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THE KINETICS OF DISSOLUTION OF HIGH MELTING POINT ALLOYING ELEMENTS IN MOLTEN ALUMINUM

by

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

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In the Name of God the Compassionate and the Merciful

To my wife,

who always was a constant source of inspiration

Abstract

Manganese and iron are two major alloying elements in various aluminum products. Since these elements have high melting points and low diffusivities in molten aluminum, their dissolution rates are very slow, when they are added to aluminum melts. In order to improve the kinetics of dissolution, several alloying methods have been introduced. All methods of alloying use mechanical stirring of some form or other to enhance dissolution rates by promoting forced convective mass transfer. In the present study, a comparison between the kinetics of dissolution of iron and manganese when added to the melt as discrete alloying particles or as compact briquettes (consisting of alloying elements and aluminum particles) was carried out. This study revealed that exothermic reactions and the local accumulation of heat within the briquettes can accelerate the kinetics of the alloy-making process.

Using the results obtained, a model for the dissolution of briquettes in molten baths of aluminum is proposed. Following disintegration of the briquettes into the melt, fine particles disperse freely into the bath, while their dissolution being controlled by mass transfer. To predict the dissolution rates, the relative velocity between fine particles entrained in the turbulent field and the fluid must be known. However, such velocities are extremely difficult, if not impossible, to clarify, since the particles will be moving erratically with a turbulent liquid, in which, random velocity fluctuations will be superimposed on mean bulk flow velocities. As such, the hydrodynamic interactions which control particle-fluid mass transfer in an agitated vessel are highly stochastic and impossible to predict, *ab initio*. In order to quantify such phenomena two theoretical approaches have been introduced by aqueous model researchers. In this investigation, for the first time, these theories

Abstract

have been evaluated for a high temperature liquid metal system involving the dissolution of alloying particles.

In the evaluation of the *terminal velocity theory* in high temperature systems, water modelling experiments in conjunction with dimensional analysis between cold model and hot temperature system were carried out to study the entrainment behaviour of (heavy) alloying particles. Then, through continuous sampling of the melt, mass transfer coefficients and rates of dissolution of suspended particles in the melt were measured. A comparison between predicted values and measured results indicated that the terminal velocity theory, in conjunction with correlations proposed for aqueous systems, was not applicable to the high temperature alloying systems studied.

In Kolmogoroff's theory of local isotropy, mass transfer in a turbulent system can be treated by a single parameter, *i.e.* energy dissipation rate. High temperature experiments revealed that this approach could be applied to stirred alloying particles-molten aluminum systems. However, at higher rates of mixing, when a fully suspended condition is reached, further increases in input mixing energy have negligible effects on dissolution rates. Thus, as a practical measure, very high mixing rates are not recommended. In this regard, a correlation for mass transfer coefficient as a function of the rate of input energy was presented.

Résumé

Le manganèse et le fer sont deux éléments d'alliage majeurs pour des produits d'aluminum variés. Comme ces éléments ont des points de fusion élévés et des coéfficients de diffusion bas dans l'aluminium liquide, leurs vitesses de dissolution dans les coulées d'aluminium sont lentes. Afin d'améliorer les cinétiques de dissolution, plusieurs méthodes d'addition d'éléments d'alliage ont été introduites. Toutes utilisent une agitation mécanique quelconque pour augmenter les vitesses de dissolution en promouvant le transfert de masse par convection forcée. Dans la présente étude, le fer et le manganèse ont été ajoutés à la coulée sous la forme de particules discrètes d'éléments d'alliage et sous la forme de briquettes compactes consistant de particules d'éléments d'alliage et de particules d'aluminium. Les cinétiques de dissolution obtenues ont été comparées. Cette étude a révélé que les réactions exothermiques et l'accumulation locale de chaleur à l'intérieur des briquettes peut accentuer les cinétiques du procédé de fabrication des alliages. Les résultats obtenus ont été utilisés pour développer un modèle pour la dissolution des briquettes dans les bains d'aluminium liquide. Après la désintégration des briquettes dans la coulée, de petites particules se dispersent librement dans le bain ; leur dissolution étant controllée par le transfert de masse. Pour prédire les vitesses de dissolution, la vélocité relative entre les petites particules entrainées dans le champ turbulent et le fluide doit être connue. Cependant, de telles vélocités sont extrêmement difficiles, sinon impossibles à clarifier, car les particules bougent d'une façon erratique dans un liquide turbulent, dans lequel les fluctuations de vélocité tout venant se superposent aux vélocités moyennes de la masse du flux.

De cette façon, les interactions hydrodynamiques qui controllent le transfert de masse fluide-particule dans un contenant agité sont très stochastiques et impossibles

Resume

à prédire, *ab initio*. Pour quantifier de tels phénomènes, deux approches théoriques ont été introduites par des chercheurs travaillant sur des modèles aqueux. Dans la présente recherche, ces théories ont été évaluées, pour la première fois, pour un système de métal à haute température incluant la dissolution de particules d'éléments d'alliage.

Dans l'évaluation de la théorie de la vélocité terminale pour les systèmes à haute température, des expériences de modélisation avec l'eau en conjonction avec une analyse dimensionnelle entre un modèle froid et un système à température élévée ont été conduites pour étudier le comportement d'entrainement des particules d'éléments d'alliage (lourdes). Ensuite, par un échantillonage continu de la coulée, les coéfficients de transfert de masse et les vitesses de dissolution des particules en suspension dans la coulée ont été mesurés. Une comparaison des valeurs prédites et des résultats mesurés indique que la théorie de la vélocité terminale associée aux corrélations proposées pour les systèmes aqueux n'est pas applicable pour les systèmes étudiés d'addition d'éléments d'alliage à haute température.

Dans la théorie de Kolmogoroff de l'isotropie locale, le transfert de masse dans un système turbulent peut être traité par un seul paramètre (ex : vitesse de dissipation d'énergie). Les expériences à haute température ont révélé que cette approche pouvait être appliquée aux systèmes agités. Cependant, pour des vitesses d'agitation élévées, quand la condition de suspension complète est atteinte, des augmentations supplémentaires d'énergie fourmxe pour le mélange ont des effets négligeables sur les vitesses de dissolution. Ainsi, il n'est pas recommandé d'utiliser des vitesses de malaxage élevées. A cet effet, une corrélation entre le coéfficient de transfert de masse et le taux d'énergie fournie est présenté.

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Appendix 1

Table 1 Diffusion coefficients of some alloying elements in liquid aluminum.



Introduction

1.1 Aluminum alloys

Aluminium alloys are used extensively in various product applications requiring high strength-to-weight ratios, as well as superior corrosion resistance, machinability, surface finishing, electrical and thermal conductivity. They are formed by processes such as casting, forging, rolling, or extrusion. Depending on the method of forming and final properties required, specific types of alloying elements have to be added to the molten aluminum before casting. These elements, in general, partly go into solid solution with the matrix and partly form intermetallic particles during the solidification process. Among the various types of alloying elements used, manganese and iron play important roles in determining the characteristics of the final products.

1.1.1 Iron in aluminum

The presence of iron in aluminum leads two different characteristic features: First, iron can be one of the most deleterious impurity elements in aluminum which has two main sources, aluminum ores (bauxite) or it can be picked up in foundry processing (melting equipments). Iron has a high solubility in molten aluminum but its solubility in solid aluminum is very low (0.04 wt pct). Therefore,

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during solidification, most of the iron present over this range is rejected from the solidifying phase into the liquid phase contained within the inter-dendritic regions.^[1,2] As a result, the enriched liquid forms a complex intermetallic second phase in combination with aluminum and, often, other elements. The volume percentage of this insoluble phase increases with iron content.^[3] This unfavourable intermetallic phase with needle-like and platelet morphology, (in the microstructure of aluminium alloys), sharply reduces the alloy's mechanical properties, particularly its elongation. In addition to this, large iron-rich needles which form during the solidification process tend to reduce cast consideration such as the flowability and feeding characteristics.^[4] In order to overcome/minimize the detrimental effects of iron several techniques such as manganese addition, rapid solidification and melt superheating are introduced. For this reason, manganese is almost always added to liquid aluminum to neutralize the irons effect.

Second, iron is not always considered as an impurity. It is sometimes added to liquid aluminum intentionally to obtain certain desirable characteristics. For instance, a higher iron content is beneficial in the die casting industry. It minimizes the driving force for molten alloys to further dissolve the steel dies while simultaneously suppressing the tendency of a condition commonly referred to as "soldering" (or welding) of the products to the steel die.^[3,5,6,7] For this reason, the majority of aluminum die casters prefer alloys with 0.8 to 1.1 wt pct iron.^[4,8,9,10,11,12] Iron also improves hot tear resistance during fabrication.^[5]

Aluminum alloys (e.g. Al-Si alloys) have some applications at high temperatures, such as their use in pistons. It has been reported that iron can dramatically increase yield strength, tensile strength, and also creep resistance, at elevated temperatures.^[13,14,15,16]

The influence of iron in wrought products is more significant where it reduces the grain size. Alloys of iron and manganese near the ternary eutectic content, such as 8006 alloy, can have useful combinations of strength and ductility at room temperature and retain strength at elevated temperatures.^[1,2] The fine grain size is stabilized at high temperature by finely dispersed, iron-rich, second phase particles such as FeAl₃, FeMnAl₆ and α AlFeSi.^[5]

1.1.2 Manganese in aluminum

Manganese is almost always added to liquid aluminum to neutralize the detrimental effects of iron in aluminum-silicon, aluminum-copper, aluminum-magnesium and aluminum-zinc-magnesium alloys.^[4,17,18,19,20,21,22,23] Note that the literature review on the neutralization of iron by manganese is quite abundant. Manganese converts the crystallization of needle-like intermetallic phases to cubic, or globular forms such as Chinese script morphology which have less harmful characteristics. This morphology improves tensile strength, elongation and ductility.^[1,11,12,17,24] Furthermore, it should be noticed that small amounts of manganese (usually Mn:Fe =1:2) play a positive role by breaking up the iron needles.^[12] When added in a higher ratio, or in the presence of chromium, depending on the melt temperature, manganese produces a hard multi-component intermetallic compound, commonly referred to as *sludge*, which affects the mechanical properties of the casting. As a simple guide for the aluminum caster, if the sum of the following elements [1x %Fe + 2x %Mn + 3x %Cr] is close to 1.8, then sludge formation will not result, for a melt temperature of 650 °C.^[11,21]

Although manganese additions are somewhat limited to casting alloys, manganese is used extensively in wrought alloys, mainly as a hardener. Manganese increases the strength in solid solution or as a finely precipitated intermetallic phase.^[1] In solid solution (with a solubility of 1.8 wt pct or more for chill casting), it is highly effective in strengthening binary alloys.^[25] However, in the presence of hard working, it offers significantly more benefits in comparison to casting products.^[26]

Altenpohl^[27] lists the aluminum alloys as casting, age-hardening and workhardening alloys. In the work-hardening alloys category, Al-Mn alloys with large production tonnages and broad applications, are the leading one. For instance, in 3xxx series alloys used for beverage containers and general utility sheets (e.g. can bodies), manganese is the main addition.^[1] It leads to the formation of complex precipitates that not only retard or inhibit grain growth during the ingot's reheating but also assists grain refinement during rolling.^[25] Furthermore, the presence of finely dispersed precipitates offers enhanced properties at elevated temperatures in alloys commonly referred to as heat resistant aluminum alloys.

Given the above introduction, it is clear that manganese and iron are important alloying additions. However, their high melting points, low dissolution rates, and their tendency to settle and accumulate on the bottom of melt after addition, always demand careful technical considerations. In dealing with this, several techniques for iron and manganese additions have been proposed.

1.2 Alloying methods

In general, molten aluminum is withdrawn from electrolytic cells and then transferred via ladles into a holding furnace, normally of the reverberatory type, where appropriate alloying additions are made and melt refining measures taken, prior to casting. For those plants far from liquid metal sources, a complete charge of scrap is melted. The shallow bath of a reverberatory furnace, and large surface area of the melt is useful for transferring heat from oil-fired flame and roof of the furnace to the metal charge to maintain a temperature about 710 °C for casting. Because of this low casting temperature and the wide, shallow furnace design, obtaining a uniform alloy composition throughout the melt prior to casting, within a reasonable time, is difficult. Alloying agent must be distributed throughout the

furnace and the molten bath should be well stirred to obtain homogenous composition.^[28]

In order to maintain or improve the alloying efficiency, or to lower the overall cost of alloying, a number of alloying techniques have been introduced. The type of the additive, the choice of where and how it is added, and the influence of the rest of the process, all combine to determine the overall alloying cost and effectiveness of addition. The most important of these techniques are discussed below.

The cheapest alloying agents are ferro-alloys such as ferro-manganese or ferro-chromium which can be added to the Hall cell. However, the advantage of low raw-material costs is overridden by the disadvantage of cell contamination. Alloying additions to the cell restrict its production to alloys containing the additive, which in turn can limit production flexibility. It also causes other major problem by lowering plant capacity due to the effect of sludge formation and accumulations on the bottom of the cell.

Alloying by electrolytic chip or powders, bagged or loose, is another economical method, but to avoid the problems of contamination and lower cell capacity, addition to the reverberatory furnace is preferable. The chip, because of its large section size and the low temperature of the reverberatory furnace, tends to dissolve rather slowly and to settle out on the furnace bottom. Powders, with much finer section sizes, exhibit fast rates of dissolution but tend to become trapped in the dross at the top of the bath. There, the powder burns, causing low recovery of the alloying elements.^[29]

Pneumatic injection of pure powder of the alloying element directly into the molten metal (using an inert gas) is another accepted method. It offers the advantages of direct powder additions with favourable dissolution rates. One disadvantage of the process is that injection equipment is needed for introducing

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the alloying elements into the melt. Furthermore, the flow of the powder, splashing and oxidation, all have to be carefully controlled during injection.

