order systems can be applied to industrial processes.

Gibbs energies of stoichiometric compounds, liquid, and solid solutions and their end-members (real and virtual) were critically evaluated and optimized. Using proper thermodynamic models considering the crystal structure of each solution phase reduced the number of model parameters and thus, enhanced the predictive ability of models, especially in high order systems. The molten oxide phase (NaO_{0.5}-FeO-FeO_{1.5}-CaO-MgO-AlO_{1.5}-SiO₂-NaAlO₂-NaFeO₂) was modeled using the Modified Quasichemical Model with the consideration of NaAlO₂ and NaFeO₂ associates. The Gibbs energy of NaFeO₂ associate in the liquid phase was constrained using experimental thermodynamic property data. The Na₂O solubility in the wüstite solid solution (FeO-FeO_{1.5}-

AlO_{1.5}-NaO_{0.5}) was modeled using polynomial expansions of excess Gibbs energy. The high-temperature (Na⁺,Va)^{Na}[Al³⁺, Fe³⁺, Si⁴⁺]^MO₂ and intermediate-temperature (NaFe⁴⁺, NaAl⁴⁺, Si⁴⁺)O₂ meta-oxide, extensive β'' -alumina Na₂(Al³⁺,Fe³⁺)₁₂O₁₉, and clino-pyroxene (Na⁺)^{M2}[Fe³⁺, Al³⁺]^{M1}{ Fe³⁺, Al³⁺, Si⁴⁺}^BSiO₆ solid solutions were treated within the framework of Compound Energy Formalism. Numerous binary and ternary stoichiometric compounds, Na₃Fe₅O₉, NaFeO₂, Na₃FeO₃, NaFeO₂, Na₂FeO₃, NaFeO₃, NaFe₂O₃, Na₂FeSiO₄, Na₈Fe₆Si₁₅O₄₀, Na₅FeSi₄O₁₂, and NaFeSi₂O₆ (aegirine formerly named acmite) were optimized using experimental thermodynamic property and phase equilibrium data. In general, experimental results and the present calculations are in good agreement. Most experimental phase diagram data in reducing and oxidizing conditions were reproduced within 3 mol % of compositional error ranges. Many unexplored phase diagrams of this system under different oxygen partial pressures were predicted within the accuracy of ± 5 mol % in composition and ± 50 K in temperature from the present thermodynamic models with optimized parameters.

- The Na₂O-FeO-Fe₂O₃ system (*Chapter 5*): A critical evaluation/optimization of experimental phase diagrams and thermodynamic properties of the Na₂O-FeO-Fe₂O₃ system was performed at 1 atm total pressure.
 - Complicated sub-solidus phase relations depending on the oxygen partial pressure and temperature were elucidated. For example, interestingly, stoichiometric compounds containing ferric oxide (NaFeO₂ and Na₃FeO₃) are also stable in the Na₂O-FeO phase diagram in equilibrium with metallic Fe.
 - o No thermodynamic properties of the Na₂O-FeO-Fe₂O₃ liquid were experimentally investigated. According to the present modeling results, it is possible to calculate any thermodynamic property of the liquid. Rather strong negative interactions in the Na₂O-FeO (in equilibrium with metallic Fe) and Na₂O-Fe₂O₃ (in air) liquid solutions were found, opposite to interactions between other network modifier components in the molten state (e.g. Na₂O-CaO). The formation of several congruently melting stoichiometric phases in these systems also supports the strong negative interactions in the liquid state. A similar behavior would be expected between alkali oxides and transition metals, e.g. Mn. Although

there is lack of information in the K_2O -FeO, K_2O -Fe₂O₃, Li₂O-FeO and Li₂O-Fe₂O₃ solutions, interaction energies similar to those of Na₂O-FeO and Na₂O-Fe₂O₃ systems could be anticipated.