In this system, however, stirring of the bath during injection increases mass transfer rates and rates of dissolution, but there are some practical limitations in terms of particle size distributions and injection velocity. Fine particles have relatively higher dissolution rates, but also tend to exhibit low recoveries: such particles have insufficient kinetic energy to penetrate the gas-liquid interface and tend to resurface with bubbles. Subsequent reactions take place with oxygen at the surface of the melt. Increasing the injection velocity provides a higher kinetic energy for the fine particles, but its usefulness is limited on account of increased splashing and dross formation.

Coarse powders, which have better penetration, exhibit slower dissolution rates due to their tendency to settle down in the liquid. The accumulation of coarse particles at the bottom of the melt may form a sludge which will dissolve more as a function of total size of the sludge heap, rather than as the diameters of the individually dispersed powders. Practically, such sludge can lower the capacity of the furnace. In Figure 1.1, a schematic representation of the behaviour of fine and coarse particles during their injection by a carrier bubble is shown.

Thus, in this method of addition, a narrow size distribution of powders is recommended so as to optimize the recovery, dissolution rate, formation of insoluble intermetallic masses and also splashing. For instance, O'Malley^[29] found that manganese powder in the size range between 40 and 140 mesh (100 to 400 μ m) provided the best combination of recovery, dissolution and intermetallic formation.

The use of master alloys (consisting of remelted solutions of alloying elements in aluminum) as an alloy addition, can provide fairly rapid rates of solution. Their main disadvantage is the need for separate alloying furnaces. If master alloys are made where primary molten aluminum is not available, additional costs for remelting aluminum are involved. Also, since master alloys sometimes have high aluminum contents, extra shipping costs from plant to plant require consideration.

Briquettes consisting of a green mixture of powders of an alloying element and aluminium, tend to replace the master alloys and injection methods. In the briquette mode of addition, the local accumulation of heat within the briquette, as a result of exothermic reactions, provides higher rates of dissolution of the high melting point additives, as compared to the use of pure powders of the alloying elements alone. Further, they are more convenient to use compared to loose particles.

1.3 Scope of the present study

In Chapter 2, the mechanisms of dissolution of manganese-aluminum and iron-aluminum briquettes has been investigated at the laboratory scale.

A microstructural study of samples taken from briquettes submerged in liquid aluminum along with a thermal analysis of the samples has revealed that, after melting of the aluminum powder within the compact, exothermic reactions between the alloying element particles and aluminum, and the formation of some intermetallic compounds around each alloying element particle, leads to an increase in the briquettes' temperatures well above the temperature of the bath, (prior to disintegration of briquettes within the melt). Based on phase diagrams for the Mn-Al and Fe-Al systems, among of the several intermetallic compounds which are stable thermodynamically at the temperature of our experiments, $MnAl_4$ and Fe₂Al₅ are the only dominant phases within the briquettes. In the present work, the kinetics of growth of the intermetallic layers forming around particles of alloying elements have been described theoretically and a model for the mechanism of briquette dissolution proposed.

A comparison between the total dissolution times of the briquettes versus discrete particles of the original powders, used in making the briquettes, has been carried out. The results showed that due to the swelling of the briquettes and penetration of liquid aluminum from the bath into the briquettes, dissolution of solid particles in the liquid proceeds while exothermic reactions and the high temperature environment within the briquettes, accelerate dissolution rates. As a consequence, immediately after disintegration of the briquettes in the melt, a very large up-taking rate of solute particles can be achieved.

In Chapter 3, the dissolution kinetics of iron and manganese particles freely dispersed in a turbulent molten aluminum has been studied. After disintegration of briquettes and dispersion in the melt, the process of dissolution is controlled by mass transfer from solid particles to the liquid, similar to the dissolution of discrete particle addition. In this study, the knowledge of the relative velocity between solid particles with irregular motions and the turbulent media is necessary. The complex hydrodynamic interactions between entrained solid particles and the turbulent fluid have lead researchers dealing with **aqueous media** to postulate either the "terminal velocity theory" or the "Kolmogoroff's theory", as a means for characterising the kinetics of dissolution.

In the present work, and for the first time, the application of the *terminal* velocity theory to a high temperature system (the kinetics of dissolution of manganese and iron particles during mechanical stirring of liquid aluminum), has been investigated. Using water modelling experiments, as well as dimensional analysis and similarity techniques, conditions for the suspension of alloying element particles in the liquid were studied. Through continuous sampling of the aluminum melt, a comparison between theoretical and measured mass transfer

coefficients and times of dissolution of fully suspended particles was possible. Significant differences between predicted and measured values were found, suggesting that more caution in the application of the terminal velocity approach to high temperature media is needed.

In Chapter 4, the potential applicability of Kolmogoroff's theory of local isotropic turbulence for solid alloying particles dissolving in mechanically stirred baths of liquid aluminium is examined. Although there are some limitations, this theory leads to the conclusion that the hydrodynamics of mass transfer can be accounted for by a single parameter, *i.e.*, the rate of input mixing energy per unit mass. For the dissolution of manganese and iron particles, Kolmogoroff's approach was found to be applicable for lower rates of input energy, before particles reached a full state of suspension. The data obtained was expressed according to two empirical correlations. The agreement between published data for the dissolution of solid particles in aqueous media and present data confirms that the rate of input mixing energy can be a useful parameter in the study of mass transfer phenomena between solid alloying particles and liquid melts. Furthermore, it was found that when alloying particles became fully suspended, further increases in rates of mixing produced negligible changes in mass transfer coefficients.

In the final chapter, conclusions of this investigation are presented.

1.4 References

1. ASM, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, *Metals Handbook*, , 1990, Tenth Edition, vol. 2, pp. 52-53.

2. J.E. Hatch, "Aluminum: Properties and Physical Metallurgy", 1984, American Society for Metals, pp. 230-231.

3. S. Gowri and F.H. Samual, "Effect of Alloying Elements on the Solidification

Characteristics and Microstructure of Al-Si-Cu-Mg-Fe 380 Alloy", *Metallurgical Transactions A*, vol. 25A, 1994, pp. 437-448.

4. A. Couture, "Iron in Aluminum Casting Alloys - A Literature Survey", AFS international Cast Metals Journal, 1981, no. 4, vol. 6, pp. 9-17.

5. ASM, "Properties and Selection: Nonferrous Alloys and Specials-Purpose Materials, *Metals Handbook*, , 1990, Tenth Edition, vol. 2, pp. 132.

6. J.E. Hatch, "Aluminum: Properties and Physical Metallurgy", 1984, American Society for Metals, p. 348.

7. A. Kaye and A. Street, " Die Casting Metallurgy", Butterworth Scientific, 1982, pp. 23-31, pp. 71-79.

8. R. Dunn, "Aluminum Melting Problems and Their Influence on Furnace Selection", *Die Casting Engineer*, 1965, Sept., pp. 8-16.

9. C.J. Simensen and R. Vellasamy, "Determination of Phases Present in Cast Material of an Al-0.5 wt. % Fe-0.2 wt. % Si Alloy", Zeitschrift Fur Metallkunde, 1977, vol. 68, pp. 428-431.

10. M.R. Ghomashchi, "Intermetallic Compounds in an Al-Si Alloy Used in High Pressure Die-Casting", *Zeitschrift Fur Metallkunde*, 1987, no. 78, H.11, pp. 784-787.

11. J.L. Jorstad, "Understanding Sludge", *Die Casting Engineer.*, 1986, Nov./Dec, pp.

 D.L. Colwell and R.J. Kissling, "Die and Permanent Mould Casting Aluminum Alloy Minor Elements", AFS Transactions, 1961, vol. 69, pp. 610-616.
 Y. Liushuan, "Effect and Elimination of Iron in Al-Si Piston Alloys", Journal of Luo Yang Engineering Institute, 1987, vol. 3, pp. 49-55.

14. Y. Liushuan, "Effect of Iron on the Mechanical Properties of Piston Alloys", *Casting Technology*, 1986, vol. 2, pp.

15. L.F. Mondolfo, "Aluminum Alloys: Structure and Properties", Butterworths,

1976, pp. 759-777.

 B. Xiufang, Z. Guohua, Z. Shengxu and M. Jiaji, "The Spheroidisation of Needle-Form Iron Compounds in an Al-Si Alloy", *Cast Metals*, 1992, No. 1, vol. 5, pp. 39-41.

17. L.F. Monodolfo, "Manganese in Aluminum Alloys", *The Manganese centre*, 1978, Paris, pp. 1-35.

18. G. Gustafsson, T. Thorvaldsson and G.L. Dunlop, "The Influence of Fe and Cr on the Microstructure of Cast Al-Si Mg Alloys", *Metallurgical Transactions* A, 1986, vol. 17A, pp. 45-52.

19. L. Grand, "Influence of some Impurities on the Quality of Aluminum Alloys", *Fonderie*, 1964, vol. 217, pp. 95-100.

20. S. Shivkumar, L. Wang and D. Apelian, "Molten Metal Processing of Advanced Cast Aluminum Alloys", *Journal of Metals*, Jan. 1991, pp. 26-32.

21. W.H. Glaisher, Metallurgia, 1951, p. 127.

22. W. Bonssack, "Effects of Minor Alloying Elements on Aluminum Casting Alloys", Part II - Aluminum-Silicon Alloys, *ASTM Bulletin*, Oct. 1943, pp.41-51.
23. D.N. Khudokormov, A.M. Galushko and S.N. Lekakh, "Influence of Modification on the Form of Fe-rich Inclusions in Alloys", *Russian Casting Production*, May 1975, pp. 198-199.

24. I. Musulin and O.C. Celliers, The Role of Manganese in 6xxx Alloys: Effect of Quench Sensitivity in 6003", *Light Metals*, 1990, pp. 951-954.

25. ASM, "Properties and Selection: Nonferrous Alloys and Specials-Purpose Materials, *Metals Handbook*, , 1990, Tenth Edition, vol. 2, p. 38.

26. E.L. Rooy, "Aluminum Scrap Recycling and Its Impact on the Metal Castings Industry", AFS Transactions, 1985, vol. 93, pp. 935-938.

27. D. Altenpohl, "Aluminum Viewed from Within", Aluminum-Verlag. Dusseldorf, 1982, pp.

28. R.I.L. Guthrie and J.F. Grandfield," Aluminum Ladle Metallurgy", *Aluminium Melt Treatment and Casting, Theory and Practice,* 1991, The University of Melbourne, Australia, 1-4 July, pp. 17:1 - 17:13.

29. R.J. O'Malley, C.E. Dremann and D. Apelian, "Alloying of Molten Aluminum by Manganese Powder Injection", *Journal of Metals*, Feb., 1979, pp. 14-19.



Fig. 1.1 A schematic representation of particle injection. Too fine or too coarse particles are major sources for alloying element losses.

CHAPTER 2

DISSOLUTION MECHANISM OF COMPACT BRIQUETTE OF HIGH MELTING POINT ADDITIVES IN STIRRED LIQUID ALUMINUM

2.1. Introduction

High quality molten metal, along with an improvement in the productivity, can be achieved by considering the effective factors and optimizing the alloying process. To this end, a study of the mechanisms of dissolution and of dissolution times of alloying agents is necessary, especially where large tonnages of various grades of aluminum alloys are involved.

In general, during the alloying process when a cold alloying agent is immersed in a bath of molten aluminum, four different routes for melting/dissolution of the additions can be identified. These depend on the heat and mass transfer conditions involved.^[1,2]

In Figure 2.1, a schematic representation of the relevant thermo-physical phenomena is shown. The first three paths refer to low melting alloying elements while the fourth depicts the case of high melting point additions. In all cases, and immediately following immersion, a solid shell freezes around the addition. For

low melting point agents below aluminum's melting point, it is possible for internal melting to begin (1C), and to be completed before the enclosing shell melts back, (1D). Following the heating up the addition to the bath melting point, the solid shell melts and the molten core will dissolve/mix rapidly into the bath. For some kinds of additions, with large diameters and low thermal conductivity immersed in a high superheat temperature, the customary chill layer melts back before complete internal melting has occurred, (2C), and the addition is re-exposed to bath.

If the addition is not fully molten by the time the first chill shell has melted, (3C), it is quite possible for another solid shell to form around solid phase remaining. Such phenomena are again associated with high superheat temperatures and large size additions, when the amount of heat being convected into the surface is below the heat demand from the colder interior. Thus, Figure (3D) shows a second smaller shell of melt which has formed around the remaining unmelted portion of the addition, after dispersion of the outer alloy liquid has occurred.

Finally, the last path (4) refers to those additions having melting points higher than the aluminum's melting temperature such as manganese, iron or chromium. They evidently must usually dissolve, rather than melt, and the present investigation is concerned with the interpretation of such phenomena.

Turning to route (4), dissolution rates are generally controlled through a mass transfer boundary layer between the solid and bulk liquid while heat transfer becomes of secondary importance. The flux of the solute can be expressed by Fick's law: $J = -D(\partial C/\partial X)$, where J is flux, D is solute diffusivity, C is solute concentration and X is effective concentration boundary layer thickness. Owing to the low values for solute diffusivities and the low solubility of iron and manganese in aluminum, the dissolution process is slow.

Mechanical stirring, which creates forced convective mass transfer, can be

considered as the major method for enhancing such dissolution rates. In this case, the flux can be expressed as: $J = K_m(C_s - C_b)$, where K_m is a solute mass transfer coefficient and C_s and C_b are the solubility and bulk concentration of solute in the liquid phase, respectively. Assuming a linear concentration distribution between C_s and C_b and remembering that K_m can be represented as a ratio of diffusivity to thickness of mass transfer boundary layer then, increasing the intensity of mixing results in a decrease in the thickness of the interfacial mass transfer boundary layer. Such a reduced effective concentration boundary layer thickness leads to enhanced mass transfer coefficients, K_m and corresponding dissolution rates.

In the aluminum industry, in addition to the methods of mechanical stirring (gas stirring or using impeller), other factors such as the price of the alloying additive, its net recovery, dissolution time, the formation of dross, impurities in alloying elements and type of furnace may be considered as the primary parameters in optimizing the process.^[3,4,5] Above all of them, methods of addition and shape of agents govern the whole process. In Chapter 1, a relatively complete survey of alloying methods was presented. In the last decade, there has been greater competition among the customary methods of addition. These include powder injection of metal, compact briquettes and master alloys. However, it seems that compact briquettes have been partially successful in replacing the other methods.^[5,6] For instance, it is reported that alloying briquettes have given reliable/consistent recovery at a cost saving over the use of an aluminum master alloy.^[7] Clearly, if a 75 wt pct manganese briquettes is added to molten aluminum instead of a 10 to 25 wt pct manganese master alloys (available in the market), the amount of addition is 7.5 to 3 times less. This fact results in substantial cost saving by reducing the amount of addition required and also times for melting.

Conclusively, due to the limited commercial information on the dissolution of such compact briquettes, a complete investigation is necessary. Furthermore, based on the author's knowledge, no comparison between the dissolution behaviour of alloying briquettes and the original particles used in the fabrication of the briquettes, has been performed, particularly in a stirred melt. In the present chapter, detailed experimental work on the dissolution kinetics of iron and manganese briquettes has been presented.

2.2. Experimental work

Elkem manganese and iron products containing 75 wt pct powders of alloying elements and 25 wt pct of aluminum powders were used for this research, (Figures 2.2). The mixture of powders of metals were compacted to an apparent density of 4300-4500 kg/m³ with a weight of 0.075-0.080 kg each one. The size distribution of the particles used is presented in Table 2.1.

Size (µm)	Fe (wt pct)	Mn (wt pct)	
<75	6.21	30.7	
75 - 105	1.73	7.75	
105 - 150	2.8	11.06	
150 - 212	14.54	13.97	
212 - 300	38.58	16.48	
300 - 425	31.70	14.80	
425 - 500	2.90	4.27	
500 - 600	1.55	0.96	

 Table 2.1. Size distribution of Fe, Mn and Al particles used in the fabrication of Elkem briquettes

Size (µm)	Al (wt pct)		
<45	15		
45 - 75	15		
75 - 150	25		
150 - 250	37		
>250	8		

A commercially pure aluminum ingot was melted in an electrical resistance furnace. The chemical composition of the molten aluminum is given in Table 2.2.

 Table 2.2. The chemical composition of commercially pure aluminum (wt pct)

Mn	Fe	Si	Cr	Ni	Zn	Cd	Ti	Al
< 0.01	0.06-0.09	0.09-0.14	< 0.02	< 0.01	<0.01	< 0.008	< 0.01	balance

In each experimental run, two iron or manganese briquettes (each one containing 60 and 56.25 grams of alloying elements respectively) were added to 18 to 20 kg melt. For discrete particles, the equivalent amount of iron or manganese powders contained in the briquettes were used. A stream of argon gas above the melt was used to prevent oxidation of the stirred melt.

To study the dissolution performance of discrete particle additions, original powders of the alloying elements used in making the briquettes were classified, (see Table 2.1), and each narrow size distribution of particles was then wrapped in aluminium foil and plunged into molten aluminum. The melt was stirred by rotating a graphite impeller placed near the bottom of the vessel. A comparison between dissolution times of briquettes and classified discrete powders was carried out by taking successive samples from the intensively stirred melt. Chemical analysis of the samples and measuring the amount of dissolved particles was
carried out using a vacuum emission spectrometer. A schematic of the experimental set-up is shown in Figure 2.3.

Furthermore, to study reactions between aluminum and alloying particles inside the briquettes after addition to the melt, a batch of samples was immersed in liquid aluminum at 720°C in a refractory basket. At intervals of five seconds, one briquette was withdrawn and rapidly quenched. This was continued up to the point of disintegration of the briquettes. Polished cross sections of the samples were prepared, and examined metallographically. The composition of the various layers were analyzed by Energy Dispersive Spectroscopy (EDS) using the TN 5500 microprobe. (Note: TN 5500 is a trademark of Tracor Northern).

A data acquisition system was also employed to record the time-temperature history at the centre and outside of the submerged briquettes in the melt, during the exothermic reactions inside the briquettes. The disintegration times of the briquettes in the molten aluminum were measured using a very sensitive load cell, when the briquettes were immersed in the melt.

2.3. Result and discussion

2.3.1 Microstructure study of solid-liquid interface

Based on the Fe-Al or Mn-Al phase diagram (Figures 2.4 and 2.5), the transformation of the alloying element from its initial solid state, at 720°C, into a liquid solution potentially occurs via the formation of several intermetallic phases that are crossed between pure alloying element and aluminum under conditions of equilibrium. The dissolution process leads to the following possible sequence of exothermic reactions:

A: Iron-aluminium system

 $Fe + Al \rightarrow FeAl \Delta H_{720^{\circ}C} = -25.14$ kJ/g.atom of Al $FeAl + Al \rightarrow FeAl_2 \Delta H_{720^{\circ}C} = -1.047$ kJ/g.atom of Al $2FeAl_2 + Al \rightarrow Fe_2Al_5 \Delta H_{720^{\circ}C} = 0$ kJ/g.atom of Al $Fe_2Al_5 + Al \rightarrow 2FeAl_3 \Delta H_{720^{\circ}C} = -1.76$ kJ/g.atom of Al $FeAl_3 \rightarrow solution in liquid aluminum$

B: Manganese-aluminium system

Mn + Al	->	MnAl	$\Delta H_{720°C} = -21.58$	kJ/g.atom of Al
MnAl+ 2Al	->	MnAl ₃	$\Delta H_{720°C} = 0$	kJ/g.atom of Al
MnAl ₃ + Al	→	MnAl₄	$\Delta H_{720°C} = 0$	kJ/g.atom of Al
$MnAl_4 \rightarrow sol$	lutio	n in liqui	d aluminum	

Thus, direct dissolution of the pure solid phase in liquid aluminum may be preferred to be replaced by the dissolution the $FeAl_3$ and $MnAl_4$ (the adjacent phases to the liquid aluminum phase in respective phases diagrams).

In this regard, thermal analyses of the immersed briquettes in the melt, using a thermocouple in the centre of the briquettes, monitored the exothermic reactions. As shown in Figures 2.6, a lot of heat was released locally within the briquette. The reaction begins immediately after the melting of aluminum particles. The melting of the aluminum particles are reflected in the temperature-time graphs which exhibit a plateau when the temperature of the heating samples approach the melting point of aluminium. Once the latent heat of fusion has been provided, the core temperature then increases sharply, peaking well above the bath temperature until disintegration takes place. These exothermic reactions conclude with thick intermetallic rims which are rapidly formed around iron or manganese particles. Figures 2.7 and 2.8 show exothermic reactions in manganese and iron briquettes withdrawn from the melt after 15 and 20 s, respectively. The photographs illustrate that exothermic reactions can continue, even outside of the melt, once melting of the aluminum particles within the briquettes has taken place.

In order to study the results of the reactions, the cross section of briquettes withdrawn from the melt and quenched, have been investigated.

The microstructure of iron-aluminum compact briquettes, immersed in the melt for 10 and 25 seconds respectively, are presented in Figures 2.9.a and 2.9.b. After 25 seconds, the iron briquettes lost their rigidity and disintegrated within the bath. No specific changes were observed in the microstructure of the samples before the melting of the aluminum particles. However, microprobe analysis (using EDS methods) of the sample withdrawn after 25 second immersion, revealed that amongst the four thermodynamically stable intermetallic phases (*i.e.* FeAl, FeAl₂, Fe₂Al₅, and FeAl₃), Fe_2Al_5 was the only dominant phase. In the Mn-Al system, amongst MnAl, MnAl₃ and MnAl₄, the only dominant phase was $MnAl_4$. The other intermetallic phases were presumably present as only immeasurably thin layers. It therefore seems that the diffusion of alloying element atoms (Mn, Fe) and aluminum atoms in the Fe₂Al₅ and MnAl₄ phases are much faster than their diffusion in the other layers of intermetallic compounds, leading to a more rapid growth of the MnAl₄ and Fe₂Al₅ phases.

The predominance of one intermetallic phase among several possible intermetallic phases has also been observed in other systems. For example, in a study of inter-diffusion in the Ti-Al system, TiAl₃ was the dominant phase among the five adjacent phases. Van Loo *et al.*^[8] annealed a specimen containing a sandwich layering of Ti-Ti₃Al-TiAl-TiAl₂-TiAl₃-Al phases at 625 °C for 15 hours. As a result, the adjacent layers, Ti₃Al-TiAl-TiAl₂, vanished completely and the situation was changed to Ti-TiAl₃-Al. It is clear that the diffusion of Ti and Al in TiAl₂ is faster than their diffusion in the other intermetallic compounds. Van Loo's

experiments also proved that any difficulties in nucleation of one of the adjacent phases cannot be the cause for their absence in the specimen.

Similar inter-diffusion experiments by Kidson *et al.*^[9] between pure zirconium and aluminum show agreement with the present work. They found that ZrAl₃ was the only phase formed during diffusion.

2.3.2 Kinetics of intermetallic layer growth

The growth rate before disintegration

When the submerged briquette is heated up close to aluminum's melting point, aluminum particles melt and flow inside the pores of the briquette, wet the alloying elements and start the reaction. An intermetallic layer of $MnAl_4$ or Fe_2Al_5 forms and grows in at the interface of aluminum and the alloying element. During the growth process two different reactions can be taken place, simultaneously. In the Mn-Al system for instance, growth can occur at both the MnAl₄-Al interface, and the MnAl₄-Mn interface. Alloying element atoms (*e.g. Mn*) move across the intermetallic layer toward the liquid aluminum, resulting in the following reaction:

$[Mn] + 4Al = MnAl_4$ at $MnAl_4$ -Liquid Al interface Reaction I

while aluminum atoms can also diffuse toward the solid manganese phase and result in the formation of $MnAl_4$ according to:

$4[Al] + Mn = MnAl_4$ at $MnAl_4$ -solid Mn interface Reaction II

Similar reactions also take place during the growth of Fe₂Al₅.

The phenomena are illustrated schematically in Figure 2.10, where the dashed lines, concerning manganese concentration, describe the growth of the intermetallic into the liquid aluminium, (*reaction I*). The solid lines, concerning aluminum concentrations, describe the growth of intermetallic into the solid manganese as a result of aluminum diffusion, (*reaction II*).

In the growth kinetics of intermetallic layers on specimens of Mo, Nb, Cr and Y immersed in liquid aluminum, Tunca *et al.*^[10] observed that the growth process was diffusion-controlled. Therefore, we assume that the growth rates of MnAl₄ and Fe₂Al₅ are also controlled by the diffusion of atoms across the intermetallic layers. Other processes, namely wetting, nucleation and chemical reaction, leading to formation of intermetallic compounds, must occur at a high rate and do not therefore affect intermetallic growth rates.

Thus, in the first reaction, diffusion of manganese through MnAl₄ layer can be treated using first Fick's law:

$$J_{Mn} = -D_{Mn} \frac{\partial C_{Mn}}{\partial Z}$$
(2.1)

where J_{Mn} is the flux of manganese atoms across the MnAl₄ phase towards the liquid aluminum phase and D_{Mn} is the diffusivity of manganese in MnAl₄.

For steady state diffusion through the intermetallic layer, the flux through every plane parallel to the face must be the same. Therefore, neglecting variations in diffusivity with temperature and composition, the concentration gradient of manganese can be considered linear as:

$$J_{Mn} = -D_{Mn} \frac{\partial C_{Mn}}{\partial Z} = D_{Mn} \frac{C_{Mn}^2 - C_{Mn}^1}{Z}$$
 (2.2)

where Z is the thickness of $MnAl_4$, also C^2_{Mn} and C^1_{Mn} are the maximum and

minimum concentration of manganese in $MnAl_4$ phase layer, see Figure 2.10. (From Mn-Al phase diagram at 720°C, $C^2_{Mn} = 32.8$ wt pct and $C^1_{Mn} = 28.3$ wt pct of manganese).

On the other hand, in the first reaction when manganese atoms, passing through the intermetallic layer, take part in reaction with aluminum instantly and increase the thickness of $MnAl_4$ as X (see Figure 2.10), then, the flux can be expressed as follow:

$$J_{Mn} = C_{Mn}^{1} \frac{dX}{dt} \qquad or \qquad \frac{dX}{dt} = \frac{J_{Mn}}{C_{Mn}^{1}} \qquad (2.3)$$

After substituting J_{Mn} from Eq. [2.2] in Eq. [2.3]:

$$\frac{dX}{dt} = \frac{1}{Z} \frac{D_{Mn} (C_{Mn}^2 - C_{Mn}^1)}{C_{Mn}^1}$$
(2.4)

or

$$\frac{dX}{dt} = \frac{\alpha_{Mn}}{Z}$$
(2.5)

where

$$\alpha_{Mn} = \frac{D_{Mn} (C_{Mn}^2 - C_{Mn}^1)}{C_{Mn}^1}$$
(2.6)

Now consider the second reaction (Reaction II) which occurs at the Mn-MnAl₄ interface (concerning the flux of aluminum atoms toward the manganese phase through the MnAl₄ layer), and the corresponding increase in the thickness of the intermetallic phase, Y. Then, after the same treatment similar to reaction one, the growth rate of the intermetallic phase inward manganese phase is:

$$\frac{dY}{dt} = \frac{\alpha_{Al}}{Z} \tag{2.7}$$

where

$$\alpha_{Al} = \frac{D_{Al} (C_{Al}^2 - C_{Al}^1)}{C_{Al}^1}$$
(2.8)

Assuming growth occurs in a nearly saturated liquid aluminum phase with negligible potential for dissolution of the intermetallic layer then, after summing two velocities for interface growths, (dX/dt and dY/dt in Eqs [2.5] and [2.7]), the total growth rate of $MnAl_4$ (inward liquid aluminum phase and solid manganese phase), can be expressed as:

$$\frac{dX + dY}{dt} = \frac{\alpha_{Mn} + \alpha_{Al}}{Z}$$
(2.9)

and due to Z=X+Y, then:

$$\frac{dZ}{dt} = \frac{\alpha_{Mn} + \alpha_{Al}}{Z} \quad or \quad Z = \left(2 \left(\alpha_{Mn} + \alpha_{Al}\right) t\right)^{\frac{1}{2}} \qquad (2.10)$$

Similarity, in the Fe-Al system the thickness of Fe_2Al_5 at each moment of reactions is :

$$\frac{dZ}{dt} = \frac{\alpha_{Fe} + \alpha_{Al}}{Z} \quad or \quad Z = (2(\alpha_{Fe} + \alpha_{Al}) t)^{\frac{1}{2}}$$
(2.11)

As a result, Eqs [2.10] and [2.11] indicate that the growth of the intermetallic layers within the briquettes obey a parabolic law with time such that growth rates decrease with increasing time, (*i.e.* decrease with increasing thickness

of intermetallic layer).