- The Na₂O-FeO-Fe₂O₃-SiO₂ system (*Chapter 6*): A critical evaluation/optimization of experimental phase diagrams and thermodynamic properties of the Na₂O-FeO-Fe₂O₃-SiO₂ system was performed at 1 atm total pressure.
 - With decreasing the FeO content of the Na₂O-FeO-SiO₂ system at Fe saturation, the position of maxima of FeO iso-activity lines for a given FeO content changes from the low basicity (Na₂O/SiO₂) side to the high basicity side: molar ratio of Na₂O/SiO₂ = 0.4 at X_{FeO} = 0.6, 1.0 at X_{FeO} = 0.2 and 2.0 at low FeO concentrations. This trend is quite different from the conventional metallurgical slag systems such as CaO-FeO-SiO₂ and MgO-FeO-SiO₂, where the maxima of FeO iso-activity lines always locate at molar ratio of CaO/SiO₂ and MgO/SiO₂ = ~ 2.0, the orthosilicate composition.
 - Based on the present optimization, iso-activity lines of SiO₂ (solid standard state) and Na₂O (liquid standard state) were calculated in the Na₂O-FeO-SiO₂ system in equilibrium with Fe at 1673 K. The activities of Na₂O and SiO₂ are mainly influenced by the basicity, Na₂O/SiO₂ ratio, and are almost independent of the iron oxide concentration in the melt.
- The Na₂O-FeO-Fe₂O₃-Al₂O₃ system. Part I: Experimental phase diagram study (*Chapter 7*): Phase diagrams of this system in air (1583 and 1698 K) and at Fe saturation (1573 and 1673 K) were investigated using the quenching method followed by EPMA and XRD phase analysis.
 - \circ The liquidus of the meta-oxide phase, the homogeneity range of the Na-β"-alumina, and two and three-phase equilibria between solids and the liquid were experimentally determined in air and at Fe saturation.
 - A complete meta-oxide solid solution between NaAlO₂ and NaFeO₂ was observed.

- An extensive solid solution of $Na_2(Al,Fe)_{12}O_{19}$ Na- β "-alumina was found in air, and the existence of a miscibility gap in this solution was confirmed.
- ο Noticeable solubility of Fe^{3+} in the NaAlO₂ meta-oxide and Na₂Al₁₂O₁₉ Na-β"-alumina phases was observed even at Fe saturation.
- ο In equilibrium with Fe, no miscibility gap in $Na_2Al_{12}O_{19}$ Na-β"-alumina was observed because the solubility of Fe³⁺ in this phase at Fe saturation is lower than the immiscibility composition.
- The solubility of Fe³⁺ in Na-β-alumina was found to be very small, most probably less than
 mol % Fe₂O₃. For the sake of simplicity, therefore, the Na-β-alumina phase was considered to be a stoichiometric compound, namely NaAl₉O₁₄ in air and at Fe saturation.
- No noticeable solubility of Na₂O was detected in the spinel solid solution.
- No ternary stoichiometric compound was found in this system in air and at Fe saturation in the experimental temperature and composition ranges studied.
- The Na₂O-FeO-Fe₂O₃-Al₂O₃ system. Part II: Thermodynamic optimization (*Chapter 8*): Mostly the present experimental data were used to optimize thermodynamic properties and phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system in air and in equilibrium with metallic Fe.
 - Based on the current experimental phase diagram data, the solidus and liquidus of the NaFeO₂-NaAlO₂ join at 1698 K could be roughly estimated.
 - As Gibbs energies of all phases present in binary and ternary sub-systems were well optimized based on a large amount of experimental phase diagram and thermodynamic property data, calculations in the Na₂O-FeO-Fe₂O₃-Al₂O₃ system would be still quite reliable even with a few amounts of phase diagram data in this quaternary system. Moreover, the present thermodynamic description was already tested in the higher order

system Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂, and accurate predictions of phase diagrams in the multicomponent system were obtained in comparison with a large body of phase diagram data, especially in air.

- The Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system (*Chapter 9*): A critical evaluation/optimization of phase diagrams and thermodynamic properties of the entire Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system was carried out at 1 atm total pressure.
 - While a couple of ternary liquid parameters were optimized to reproduce phase equilibria at Fe saturation, phase relations in air were well predicted from the thermodynamic models with optimized model parameters in binary and ternary sub-systems without any additional parameter. As a result of thermodynamic optimization for all phases, unexplored phase diagrams of the Na₂O-FeO-Fe₂O₃-Al₂O₃-SiO₂ system important for various pyrometallurgical applications, especially for refining processes were predicted. The accuracy of the calculated diagrams would be about maximum \pm 50 K in temperature and \pm 5 wt.% in composition from our experience in oxide systems where the number of experimental data is very limited to validate calculation results.
 - The predicted Na₂O-FeO-SiO₂ section with 20 wt.% Al₂O₃ at Fe saturation showed that the liquid phase is stable in a large composition area. The prediction indicated that the Na₂O-FeO-SiO₂ flux with maximum about 20 wt.% Al₂O₃ can be used as a liquid agent for the desulfurization and dephosphorization of steel. Of course, the sulfur removal capacity of the flux is expected to be better at higher Na₂O and FeO regions but once solid phases form, the desulfurization capacity drastically decreases. Therefore, the proper adjustment of composition can be calculated from the phase diagram information. The dephosphorization reaction is more complex since it occurs at a higher oxygen potential. Hence, a good balance of Na₂O and FeO is required to maximize the dephosphorization capacity.
- The Na₂O-FeO-Fe₂O₃-X (X = CaO and MgO) systems (*Chapter 10*): The Na₂O-FeO-Fe₂O₃-CaO and Na₂O-FeO-Fe₂O₃-MgO systems were treated as ideal solutions in the present

research. Based on only a couple of experimental data, the thermodynamic optimization of the Na₂O-Fe₂O₃-CaO system in air was carried out. No ternary model parameters were introduced into the liquid solution. No experimental data are available in the other sub-systems.