The above theoretical consideration also helps us to describe the interesting phenomena observed in the growth kinetics of intermetallic layers. A comparison between the morphology of the MnAl₄ and Fe₂Al₅ intermetallic phases, presented in Figures 2.11 and 2.12, shows that in the Mn-Al system the intermetallic phase(s), MnAl₄, has preferentially grown inside the liquid aluminum phase, while in the Fe-Al system, conversely, the intermetallic phase(s), Fe₂Al₅, has grown inside the solid iron phase. This indicates that in Al-Mn system, the growth kinetics via the outwards reaction I is faster than it is via the inwards reaction II, while in the Al-Fe system, the inwards reaction II is faster. One should note that for equal growth rates of intermetallic: inside both solid and liquid phases, continuity requires that the flux of manganese should be equal to one quarter that of the inwards flux of aluminum, i.e. $J_{Mn} = 1/4 J_{AL}$. Similarity, for the Fe₂Al₅ phase, for equal growth inwards and outwards of the intermetallic phase, the flux of iron should be equal to 2/5 that of aluminum, i.e. $J_{Fe} = 2/5 J_{AI}$. The present microstructural observations show that $J_{Mn} > 1/4J_{Al}$ while $J_{Fe} < 2/5J_{AL}$. For this reason, in Figure 2.10, the original interface for the Mn-Al system is depicted closer to the solid phase than the liquid phase (X > Y), whereas for the Fe-Al system, it is closer to the liquid phase (X < Y).

The growth rate after disintegration

Following disintegration of the briquettes, particles will be freely dispersed into an unsaturated melt. As a result, the outer surface of the intermetallic phase formed in contact with the liquid phase will be exposed to dissolution. In this circumstance, the growth rate shows some deviation from growth in a saturated melt with no dissolution of solute. For a given temperature, the thickness of the intermetallic layer can be expressed as:

$$Z = (2 \alpha t)^{\frac{1}{2}} - (R_d - R_t)$$
 (2.12)

where $\alpha = \alpha_{Al} + \alpha_{Mn}$ or $= \alpha_{Al}^{\prime} + \alpha_{Fe}$, R_d in the initial radius of the particle at time of disintegration and R_t is the particle radius at time t of dissolution (at time t after disintegration). Calculation of R_t is difficult, if not impossible, because it depends on the relative velocity between the dispersed particles and turbulent liquid media. In Chapter 3, proposed theories available for the calculation of R_t , in both theoretical and experimental manners, are investigated.

2.3.3 Disintegration times of compact powders in the melt

Dissolution performance of the briquettes is greatly influenced by the duration that briquettes can maintain their rigidity within the melt. Using a load cell, it was shown that manganese briquettes could only retain their rigid skeletons for about 35 seconds and iron briquettes for about 25 seconds, following immersion in the aluminum melt, (see Figure 2.13). During the first period of immersion, the load cell registered some vibrations before reaching a stable condition. During the second period, the downward force remains constant. In heating such samples outside of the bath, Perry^[11] observed that the apparent density dropped from 4.45 to 2.24 gr/cm³. Samples withdrawn from the melt also showed expansion of the immersed sample in melt, see Figures 2.7 and 2.8. Now, one may ask " why does the downward force remain constant when the briquette is expanding ?" In the other words, when an immersed sample in the melt swells, the buoyancy force applied increases and consequently, a decrease in downward forces is expected. But, load cell experiments indicate a constant downward force during swelling periods. It transpires that during this period, when the porosity of the sample increases, penetration of liquid aluminum compensates for increased buoyancy forces and the result is a constant downward force until disintegration

takes place, as seen from Figure 2.13. Furthermore, a comparison between the microstructure of subsequent quenched samples confirmed the penetration of liquid aluminum into the briquette during the period of immersion.

The findings from the thermal analysis experiments along with the load cell experiments results (penetration of liquid aluminum in expanded briquettes and constant downward force or apparent weight) allow one to propose the followings model for the dissolution of such briquettes.

2.3.4 Proposed mechanism for dissolution of compact powder

When a cold powder compact briquette is first added to liquid aluminum, a solid shell chills around it, a shell whose thickness depends upon the superheat of the bath, the thermal conductivity of the sample and the latent heat of aluminum.

In Figure 2.14.a, a schematic representation of the cross section of the additives is shown. Within a short period of heating, the sample reaches the aluminum's melting point, the solid shell disappears and an exothermic reaction between the alloying elements and the aluminum powders raises the temperature of the sample above the bath temperature. The exothermic reaction leads to the formation of several layers of intermetallic compounds on the surfaces of the alloying element particles. The release of heat keeps the reaction-site temperature high enough to have an appreciable solid-state diffusion of aluminum into the solid-metal particles and, at the same time, allows diffusion of alloying elements through the intermetallic reaction zones. Furthermore, due to the swelling of briquettes and increasing amounts of void, (see Figure 2.14.b), liquid aluminum can penetrate from the bath and continue the intermetallic reactions as well as dissolution of the intermetallic phases in liquid aluminum. For this reason, the amount of swelling may play a critical role in the characteristic dissolution

behaviour of alloying briquettes. Clearly, larger amounts of liquid aluminum can penetrate into the briquettes from the bath, due to an enhanced swelling. Hence, this can provide a higher potential for dissolution of solute in the aluminum inside the briquettes (by delaying the onset of saturated conditions).

Finally, at a certain point, the rigid skeleton of the briquette disintegrates and the dissolution process of freely dispersed particles within the liquid bath begins (Figure 2.14.c).

2.3.5. Briquettes swelling

As mentioned, the amount of swelling obtained before disintegration can have a strong effect on rate of dissolution of compact briquettes. So, process details and also relevant parameters which contribute to briquette swelling will be illustrated.

In a binary compact mixture powder system, there is a general rule in determination of shrinkage or swelling of the compact. The case can easily be resolved from the latter's constitution diagram. Here, the focus is on the processes occurring during heating the mixture and after melting of the minor component while the major component is solid. A high solubility of liquid phase in the solid phase (as solid solution or intermetallic compounds formation) coupled to a low solid solubility in liquid causes swelling. Conversely, a high solubility of solid in liquid coupled to low solubility of liquid in solid aids densification.^[12,13]

High solubility of one component in the other is indicative of the existence of a relatively unidirectional flux of one element toward the solvent. Because of this, a compact whose basis element is solvent grows whereas compacts based on a solute metal exhibits shrinkage. The direct reason of growth of solid particles, during diffusion of atoms from a liquid phase into them, is an increase in particles mass where there is actually no migration of atoms in the reverse direction, from solid phase into the liquid. The change in volume of the particles results in the change in volume of the briquettes.

The role of high solubility of solid particles in a liquid phase on densification is related to lubrication, sliding and surface smoothing. Then, the capillary forces will pull the particles into a dense package^[14], and rearrange the particles to minimize interfacial energy. Consequently, the compact as a whole experiences a shrinkage.^[12] In Figure 2.15 a schematic diagram on the effect of solubility on swelling or densification is shown.

In general, for a wetting liquid component in a mixture, the small pores in the compact are filled first because of favourable interfacial energy reduction (unless the liquid has a high contact angle). In an Fe-Al or Mn-Al system, after aluminum particles melt, the liquid phase, due to its good wettability, readily spreads throughout the compact, allowing the alloying element particles to react with the melt over the whole of the their surfaces. Due to the high solubility of liquid aluminum in the solid iron or manganese phase, there is preferential diffusion of aluminum atoms into the solid phases. As a result of this, the solid particles grow, resulting in an expansion of the briquettes. Moreover, as a pore will be left at the site of the original particles of aluminum, there will be a net increase in the volume of the compact. In Figure 2.16, a scanning electron micrograph demonstrates a pore formation in position of aluminum particles in an Al-Fe system during heating.^[13,15]

In another study on the iron-aluminum system, Sheasby^[16] has shown that the Kirkendall effect can also contribute to about 15 pct swelling of the mixture of the powders. Aluminum diffuses more rapidly through the Fe_2Al_5 rim, causing a localized expansion that tends to push the alloying particles apart.

Concerning the swelling of the compact mixture of metal powders, some analytical relations between the end porosity of the compact and the porosity of the green compact of binary element powders has been suggested.^[17,18,19] For a system with low solubility in the liquid phase and a wide range of solubility in the solid phase (such as Fe-Al or Mn-Al system), Savitskii *et al.*^[17,18] has shown a correlation as:

$$\varepsilon = \varepsilon_{o} + C (1 - \varepsilon_{o})$$
 (2.13)

where ε and ε_0 are end porosity and green porosity of the compact respectively, and C is the volume fraction of aluminium which has reacted with the solid phase, as a solid solution or intermetallic compounds. (Note that in this equation porosity is defined as the ratio of the volume of inter-particles voids to the total volume of the briquette.)

Apart from the effects of solubility, the diffusion of aluminum atoms into the solid alloying elements may change the parameters of the lattice of the solid phase or cause a complete reorganization in structure due to the formation of an intermetallic compound. Since in Mn-Al or Fe-Al systems the specific volume of the intermetallic compounds formed around alloying particles are larger than the volume of the pure metals, the total radius of the particles increase during reactions. This, in turn, increases the volume of the sample. (Note: The average volume per aluminum atom (V_{Al}) in the cell of aluminum phase = 16.6 Å³, V_{Fe} in the cell of iron phase = 11.7 Å³, V_{Mn} in the cell of manganese phase = 12.2 Å³, while V_{Fe} in the cell of Fe₂Al₅ phase = 48.2 Å³, V_{Mn} in the cell of MnAl4 phase = 78.7 Å³).

Therefore, as a result of increasing the amount of porosity and forming more voids in the briquettes, liquid aluminum can penetrate from the bath into the expanding compact, to continue the dissolution of the solid particles, within the briquettes. Concluding, it is suggested that the swelling of the briquette and the size of pores can be maximized by making the average size of the aluminum particles relatively large.

2.3.6. Dissolution time of dispersed particles

A comparison between the time for complete dissolution of a briquette and the dissolution time of original particles, used in making the briquettes, for full entrained conditions of particles in highly stirred systems is shown in Figures 2.17 and 2.18. The results show that the dissolution of briquettes into the bath starts at 25-35 seconds, immediately following their disintegration, such that a high rate of up-take of iron or manganese particles by the liquid aluminum can be achieved quickly.

The phenomena can be described as follows; 25 wt pct original aluminum powder inside the briquettes, along with liquid aluminium penetrating into the expanded sample, provide some liquid metal around of solid particles. So, the solute iron or manganese can dissolve in unsaturated liquid aluminum, before disintegration. Furthermore, local accumulation of heat released in the briquettes, increases the maximum solubility of solute in the liquid aluminum, as well raising the diffusion rate of solute from solid to liquid. Therefore, the present conditions in the sample provide for a relatively high driving force for dissolution of the alloying elements before disintegration. The dissolution process proceeds until a saturated condition is achieved. Hence, the saturated liquid aluminum inside the briquettes (contained a high content of solute), supplies some dissolved agent into bath instantly after disintegration. Chemical analysis of withdrawn and quenched samples before disintegration confirms the idea. Turning to the microstructure of iron or manganese briquettes withdrawn before disintegration (Figure 2.11 or 2.12), has shown a super saturation condition of solute in the matrix such that a lot of low melting point phases are formed during quenching. (e.g. MnAl₆ with 25.34 pct Mn, small white areas in aluminum matrix).

Consequently, by spreading this saturated liquid aluminum in melt, following the collapsing of the briquettes, a sharp rise in concentration of solute can be achieved.

However, in the case of alloy making by the addition of discrete particles of pure alloying elements, the dissolution performance is different. There, two periods can be observed, particularly for manganese particles. During the first period, some physical actions such as dispersion and heating or chemical reactions such as removing of oxide layers and nucleation of soluble intermetallic compounds may delay or slow the initial dissolution process. The results shows that this period is roughly independent of particle size and takes place over the first 80 seconds or so for manganese and 40 seconds for iron powder. The second period which takes up the most time for dissolution is controlled by mass transfer through the boundary layer, similar to dissolution of particles dispersed in the melt following disintegration of briquettes.

From the point of recovery, since during the whole experiments, for both of briquettes and discrete particles, the surface of the melt was highly covered by argon gas, a comparison between the recoveries of the two systems may not be accurate, particularly with a subsurface addition mode for discrete particles. However, the final recoveries for manganese briquettes was more than 98% and for iron briquettes more than 98.5%. For discrete particles, it was close to 0.4% lower.

2.4. Conclusions

Among the several methods which have been introduced for alloy making additions to liquid aluminum, compacted powders of high melting point elements and aluminum can improve the kinetics of dissolution of alloying agents.

Microstructural studies along with thermal analysis of immersed briquettes

of Fe-Al and Mn-Al in the bath indicated that after the melting of the aluminum particles in the briquettes, exothermic reactions between aluminum and solid particles ($\Delta H_{720 \circ C}$ Fe₂Al₅ = 10.47 and $\Delta H_{720 \circ C}$ MnAl₄ = 5.4 kJ/g.atom Al) and the local accumulation of heat inside the briquettes, increased a briquettes's temperature sharply, well above the bath temperature. As a result, a high temperature atmosphere not only accelerates diffusional reactions, concerning the formation of intermetallic rims around particles of alloying elements, but also offers a high driving force for dissolution of alloying elements inside the liquid aluminum available in the compact. As well, penetration of liquid aluminum from the bath into the expanded sample, delays achieving the maximum solubility by increasing the amount of liquid. Then, the dissolution of solid particles proceed in the present liquid inside the briquettes until disintegration occurs.

The microstructural study of the immersed briquettes indicated that among several thermodynamically stable intermetallic compounds at the temperature of the experiment, Fe_2Al_5 and $MnAl_4$ are the only dominant intermetallic phases in the structure of the respective briquettes.

A theoretical analysis aided by some experimental observations (see Figure 2.9) revealed that in the growth of intermetallic compounds within the briquettes, which obey a parabolic law with time, the diffusion rate of manganese in $MnAl_4$ is higher than is one quarter of the diffusion rate of aluminum. As a result, the intermetallic region penetrates the liquid aluminum phase preferentially. In the growth of Fe₂Al₅, the opposite phenomenon is observed. The intermetallic phase grows preferentially inward towards the centre of the iron particle, see Figure 2.10. In this case, the flux of iron is grater than 2/5 of the flux of aluminum.

A comparison between dissolution times of briquettes and original classified particles, used in their fabrication, showed that a high up-take rate of alloying particles can be reached immediately following the briquettes disintegration. Dispersion of some saturated liquid aluminum (present inside the briquettes), in the melt, supplies solute to the bulk instantly. As a consequence, it can lead to a sharp rise in concentration of solute in the bulk following disintegration. This saturated liquid aluminum in the briquettes was provided by former 25 wt pct solid aluminum particles plus liquid aluminum penetrated from the bath due to swelling of the briquettes. Furthermore, one should remember that exothermic reactions and local heat accumulation in the briquettes hasten the dissolution process. In the dissolution of discrete powders, however, the process is rather different. It seems the initial dissolution process is delayed by some physical and chemical reactions (particularly for Mn particles) and therefore, initial up-take rates are low. However, during the second period of dissolution, the process is controlled by mass transfer from solid to liquid, similar with dissolution of disintegrated briquettes. Given that the briquettes were totally dissolved within periods of 420 seconds (Mn) and 330 seconds (Fe), while the larger sized particles from which they were fabricated required some 150 seconds further for complete dissolution.

It is concluded that alloying liquid aluminum with briquettes provides enhanced rates of dissolution, as well as facilitating its method of addition, compared to discrete particles.

2.5 Nomenclature

- C solute concentration
- D solute diffusivity

J flux

- V the average volume per solute atom in the cell
- X thickness of intermetallic layer made via reaction I
- Y thickness of intermetallic layer made via reaction II
- Z total thickness of intermetallic layer made via reactions I and II

- ε_{o} green porosity
- ε end porosity

2.6 References

1- R.I.L. Guthrie, "Addition Kinetics in Steelmaking", *Electric Furnace* Proceedings, 1977, PP. 30-40.

2-S.A. Argyropoulos and R.I.L. Guthrie, "Appendix to Heat and Mass Transfer Principles Applied to Alloying", *Aluminium Melt Refining and Alloying*, 1989, The University of Melbourne, July 10-12, pp. E1.1-E1.12.

3. T.A. Engh, "Alloy Addition to Aluminium by Pneumatic Injection", *Aluminium Melt Refining and Alloying*, 1989, The University of Melbourne, July 10-12, pp. H1-H15.

4. T. Pedersen and E. Myrbostad, "Refining and Alloying of Aluminum by Injection", *Light Metals*, 1986, pp. 759-765.

5. R.J. O'Malley, C.E. Dremann and D. Apelian, "Alloying of Molten Aluminum by Manganese Powder Injection", *Journal of Metals*, 1979, Feb., pp. 14-19.

6. D.A. Granger, "Master Alloys: Quality and Performance Expectations of Alcoa", *Light Metal Age*, 1987, June ,pp. 17-24.

 G.T. Campbell qnd R.E. Bridges, "New Generation Manganese Additive for the Cast Shop; 85% Manganese ALTAB HC", *Light Metals*, 1994, pp. 1093-1097.
F.J.J. van Loo and G.D. Rieck, "Diffusion in the Titanium-Aluminum System: I. Interdiffusion between Solid Al and Ti or Ti-Al Alloys", *ACTA Metallurgica*, 1973, vol. 21, pp. 61-71.

9. G.V. Kidson and G.D. Miller, *Journal of nuclear Materials*, " A Study of the Inter-diffusion of Aluminum and Zirconium", 1964, vol. 12, pp. 61-69.

10. N. Tunca, G.W. Delamore, and R.W. Smith, "Corrosion of Mo, Nb, Cr and

Y in Molten Aluminium", Metallurgical Transactions A, 1990, vol. 21A, pp. 2919-2928.

11. W.H. Perry, "Aluminum Recovery from All Metallic Hardener Briquettes", Light Metals, 1994, pp. 841-848.

12. A.P. Savitskii, "Some Characteristic Features of the Sintering of Binary Systems", *Poroshkovaya Metallurgiya*, 1980, no. 7, vol. 211, pp. 62-69.

13. R. M. German, Liquid Phase Sintering, 1985, Plenum Press, New York and London, pp. 23 and 67-74.

14. R. M. German, "Particle Packing Characteristics", 1989, Metal Powder Industries Federation, New Jersey, pp. 316-327.

15. D.J. Lee and R.M. German, "Sintering Behaviour of Iron-Aluminum powder mixes", *The International Journal of Powder Metallurgy & Powder Technology*, 1985, vol. 21, no. 1, PP. 9-21.

16. J.S. Sheasby, "Powder Metallurgy of Iron-Aluminum", *The International Journal of Powder Metallurgy & Powder Technology*, 1979, vol.15, pp. 301-305.

17. A.P. Savitskii and N.N. Burtsev, "Theory and Technology of Sintering, Thermal, and Chemicothermal Treatment Processes; Compact Growth in Liquid-Phase Sintering", *Poroshkovaya Metallurgiya*, 1979, no. 2, vol. 194, pp. 31-38.

18. A.P. Savitskii, L.S. Martsunova and M.A. Emel'yanova, "Theory and Technology of Sintering, Thermal, and Chemicothermal Treatment Processes: Compact Porosity Changes in Liquid-Phase Sintering due to Diffusional Interaction between Phases", *Translated from Poroshkovaya Metallurgiya*, 1981, no. 1, vol. 217, pp. 6-12.

19. A.P. Savitskii, N.N. Burtsev, and L.S. Martsunova, "Theory and Technology of Sintering, Thermal, and Chemicothermal Treatment Processes: Volume Changes Experienced by Al-Zn Compacts during Liquid-Phase Sintering", 1982, *Poroshkovaya Metallurgiya*, 1982, no. 10, vol. 238, pp. 11-16.



Fig: 2.1 A schematic representation of four kinetic paths for alloying additions melting or dissolution in bath.



Fig: 2.2 Elkem alloying briquettes.



5 : Tachometer

Fig: 2.3 A schematic of the experimental set-up, $(T=720^{\circ}C)$.



 θ , " θ -Al₃Fe", with a very complex end-centered monoclinic structure η , " η -Al₅Fe₂", with an end-centered orthorhombic structure β ', "AlFe", with an ordered bcc (B2) structure β '', "AlFe₃", with an ordered bcc (D0₃) structure

"Al₆Fe", with an orthorhombic structure isotypic with Al₆Mn. This phase is not shown on the phase diagram.

 ζ , " ζ -Al₂Fe", with a complex rhombohedral structure ϵ , with a complex bcc structure

Fig: 2.4 Al-Fe phase diagram



 ϵ , "Al₆Mn", with the orthorhombic (D_{2h}) prototype structure ζ , "Al₄Mn", with a hexagonal structure. θ , " Φ -Al₁₀Mn₃", with a hexagonal structure i, "Al₃Mn", with an orthorhombic structure λ , " δ -Al₁₁Mn₄", with a triclinic structure. μ , "Al₆Mn₅(?)", with the bc rhombohedral (D8₁₀) structure ν , " η Al-Mn", with a hexagonal structure $\hat{\xi}$, ϵ Al-Mn", with a hexagonal structure

Fig: 2.5 Mn-Al phase diagram.



Fig: 2.6 Thermal analysis of iron and manganese briquettes submerged in molten aluminum, $(T=720^{\circ}C)$.



Fig 2.7 An example of exothermic reactions and expansion in manganese briquette immersed in melt, a) green briquette; photographs b, c, d, e) show the sample withdrawn from the melt, containing its exothermic reactions within the body of the briquette.



Fig 2.8 An example of exothermic reactions and expansion in iron briquette immersed in melt, a) green briquette; photographs b, c, d, e) show the sample withdrawn from the melt, containing its exothermic reactions within the body of the briquette.



Fig: 2.9 Microstructure of Fe-Al briquette: a) 10 seconds, b) 25 seconds, after immersion in liquid aluminum, (T=720°C).



Fig: 2.10 A schematic representation of the concentration distribution of manganese and aluminum during the growth of an intermetallic layer of $MnAl_4$.



Fig: 2.11 The preferential growth of MnAl₄ phase at Mn-Al interface within liquid phase.



Fig: 2.12 The preferential growth of Fe₂Al₅ phase at Fe-Al interface within solid phase.



Fig: 2.13 Disintegration times of manganese and iron briquettes submerged in liquid aluminum using a load cell, (T=720°C).



Fig: 2.14 Proposed mechanism for the dissolution of compact briquettes in liquid aluminum.



Fig: 2.15 A schematic plot of the solubility effect on densification or swelling the briquettes during the heating. S represents the solubility and the subscript denotesB for base (major phase) solubility in the additive and A for additive (minor phase) solubility in the base.^[13]



Fig: 2.16 Pore formation at the prior aluminum particle sites in a powder mixture of iron and aluminum due to the outward flow of aluminum into the iron particles.^[13]



Fig: 2.17 A comparison between dissolution time of manganese briquettes and original particles used in making the briquettes in a highly stirred system, $(T=720^{\circ}C).$


Fig: 2.18 A comparison between dissolution time of iron briquettes and original particles, used in making the briquettes in a highly stirred system, $(T=720^{\circ}C)$.

CHAPTER 3

DISSOLUTION KINETICS OF Fe AND Mn PARTICLES IN STIRRED LIQUID ALUMINUM

Evaluation of Terminal Velocity Theory in High Temperature Melts

3.1 Introduction

Following disintegration of the briquettes in the liquid melt, fine particles disperse freely in the bath and dissolution continues. In such transport controlled processes, the degree of mass transfer from a solid to the liquid is a measure of the relative velocity between them. In a mechanically stirred system, both liquid and entrained particles will have turbulent motions (in three dimensions with different mean velocities and random fluctuations). So that particles will be in irregular motion within a turbulent stirred liquid. Moreover, small scale turbulent eddies in the system, smaller than the size of the particles, or rotation of particles within the liquid, could also contribute to relative motion between the liquid and

the surfaces of particles. Therefore, in such turbulent systems, measuring relative velocities of particles is not simple, if not impossible.

However, in aqueous model systems, some approaches have been introduced, (terminal velocity theory and Kolmogoroff's theory). In the present study, (for the first time) these proposed theories have been examined in high temperature liquid metal system.

Mechanical modes of stirring

In general, alloying additions to turbulent liquid melts of aluminum is accomplished by mechanical stirring. Since the dissolution process of most alloying particles in liquid aluminum is slow and is controlled by mass transfer through a boundary layer between solid particles and the liquid, mechanical stirring can be very helpful for enhancing the kinetics of the dissolution process. Mechanical stirring of liquid aluminium is usually carried out by one of the following methods:

In the first commonly-used method, stirring is done in an alloying furnace by moving a massive flat blade back and forth over a heaping of alloying elements. Shorter dissolution times can be achieved by this mixing operation, by exposing a greater surface area of solids to the dissolution process.

In more sophisticated methods, a rotor is employed in the "ladles" which are used to convey the primary melt from the reduction cell to the alloying/holding furnace. The high temperature of the melt, as well as the well-designed geometry of these transport ladles (narrow and tall), helps to generate an effective turbulent flow and decreases dissolution time of alloying elements.

Beyond these approaches, gas stirring (using argon), which is sometimes used to carry the alloying particles in the beginning of the injection process, is also another accepted addition method in the aluminum industry.

3.2 Previous work on high temperature systems

Kinetic studies of alloying additions to aluminum melts has received comparatively little study, even though the alloying process can be one of the rate limiting steps which can influence the rate of production of aluminum alloys.

To the best of author's knowledge, except for some limited work in conjunction with pneumatic powder injection techniques^[1,2,3], no systematic research has yet been carried out to study the kinetics of dissolution of fine particles of alloying elements in turbulently stirred systems of molten aluminum (nor any other metal). More specifically, no study has yet been reported concerning the kinetics of dissolution of *fully suspended* particles of iron and manganese in a mechanically stirred system of liquid aluminum.

Nearly all previous kinetic studies of the dissolution of alloy additions to aluminum have been limited to the rotating disk method. This technique has been popular among most researchers and it is shown that dissolution rates depend strongly on the hydrodynamic conditions within the liquid. Since the method can be used to measure diffusion coefficients of high melting alloying elements in liquid aluminum and to test whether a dissolution process is controlled by mass transfer from solid to liquid, it is useful to provide a more detailed description of the method.