- Thermodynamic modeling of sulfide capacity of Na₂O-containing oxide melts (*Chapter 11*): Thermodynamic modeling of the sulfide dissolution in the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ slag was performed to investigate the desulfurization of hot metal using Na₂O-containing fluxes. The dissolution behavior of sulfur in the melt was modeled using the two-sublattice Modified Quasichemical Model in the quadruplet approximation. The developed database was applied to predict the sulfide dissolution in the Na₂O-Fe_tO-CaO-MgO-MnO-Al₂O₃-SiO₂ melt, which is of high importance for the production of low sulfur steels.
 - In addition to two previously optimized model parameters for the MnO-MnS-SiO₂ and CaO-Al₂O₃-CaS systems, one model parameter for the Na₂O-Na₂S binary melt was newly introduced in the MQM to reproduce experimental data. All data in the current systems were relatively well predicted from the present model with optimized parameters within experimental scatter ranges.
 - It was demonstrated that the sulfide capacity concept cannot give a unique sulfide capacity value for a given slag composition containing a noticeable amount of Na₂O. Since the sulfide solubility in Na₂O-containing slags is very significant, the Henrian activity coefficient of sulfide cannot be satisfied. That is, the sulfide capacity of slag varies depending on partial pressures of oxygen and sulfur. Large scatters in experimental sulfide capacity data might be pertinent to the limitation of the sulfide capacity approach.
 - The MQM with optimized parameters may be used along with other thermodynamic databases in the FactSage system to predict the sulfur distribution between slag and metal for Na₂O-containing fluxes.

12.2 Suggestions for future work

Although the optimization of all thermodynamic properties of solid and liquid phases was performed reasonably well in comparison with available experimental data, there are still certain limitations in terms of modeling and experimental data. These will be disclosed below:

- Experimental phase diagram data in the Na₂O-Fe₂O₃ system in air at high Na₂O region are very limited, and thus, the liquidus in this area is purely prediction. Further experimental phase diagram studies for high Na₂O concentrations are then recommended. Thermodynamic data for many stoichiometric compounds in the Na₂O-FeO-Fe₂O₃ system are also missing. These should be investigated to fully understand this system.
- Calculated primary phase fields and various sections of the Na₂O-FeO-SiO₂ system at Fe saturation are in agreement with experimental data considering scatters of available data. However, it is necessary to reinvestigate the phase diagram of the Na₂O-FeO-SiO₂ system at Fe saturation.
- There is certainly room to improve the thermodynamic description of the Na₂O-FeO-Fe₂O₃-Al₂O₃ system.
 - Further phase diagram experiments regarding the miscibility gap in the Na-β"-alumina solid solution are essential to better constrain the Gibbs energy of the phase, which is considered to be a potential candidate for solid solution electrodes in electrochemical cells. The width of miscibility gap was reasonably determined only at 1698 K; its temperature dependence could not be well constrained.
 - \circ The inhomogeneity range of Na- β -alumina should be also further investigated.
 - The liquidus above 1673 K has not been studied yet.
- The primary crystalline region of SiO₂ in the NaAlSiO₄-FeO-SiO₂ system at Fe saturation was calculated to be much larger than that experimentally measured. Therefore, to better reproduce

the NaAlSiO₄-FeO-SiO₂ phase diagram, four temperature-independent ternary parameters were added into the NaAlO₂-FeO-SiO₂ liquid solution. From our experience, rather large number of parameters is not common. However, even with these parameters, the primary phase region of spinel could not be well represented, and the wüstite solid solution was calculated to be stable instead. Further phase diagram experiments are necessary to resolve the spinel and wüstite phase boundary in this system.

No complete and systematic experimental investigations were performed in the Na₂O-FeO-Fe₂O₃-X (X = CaO, MgO) systems either in air (P_{O2} = 0.21 atm) or at Fe saturation (a_{Fe} = 1). A couple of studies focused on phase relations between Na₂Fe₂O₄, Na₂Al₂O₄, and Ca_xFe_yO_z compounds in the Na₂O-Fe₂O₃-CaO system in air. Therefore, more experimental investigations in these systems are required to better constrain Gibbs energies of solid and liquid phases present in the systems.