3.2.1 Rotating disk mass transfer

In the kinetic study of the dissolution of high melting point elements, the rotating disk technique is not only used for studying the dissolution of high melting alloying elements such as molybdenum^[4,5], niobium^[4,5], chromium^[4,6,7,8], yttrium^[4], iron^[7,8,9,10,11,12], manganese^[7], titanium^[7,8,10], nickel^[8,13], vanadium^[8], ferrous alloys^[9] and iron-nickel alloys^[14] in liquid aluminum, but is also used for dissolution studies of high melting point alloys in liquid steel. In the rotating disk method, small

cylindrical specimens with a polished surface are first prepared, then pressed into a high-purity graphite tube to protect the specimen's lateral surface from the melt. Thus, only the disk surface dissolves during the rotation.

The dissolution of a solid metal in a liquid metal can be described by the mass balance equation:

$$\frac{dC_b}{dt} = K_m \frac{S}{V} (C_s - C_b)$$
(3-1)

After integrating, and applying the initial condition, $C = C_o$ at t = 0, :

$$\ln \frac{C_s - C_o}{C_s - C_b} = K_m \frac{S t}{V}$$
(3-2)

where C_s and C_b (kg/m³) are the saturation and bulk concentrations of solute, S is the surface area of solid (m²), t is time (s), V is the volume of the melt and K_m is mass transfer coefficient. Thus, the concentration measured (C_b) by periodical sampling, can readily be analyzed using above equation. For a given temperature and speed of rotation, it was found that there is a linear relation between ln{(C_s - C_o)/(C_s - C_b)} and St/V, which indicates a constant mass transfer coefficient (K_m).

In the rotating disk technique, the flux $J(kg m^{-2}s^{-1})$ of material from the surface of the solid to liquid can also be calculated using Levich's^[15] equation:

$$J = 0.6^{2}_{*} D^{2/3} v^{-1/6} \omega^{1/2} (C_s - C_b)$$
(3-3)

where D is the diffusion coefficient of the solute element, ν is the kinematic viscosity and ω is the angular velocity of disk. This equation was applied for liquid flow over the surface of the disk which occurs in the rotational speed range of 100-1000 rpm for a disk with an area of about 1 cm².

From Levich's equation, the mass transfer coefficient, K_m, is related to

angular velocity through the equation:

$$K_{m} = 0.62 \ D^{2/3} \ v^{-1/6} \ \omega^{1/2} \tag{3-4}$$

The results obtained for most transition metals (such as iron and manganese) reveal a linear relation between mass transfer coefficient and the root square of angular velocity of disk, $\omega^{1/2}$. This indicates that the *dissolution process is controlled by diffusion of atoms through the liquid-metal boundary layer* adjacent to the disk, even at excessive speeds of rotation.^[5,6,7,8,9,11,12,13,14,16]

The rotating disk technique has also been used to measure solute diffusion coefficients of the following binary systems: $D_{Cr-Al}^{[6,7]}$, $D_{Si-Al}^{[7]}$, $D_{Fe-Al}^{[7,10,11,12]}$, $D_{Cu-Al}^{[7]}$, $D_{Ti-Al}^{[7,10]}$, $D_{Ni-Al}^{[7,13]}$, $D_{Mn-Al}^{[7]}$, $D_{W-Al}^{[5]}$ and $D_{stainless steel-Al}^{[16]}$. Measuring mass transfer coefficients from Eq. [3.2] for different rotational speeds, and substituting in Eq. [3.4], diffusion coefficients can be obtained. Diffusion coefficients are a function of temperature and, for different temperatures of the experiment, the result can be analyzed using an Arrhenius type equation, (more details are given in Appendix 1).

The rotating disk method can also be used in studying the growth kinetics of intermetallic layers. In this method, the crucible, together with the flux, the melt and the specimen, are shot into water to arrest the metal-aluminium reaction in the interface. It is important that the specimen continue to rotate until complete solidification of the melt. After cooling, the bimetallic specimen obtained by this method is cut along the cylindrical axis and, after polishing, the cross section of the sample is metallographically examined. The results have shown the existence of an intermetallic layer over the surface of sample.

Finally, from rotation disk technique, it can be concluded that chemical reactions such as the formation of intermetallic compounds have no effect on the dissolution rate such that in high rotation speed the dissolution process is still controlled by mass transfer.

3.3 Previous work on cold systems

In liquid metal systems, essentially no work seems to have been carried out on the dissolution of solid alloying particles in a turbulently stirred system. However, in "cold" temperature systems, the extent of the work is so substantial that gathering them into a unit collection proved difficult. The author, through a literature survey (mostly of chemical engineering research), attempted to simply introduce the theories proposed for the dissolution of solid particles in low temperature liquid systems and to evaluate these theories in high temperature molten metal systems.

In general, in studying mass transfer between a solid phase and liquid media, the simplest case is that of mass transfer from a single-fixed particle in stagnant bath or one in flow. Mass transfer from suspended particles in a stirred turbulent system is more complex.

3.3.1 Single particle mass transfer

Mass transfer coefficients for rigid, fixed particles in a flowing fluid are represented by the equation :

$$Sh = 2 + A Re^{m} Sc^{n}$$
 (3-5)

where m, n and A in the above equation are a function of the particle Reynolds number (Re) and Schmidt number (Sc), where;

$$Sh = \frac{K_m d_P}{D}$$
, $Re = \frac{U d_P}{v}$, $Sc = \frac{v}{D}$ (3-6)

One can readily show that in the transfer of mass between a solid sphere

and a Equid, the Sherwood correlation, in the absence of any convection, involves a Sherwood diffusion term with a limiting value of 2.0, while the second term corresponds to the forced convection component of Sherwood number. It seems that natural convection phenomena, resulting from density differences in concentration boundary layers around solute particles, was neglected in the presence of a force convection condition. In determination of m, n and A in the Sherwood correlation, Hughmark^[17,18] analyzed the heat and mass-transfer data of many investigators and proposed several equations for mass transfer. However, turbulent intensity around an entrained particle in agitated vessels will differ from that for a fixed particle in a flowing liquid. Therefore, some modification is necessary.

3.3.2 Mass transfer from suspended particles

In order to be able to quantify the dissolution kinetics of small particles in stirred liquids under conditions of transport control in the liquid phase, the relative velocity between the particles and the fluid must be known. However, these are extremely difficult, if not impossible, to clarify, since the particles will be moving erratically with a turbulent liquid, in which random velocity fluctuations will be superimposed on mean bulk flow velocities. In addition, the relative effects of turbulent motions within the fluid on dissolution kinetics will depend upon the size of the particles relative to the scale of turbulence. It is even possible that the rotation of the entrained particles within the fluid, by providing a relative motion of liquid at the surfaces of the particles, may affect the dissolution rates.

As such, the hydrodynamic interactions which control particle-fluid mass transfer in an agitated vessel are highly stochastic and impossible to predict, *ab initio*.

However, several approaches have been introduced. Most recent workers have used either terminal velocity theory or Kolmogoroff's theory (local isotropy in Λ

turbulent systems) to explain and solve this problem. By simplification, the terminal velocity theory implies that mass transfer coefficient in a agitation system is related to velocity which would be obtained if the particle moves at its terminal velocity in a stagnant bath. The Kolmogoroff's theory on the other hand, suggests that mass transfer is related to the rate of input mixing energy into the system, such that in systems with different agitation systems, equal mass transfer coefficients are achieved by equal input power per unit mass of the melt. In this chapter and the next, while explanations the terminal velocity theory and Kolmogoroff's theory respectively, their applicabilities in molten metal system, for the first time, have been evaluated.

3.3.3 Terminal velocity theory

Based on the terminal velocity approach (Harriott^[19], Nienow^[20,21], Levins and Glastonbury^[22], Conti and Sicardi^[23], Calderbank and Moo-Young^[24], Sykes and Gomezplata^[25]) terminal settling velocity of solid particles in a quiescent liquid is used to calculate the mass transfer coefficient of suspended particles in an agitated system. The suspension of solids particles in a liquid media will be obtained when the rising velocity of the fluid phase equals, or exceeds, the settling velocity of the particles. It is envisaged that counter-current flows apply some turbulence forces on descending particles as so to keep them suspended. If so, the mass transfer rates are expected to be close to those for particles moving freely under gravity.^[24]

This theory was later modified by Nienow.^[21] It was found that using the terminal velocity as relative velocity in Sherwood correlation, the minimum expected value for the mass transfer coefficient is obtained. The minimum coefficient is then multiplied by a correction factor, which is obtained from experimental results and justifies using such theoretical mass transfer

considerations.

In theoretical calculations of the mass transfer coefficient, Nienow^[20] used Rowe's^[26] equation :

$$Sh = 2 + 0.72 Re^{1/2} Sc^{1/3}$$
 (3-7)

Limitation of theory

Although the theory has been accepted by some researchers and they were able to analyze their experimental results via this theory satisfactorily, it has a significant limitation. The theory will break down when the density difference between a particle and the liquid approaches zero, regardless of particle diameter, due to particle Reynolds number approaching zero. It is clear that for a neutral buoyancy particle, the Sherwood correlation is greater than 2.0 (the diffusion term), because the fluid around the particle is always in a state of turbulent interchange. To solve this difficulty, Harriott^[19] has proposed that for neutrally buoyant particles, an adhoc density difference of 0.3 g/cm^3 should be taken rather than the true value.^[19]

3.3.4 Minimum suspension speed

The determination of the minimum speed of agitation needed to raise particles off the furnace bottom plays an important role in the kinetics of dissolution. It is observed from studies in aqueous medium that below a critical speed, due to the settling of particles to the bottom of the vessel, the total surface area of solids is not efficiently available for the dissolution process, therefore, dissolution rate is slow. Above this critical speed, the rate of mass transfer may increase slowly.^[19,24,27] In a complete suspension, it is sufficient that the whole of the solid surfaces be exposed to the liquid, and it is often unimportant that the upper layer of liquid contains smaller and lighter particles, whereas coarse and heavy particles remain in the lower part of the vessel.

The critical speed for full suspension has been defined as the speed at which no solids remain on the base of the vessel for longer than one second.^[28]

Zwietering^[28] presented a correlation for the critical speed (N_s) to obtain a full suspension of solid particles:

$$N_s = \frac{S v^{0.1} d_P^{0.2} (g \Delta \rho / \rho_L)^{0.45} X^{0.13}}{D_L^{0.85}}$$
(3-8)

where S is a dimensionless constant, v is the kinematic viscosity, d_P is particle diameter, g is the gravitational constant, $\Delta \rho$ is density difference between solid and liquid, ρ_L is density of liquid, X is the concentration of solid in liquid (mass per mass of liquid, times 100, dimensionless), and D_I is the diameter of the impeller. However, dimensionless constant (S) depends on system geometry, and several graphs were presented in his paper to give values of S for five impeller types at various V_D/D_I and various impeller clearances. (V_D is diameter of the vessel.)

The following equation has also been proposed by K. Raghava Rao et al. [29]

$$N_{s} = \frac{C v^{0.1} (g \Delta \rho / \rho_{L})^{0.45} X^{0.1} d_{P}^{0.11} D_{V}^{0.31}}{D_{L}^{1.16}}$$
(3-9)

while G. Baldi et al.^[30] presented:

$$N_s = \frac{C \ \mu^{0.17} \ (g \ \Delta \rho)^{0.42} \ d_P^{0.14} \ X^{0.125}}{\rho_L^{0.58} \ D_I^{0.89}}$$
(3-10)

and C.M. Chapman et al.^[31] reported:

$$N_s = \frac{C v^{0.17} (g \Delta \rho / \rho_L)^{0.42} (D_I / D_V) d_P^{0.14} X^{0.11}}{P_N^{0.28} D_I^{0.89}}$$
(3-11)

where P_N is power number (dimensionless) = (input power/ $\rho_L N^3 D_I^5$), and C is a constant.

While there is some discrepancy among these equations, Zwietering's equation^[28] has received more support than the others because it represents the most complete investigation of N_s in terms of its extensive range of geometries and materials studied for aqueous systems.

Furthermore, in study of minimum suspension speed, it was observed that N_s depends strongly upon the impeller clearance from the bottom and decreases as the impeller is moved closer to the base.

Most of the investigations on this subject have been carried out using single impeller systems, however, Armenante *et al.*^[32] has also investigated the role of a multiple impeller agitation system mounted on the same shaft. He found that the presence of multiple impellers may not necessarily be beneficial to the achievement of suspension conditions. In this case, while the critical agitation speed decreases with the number of impellers on the shaft, the power required is higher.

In conclusion, a literature review on the present topic reveals an abundance of work and numerous correlations for the suspension of particles. This extensive research discloses the importance of mixing, as well the critical effect of suspension of particles, on solid-liquid mass transfer processes. One can conclude that in a solid-liquid system, special care should be taken in assuring an appropriate degree of suspension.

Degree of suspension

In general, three categories for the suspension of solids can be identified:

a:) On bottom motion, in which coarse particles are moving on the bottom of the vessel, whereas fine particles will be suspended off the bottom.

b:) Off bottom suspension, in which all particles are suspended, but not uniformly throughout the vessel content.

c:) Uniform suspension, in which all particles, fine or coarse, are suspended uniformly.

It is well known that in the dissolution of solid particles in a liquid, a complete and uniform suspension is not necessary. Therefore, the off bottom suspension condition as defined by Zwietering, (no solid particles remains on the base for longer than one second), was adopted for this investigation.

3.4 Experimental procedures

In the present work, two series of experiments were carried out.

a) Some aqueous model experiments were used to study the suspension behaviour of particles in turbulent system. b) Water model experiments were followed by high temperature experiments to determine actual mass transfer coefficients and dissolution times of high melting point alloying elements particles in liquid aluminum.

The case of iron and manganese were chosen for the present investigation since these alloying elements are very important alloying additions in the improvement of mechanical properties of die casting and wrought aluminium products.

3.4.1 Water modelling experiments

As noted, the contact area between solid particles and the liquid should be maximised, and this is possible by generating effective turbulence throughout the melt and by bringing the highest density materials into suspension. In the actual liquid metal system, due to its inherent opaqueness, it is not easy to evaluate the degree of suspension of particles during stirring. Substituting water as the modelling medium is an appropriate and reliable method to elucidate such complexities.

In Table 3.1, some of the relevant physical properties pertaining to the present water model and the high temperature system are provided.

Item		Water model	Prototype	
Particle density $(\rho_{\rm P})$	kg/m ³	Lead particles: 11680	Fe:7830, Mn:7300	
Particle diameter (d _P)	μ m	90-550	90-550	
Liquid density (ρ_L)	kg/m ³	999	2370	
Liquid viscosity (µ)	kg/m.s	1.05x10 ⁻³	1.1x10 ⁻³	
Impeller diameter (D _I)	m	0.07	0.07	
Vessel diameter (D _v)	m	0.14	0.14	
Clearance	m	0.01	0.01	
Temperature (T)	°C	15	720	

 Table 3.1 Physical properties of water model and prototype

3.4.1.1 Measurement of critical rotational speed in water

Turning to section 3.3.4, several correlations for the suspension of the particles have been suggested, based on experiments using cold model systems. However, due to the discrepancies which exist among current empirical correlations, determination of critical speed of impeller needed for a full entrainment of iron and manganese particles within the liquid aluminum was necessary. In particular, in the case of this study, a high density difference between iron or manganese particles and molten aluminium (≈ 5.4 gr/cm³) is

involved, which is essentially not compatible with previous experiments. Furthermore, in liquid metal experiments, it was not easy to obey the proposed standard geometric dimensions which are used in aqueous model for mixing. For instance, thick-bladed graphite impellers which were used in liquid aluminium experiments are entirely different from the stirrer types recommended for cold models. Hence, the present practical limitations lead the author to adopt another approach, involving water modelling experiments in company with dimensional analysis, so as to correlate the results of the cold model with high temperature systems.

In water model experiments, the critical speed of rotation in water, N_s , was measured by observing the suspension of lead particles as seen via a mirror placed below the bottom of the plexiglass vessel, which was well illuminated. These experiments were performed for a variety of classified particle sizes ranging from 90 to 550 μ m diameter. The data obtained is shown in Figure 3.1. By dimensional analysis, and using the current water model results, one can predict the minimum speed of rotation of the impeller required to obtain a full entrainment of iron and manganese particles in liquid aluminium.

3.4.2 Dimensional analysis

In a dimensional analysis, at first, the variables involved in the problem should be identified. In Table 3.2, the variables: density of liquid (ρ_L), diameter of the particles (d_P), apparent weight of particles ($W = (\pi d_P^3/6)(\rho_P - \rho_L)g$), liquid viscosity (μ), impeller diameter (D_L), vessel diameter (D_V), and impeller speed (N_P) as well the respective dimension of each variable have been shown, (where ρ_P and g are particle density and acceleration of gravity, respectively).

ρ_L	d _P	W	μ	Dı	D _v	N _s
ML-3	L	MLT ⁻²	ML-1T-1	L	L	T -1

Table 3.2 The dimension of variables involved

In our system, seven variables with three dimensions; mass M, length L and time T, are available. Then, due to difference between the number of variables and dimensions (7 - 3 = 4), only four dimensionless pi groups (π_i), with combination of variables, can be defined. The combination procedure is:

$$\pi_{1} = D_{1}^{a} \cdot \rho_{L}^{b} \cdot \mu^{c} \cdot N_{s}$$

$$M^{0}L^{0}T^{0} = (L)^{a} \cdot (ML^{-3})^{b} \cdot (ML^{-1}T^{-1})^{c} \cdot (T^{-1})$$

$$\pi_{1} = D_{1}^{2} \cdot \rho_{L} \cdot N_{s} / \mu$$

$$\pi_2 = D_I^{a} \cdot \rho_L^{b} \cdot \mu^{c} \cdot D_V$$

M⁰L⁰T⁰ = (L)^a. (ML⁻³)^b. (ML⁻¹T⁻¹)^c. L
 $\pi_2 = D_V/D_I$

$$\begin{aligned} \pi_3 = D_I^{a} \cdot \rho_L^{b} \cdot \mu^c \cdot d_P \\ M^0 L^0 T^0 = (L)^{a} \cdot (ML^{-3})^{b} \cdot (ML^{-1}T^{-1})^c \cdot L \\ \pi_3 = d_P / D_I \end{aligned}$$

$$\pi_4 = D_I^a. \ \rho_L^b. \ \mu^c \ . \ W$$
$$M^0 L^0 T^0 = (L)^a. \ (ML^{-3})^b. \ (ML^{-1}T^{-1})^c. \ (MLT^{-2})$$
$$\pi_4 = \rho_L. W/\mu^2$$

Therefore, four dimensionless pi groups, involved in the system, have been

introduced:

$$\pi_1 = \frac{D_I^2 \cdot \rho_L \cdot N_S}{\mu} \quad \pi_2 = \frac{D_V}{D_I} \quad \pi_3 = \frac{d_P}{D_I} \quad \pi_4 = \frac{\rho_L \cdot W}{\mu^2}$$

Based on dimensional analysis and similarity (Buckingham pi theorem), each pi group can be defined as a function of other involved pi groups in the system as: $\pi_1 = f(\pi_2, \pi_3, \pi_4)$, or:

$$\frac{D_{I^{*}}^{2} \rho_{L^{*}} N_{s}}{\mu} = f\left(\frac{D_{V}}{D_{I}}, \frac{d_{P}}{D_{I}}, \frac{\Pi_{s} d_{P^{*}}^{3} g_{s} \rho_{L^{*}} (\rho_{P} - \rho_{L})}{6\mu^{2}}\right)$$
(3-12)

According to the modelling theory provided, if π_2 , π_3 and π_4 in the cold system are selected such as to be equal to respective π_2 , π_3 and π_4 groups in high temperature system, then it leads to the equality of amount of the dependent function for both systems, *i.e.* π_1 .

To assure these similarities, the geometrical configurations of the hot and cold model systems (D_V/D_I) and d_P/D_I as well as $\rho_L.d_P{}^3(\rho_P-\rho_L)/\mu^2$ for both systems, were selected such that π_2 , π_3 and π_4 were identical in water and liquid experiments, (see Table 3.1). Noting that in order to get equal π_4 for both system, density of particles in the water should be equal to 11650 kg/m³. For this reason, lead particles with density of 11680 kg/m³ selected for water modelling experiments. These conditions resulted in the equality of π_1 for both systems:

$$\left(\frac{D_{I^{*}}^{2} \rho_{L^{*}} N_{S}}{\mu}\right)_{Liquid metal} = \left(\frac{D_{I^{*}}^{2} \rho_{L^{*}} N_{S}}{\mu}\right)_{Water}$$
(3-13)

3.4.3 Prediction of critical rotational speed of suspension in liquid metal

As mentioned, the critical impeller speed in molten aluminum can be determined using water modelling results and a dimensional analysis between water modelling scale and prototype. Inserting respective values for ρ_L , μ and D_I for water and liquid aluminium from Table 3.1 into correlation obtained, Eq. [3.13], the relation between critical rotational speed of impeller (N_s) in liquid aluminium and water for complete suspension will be as follows:

$$N_{S_{L^{i}guid}Al} = 0.4 N_{S_{Water}}$$
(3-14)

Therefore, applying the results obtained from water modelling experiments (Figure 3.1) in the Eq. [3.14], the critical impeller rotational speed in liquid melt was predicted, (Figure 3.2). To ensure full suspension, the melt was stirred 20% higher than the predicted rotational speeds for each specific size of solute particles.

3.4.4 High temperature experiments

The main objectives of the hot metal work was to study the dissolution process for alloying particle, using two entirely independent methods, namely the conventional analysis method and the more sophisticated on-line particle detection technique, known as **LiMCA**, the acronym for Liquid Metal Cleanliness Analyzer. The latter method is based on the resistance pulse principle. In this work only the results obtained based on the conventional method have been presented.

To prevent electrical noise in the system compromising LiMCA signals, an air drive motor was used for stirring. Using a tachometer on top of the motor shaft, desired mixing rates and speeds of rotation could be reached by changing input air-flows. Aluminium melts were prepared in an electrical resistance furnace having a capacity to hold 15-20 kg of aluminium. The melt temperature was controlled in the range of 720-725 °C. To minimize the oxidation of particles and the melt, a stream of argon gas covered the surface of the liquid during the experiment. The melt was stirred by a four-bladed graphite impeller, 70 mm diameter, 35 mm high and 10 mm thick, connected to the motor by a graphite shaft. The impeller was placed in the melt with a clearance of 10 mm from the bottom of crucible. The LiMCA tube and the thermocouple tube served as baffles prevented vortex formation. A schematic of the high temperature experimental setup is shown in Figure 3.3.

Considering the sensitivity of the LiMCA, the iron and manganese particles in the range of 90-550 μ m diameter were sieved and classified. In Table 3.3 equivalent spherical diameters of classified powders and the relevant range of the particles are shown.

size range (µm)	equivalent diameter (µm)
75 -105	90
105-150	127.5
150-212	181
212-300	256
300-425	362.5
425-500	462.5
500-600	550

Table 3.3 Size range of classified iron and manganese particles used.

Alloying was carried out by plunging a thin cored wire consisting of 0.5 to 0.6 wt pct of alloying powders wrapped in an aluminium foil. Sampling was carried out

periodically by stopping the mixing and taking the sample from the surface (and bottom of the melt). Ensuring that no particle was entrapped inside the surface samples taken, a vacuum emission spectrometer method was employed to clarify the amount of dissolved alloying elements in the bulk. Differences between the initial concentration of solute before the alloying addition and the concentrations of solute measured subsequently, were used to calculate changes in the average size of particles during dissolution. Further details in calculation procedure will be given later, (or see Appendix 2). Due to intensive mixing, one can be sure that the liquid is sufficiently homogenous i.e., any difference between the concentration of dissolved alloying elements in the surface and bottom layers of the melt are negligible. Therefore, the amount of dissolved alloying elements measured in the bulk can be a reliable method to deduce variations in the mean size of particles during dissolution. In addition, a few of the bottom samples, which included entrapped particles, were analyzed by Energy Dispersive Spectroscopy (EDS) using the TN 5500 microprobe. The measured amount of dissolved iron and manganese in the matrix of the bottom samples (using EDS method of analysis), confirmed top to bottom bulk homogeneity.

3.5 Results and discussion

3.5.1 Theoretical mass transfer coefficient

It has been suggested that the relative velocity between solid particles and liquid, in full suspension, is equal to the terminal settling velocity. This would seem almost reasonable because the gravity force is balanced by the upward forces of rising fluid. When a free-falling particle reaches terminal velocity, the sum of applied forces (ΣF_z), acting on it is equal to zero, therefore:

$$\sum F_{z} = F_{g} + F_{B} + F_{D} = 0$$
 (3-15)

where

$$F_g = \frac{4 \pi R^3}{3} g \rho_P$$
 (3-16)

$$F_B = -\frac{4 \pi R^3}{3} g \rho_L$$
 (3-17)

$$F_D = \frac{1}{2} C_D \rho_L U_t (\pi R^2)$$
 (3-18)

where F_g , F_B and F_D are gravity, buoyancy and drag forces applied on the particle respectively, R is the radius of the particle, g is the gravitational constant, ρ_P is particle density, ρ_L is liquid density, C_D is the drag coefficient and U_t is the terminal settling velocity. Inserting F_g , F_B and F_D from Eqs [3.16, 3.17 and 3.18] in Eq. [3.15], then, the terminal velocity is:

$$U_{t} = \left(\frac{8 g R \Delta \rho}{3 C_{D} \rho_{L}}\right)^{1/2}$$
(3-19)

In general, the drag coefficient (C_D) is a function of particles Reynolds number (Re). In this regard, three regions for relation between Re and C_D have been identified.

Substituting $C_D = 0.44$, $C_D = 18.5 \text{Re}^{-0.6}$, and $C_D = 24 \text{Re}^{-1}$ in Newton's, intermediate, and Stokes' region respectively,^[33] the terminal velocity in each region is:

$$U_t = 2.46 \ (\frac{g \ R \ (\rho_P - \rho_L)}{\rho_L})^{1/2} \qquad 500 < Re < 200000 \qquad (3-20)$$

in Newton's region

$$U_t = \frac{0.337 \ g^{0.71} \ R^{1.14} \ (\rho_P - \rho_L)^{0.71}}{\rho_L^{0.29} \ \mu^{0.43}} \quad 2 < Re < 500 \quad (3-21)$$

in intermediate region

$$U_t = \frac{2g R^2 (\rho_P - \rho_L)}{9\mu} \qquad 0.0001 < Re < 2 \qquad (3-22)$$

in Stokes' region

It is now appropriate to identify the regimes applying to the iron and manganese particles, selected for this study. The critical particle size above which each law will not apply is obtained by taking the maximum Reynolds number for each region and deducing U_t . The maximum diameter of the particles in each region, for iron and manganese particles is given in Table 3.4.

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Region	Max. d _{Fe} (m)	Max. d _{Mn} (m)
Stokes' law	4.7x 10 ⁻⁵	4.98x10 ⁻⁵
Intermediate law	5.42x10 ⁻⁴	5.8x10 ⁻⁴
Newton's law	2.26x10 ⁻²	2.44x10 ⁻²

Table 3.4 Maximum valid diameter for Fe and Mn particles in each region

In the present study, the iron and manganese particles with equivalent diameter between 90 to 550 μ m are seen to obey Eq. [3.21], *i.e.*, the intermediate region. As such, the terminal velocity is:

$$Fe \quad U_{r} = 1508.5 \ R^{1.14} \qquad m/s \qquad (3-23)$$

$$Mn \quad U_{\star} = 1403.0 \ R^{1.14} \qquad m/s \qquad (3-24)$$

Considering the diffusion coefficients and also Schmidt numbers of iron and manganese particles in liquid aluminium at (720°C), ($D_{Fe-AI} = 1.95 \times 10^{-9}$, $D_{Mn-AI} = 0.85 \times 10^{-9} \text{ m}^2/\text{s}^{[7]}$ and $\text{Sc}_{Fe} = 238$, $\text{Sc}_{Mn} = 546$), then, inserting U₁ from Eqs [3.23] and [3.24] in the Sherwood correlation, (Eq. [3.7] which is proposed by Rowe^[26] and used by Nienow^[20]), for dissolution of suspended particles in a highly turbulent system, the theoretical mass transfer coefficient based on terminal velocity theory can be calculated:

$$Fe \quad K_{s} = 1.95 \times 10^{-9} R^{-1} + 6.375 \times 10^{-4} R^{0.07} \quad m/s \quad (3-25)$$

$$Mn \quad K_{\star} = 0.85 \times 10^{-9} R^{-1} + 3.413 \times 10^{-4} R^{0.07} \quad m/s \quad (3-26)$$

Justified mass transfer coefficient (K_i)

In the aqueous model study, it was quoted that terminal velocity theory gives the minimum mass transfer coefficients. Therefore, in order to justify the theory with experimental results, Nienow^[21] suggested that the actual mass transfer coefficient for complete suspension should be between 6 pct to 50 pct above this calculated mass transfer coefficient and should depend on particle size. The enhancement in the mass transfer coefficient with particle size can be approximately expressed by the empirical equation:

$$\frac{K_j}{K_t} = E = \left(\frac{R}{R = 20 \ \mu m}\right)^{0.08}$$
(3-27)

where K_j is the justified mass transfer coefficient for full suspension of particles and K_t is the theoretical mass transfer coefficient based on terminal velocity. E is a dimensionless ratio, and the value of R=20 μ m is the particle size below which the enhancement is negligible; since the mass transfer contribution from the 2.0 term in Rowe's equation, Eq. [3.7], begins to swamp the Reynolds group in the typical solid-liquid system.^[21]

Applying the proposed correction factor, the justified mass transfer coefficients for the full suspension condition are:

$$Fe \quad K_i = 4.63 \times 10^{-9} R^{-0.92} + 1.515 \times 10^{-3} R^{0.15} \quad m/s \quad (3-28)$$

$$Mn \quad K_j = 2.02 \times 10^{-9} R^{-0.92} + 8.11 \times 10^{-4} R^{0.15} \quad m/s \quad (3-29)$$

The relation between theoretical mass transfer coefficient (K) and the

justified mass transfer coefficient (K_j) for manganese and iron as a function of particle diameter are shown in Figure 3.4. Increasing the particle diameter, a small increase in mass transfer coefficient was observed for particles beyond Stokes' law. (Note: For fine particles which obey Stokes' law (Re < 2), mass transfer coefficients decrease with increasing particle size.)

3.5.2 Theoretical dissolution time

While the dissolution rate of suspended iron and manganese particles in an agitated liquid aluminium is mass transfer controlled, the dissolution time can be predicted as :^[34,35]

$$\rho_P \frac{dR}{dt} = -K_m (C_s - C_b) + \frac{\rho_P C_s}{\rho_L} \frac{dR}{dt}$$
(3-30)

where dR/dt is the rate of change of the particle radius, C_s and C_b are the saturation limit and bulk concentrations, and K_m is the mass transfer coefficient. Both diffusion and bulk flow terms are included in the above mass balance correlation. Dissolving small amounts of solute in bulk, C_b is close to zero then, integrating and rearranging Eq. [3.30] as:

$$t_D = \int_0^{t_D} dt = \frac{\rho_P (C_s - \rho_L)}{\rho_L C_s} \int_{R_s}^0 \frac{dR}{K_m}$$
(3-31)

where t_D is dissolution time of the particle and R_o is initial particle size.

The mass transfer coefficient can be fitted to an Arrhenius type correlation with temperature according to: $K_m = K_o \exp(-Q/RT)$, where K_o is frequency factor, Q is the activation energy, R is gas constant and T absolute temperature. Higher temperatures lead to higher K_m and also C_s , resulting in lower dissolution times. The maximum solubility at given temperature is determined by the phase diagram for pure elements in solution with liquid. For the present study the solubilities of iron and manganese at the temperature of the experiment (720°C) were found as: $C_{s,Fe} = 90$ and $C_{s,Mn} = 140 \text{ kg/m}^3$.

In calculations of the theoretical dissolution time based on terminal velocity theory, the correlations previously obtained for mass transfer coefficients, K_t and K_j , (Eqs [3.25] and [3.28] for iron particles and Eqs [3.26] and [3.29] for manganese particles), can be substituted in above equation (Eq. [3.31]), and the equations integrated. The predicted dissolution times as a function of particle size are shown in Figure 3.5.

At the end, one important point which has been considered in the calculation of dissolution times should be noted. As the dissolution process continues, once a particle reaches a radius smaller than 24 μ m, it no longer obeys the proposed K, or K_j correlations for the intermediate region; rather, in this period of dissolution, Stokes' law and relevant equations must be applied in calculation, see Table 3.4.

Furthermore, assuming $C_b = 0$ may increase the degree of uncertainty in the results obtained. Hence, in order to improve the accuracy, the amount of manganese or iron added to the melt was kept as low as possible and not more than 0.5 to 0.6 wt pct. In subsequent calculations of mass transfer coefficients and dissolution times, C_b was taken to be equal to the average of the initial and final concentrations of the solute in the system.

3.5.3 Measured mass transfer coefficients

When a solid solute particle is immersed in a solvent liquid, it becomes smaller and smaller, due to the transfer of mass from solid to liquid. In deducing the experimental mass transfer coefficients, the rates of change in the initial size of particles during the dissolution process were measured. In this regard, knowledge of initial particle diameters, the initial concentration of solute in the melt before the addition and the concentration of the solute in the bulk at time t after addition, are necessary.

Assuming a spherical shape for particles with an equivalent radius of R_0 , then the solute concentration in the bulk measured at time t after addition, can be related to the mean radius of the particle via:

$$R_{t} = R_{o} \left(1 - \frac{C_{t} - C_{o}}{C_{f} - C_{o}} \right)^{1/3}$$
(3-32)

where R_o is the initial radius, R_t is the radius of particles at time t, C_o , C_f and C_t are initial, final and transient bulk concentrations at time t of dissolution, respectively. (More details in the calculation procedure of particle size from concentration measured are given in Appendix 2).

The variation in the diameter of iron and manganese particles which were exposed to dissolution process in the molten aluminum are shown in Figures 3.6 and 3.7 respectively. The existence of plateaux at the beginning of the graphs, suggests a mixed controlled process at the start of dissolution. It seems that these *incubation* periods are needed for dispersion, heating of the particles and removal of any adsorbed interfacial layers together with the formation of intermetallic compound layers around particles.

Taking the slope of each curve (dR/dt), and substituting it in the mass balance equation (Eq. [3.30]), mass transfer coefficients for each size of particle can be obtained. (Note: since the procedure for the calculation of the theoretical mass transfer coefficients is established on the basis of mass transfer controlled dissolution and also in order to have an accurate comparison between the theoretical and measured mass transfer coefficients the first periods of dissolution (incubation times) were ignored in measuring slopes in diameter changes with time). A comparison between theoretical mass transfer coefficient, as calculated from the terminal velocity approach, and measured values are shown in Figure 3.8. The results indicate significant differences between the actual and predicted mass transfer coefficients. For manganese particles, the measured values are only in the order of 13 to 15 pct of the theoretical values (calculated from Rowe's equation), while for iron particles they are as small as 14 to 16 pct of theoretical results. In these aspects, it would seem that the terminal velocity theory is not applicable in dissolution of iron and manganese in stirred liquid aluminum.

3.5.4 Other proposed correlations for mass transfer

Since a number of correlations, (as well as that proposed by Nienow, Eq. [3.7]), have been developed for particles dissolving in aqueous systems, it was decided to test whether any of these might be more adequate in quantifying mass transfer phenomena in the present high temperature system.

In Figures 3.8 and 3.9, comparisons between measured mass transfer coefficients and theoretical mass transfer coefficients, calculated from the various correlations proposed^[36,37,38,39,40,41], are shown. The differences are remarkable, as can be seen from Tables 3.5 and 3.6, which make this comparison easier. As seen, the experimental results for manganese particles, depending on particle size, are only in the range of 25 to 33 pct of the lowest predicted values (calculated from Kudryashev's equation^[41]). For iron particles (Table 3.6), they are also as small as 28 to 35 pct of theoretical results.

Table 3.5 A comparison between measured mass transfer coefficients (μ m/s), for <u>manganese</u> particles, and theoretical mass transfer coefficients (μ m/s) as calculated from proposed correlation: $Sh = 2 + A.Re^{1/2}.Sc^{1/3}$

$d_{Mn} \pm W_d$ (μ m)	K _m A=0.72	K _m A=0.6	K _m A=0.55	K _m A=0.5	K _m A=0.49	K _m A=0.33	$K_m \pm W_{Km}$ experiment
540 ± 47	195	163	150	1.36	135	90.1	29.7 ± 2.8
460 ± 37	194	162	149	136	134	89.7	29.2 ± 2.9
358 ± 61	191	160	148	134	132	89.2	28.3 ± 6.5
250 ± 43	189	158	146	133	131	89.2	28.5 ± 6.2
178 ± 30	187	158	146	133	131	, 190	26.6 ± 6.6
124 ± 22	187	158	147	134	132	92.1	26.7 ± 6.9
89 ± 15	188	160	149	137	135	95.7	24.2 ± 6.1

Table 3.6 A comparison between measured mass transfer coefficients (μ m/s), for *iron* particles, and theoretical mass transfer coefficients (μ m/s) as calculated from proposed correlation: $Sh = 2 + A.Re^{1/2}.Sc^{1/3}$

$d_{Fo} \pm W_d$ (μ m)	K _m A=0.72	K _m A=0.6	K _m A=0.55	K _m A=0.5	K _m A=0.49	K _m A=0.33	$K_m \pm W_{\kappa_m}$ experiment
538 ± 46	366	306	282	256	253	170	59.4 ± 6.2
457 ± 36	363	304	280	255	251	169	59.0 ± 6.2
356 ± 61	359	301	278	253	249	169	59.7 ± 13.6
245 ± 42	355	299	276	252	248	170	56.4 ± 13.2
177 ± 30	354	298	276	252	249	172	53.3 ± 13.5
126 ± 22	355	301	279	256	253	178	52.8 ± 13.9
87 ± 14	360	308	287	264	261	188	52.6 ± 13.6

Note: In Table 3.5 and 3.6, W_d and W_{Km} represent uncertainties (99.5% confidence limits) in the measurement of diameter of particles and measured mass transfer coefficients. An uncertainty analysis section given in Appendix 3 provides further details. Moreover, if we assume a Gaussian distribution for the sizes of the particles in each range, (the average diameters are given in the first columns of the prior tables), then standard deviations of the particles will be equal to one-third of the uncertainties of the particles' diameter or S.D. = $W_d/3$. As a result, the standard deviations for K_m will be much lower than Wk_m given in last columns of the tables.

Finally, one should remember that the terminal velocity approach gives the minimum mass transfer coefficient and cold model experimental findings have been analyzed via an increment modification factor, which increase the theoretical mass transfer coefficients from 6 to 50 pct. However, in the current study, even without applying any the increment factor on theoretical values, they are still much higher than the experimental results presently attained.

Concluding, the significant gap between theoretical and experimental results is a sign of the weakness of the terminal velocity approach for predicting the mass transfer coefficients for alloying particles entrained in a molten aluminum system.

3.5.5 Measured dissolution times

Considering the changes in particle diameters during dissolution, the results indicate short incubation times preceding the start of dissolution, and particularly so for manganese particles. Based on the Fe-Al and Mn-Al phase diagrams, the transfer of solid element to the liquid phase occurs via the formation of several intermetallic compounds. Microscopic studies of samples withdrawn from the lower layers of the melt verified the existence of layers of Fe₂Al₅ or MnAl₄ around iron and manganese particles during their dissolution, respectively. It seems that

this incubation time is necessary for formation of soluble intermetallic compounds together with the time required for heating and dispersion of particles into the melt following their addition.

As mentioned earlier, in order to gain an accurate comparison between theoretical dissolution times (established on the basis of mass transfer controlled correlations) and measured dissolution times from experiments, this incubation period was subtracted from total measured dissolution time.

After addition of alloying particles to the stirred melt, followed by measuring the changes in bulk solute concentration, the time for complete dissolution is marked by the start of the plateau region of highest bulk concentration. A comparison between measured and predicted dissolution times as a function of particle size for iron and manganese particles are shown in Figures 3.10 and 3.11, respectively. As the results show, differences are considerable. Theoretical dissolution times are just only between 13 pct to 16 pct of the actual results, for coefficient A = 0.72 in the Sherwood correlation. While for coefficient A = 0.33, they are only in the order of 25 to 33 pct of measured values, which depends on particles diameter. Hence, the results indicates the weakness of terminal velocity theory in prediction of mass transfer coefficients or dissolution times of alloying particles in molten aluminum.

Nevertheless, one may assert that the possible agglomeration of the particles in the melt reduces the total surface of particles exposed to dissolution, thereby causing a significant difference between measured and predicted values. However, several melt samples indicated the exclusive existence of discrete particles in the melt with no agglomeration. In order to be certain of complete suspension, not only was the critical suspension speed of impeller selected to be 20 pct above these predicted, but another set of experiments at very high rates of stirring was carried out, to check any differences. For particles in the range of 212-250 μ m, it was found that even there, mass transfer coefficients still remained much lower than the theoretical value, (see Chapter 4).

The significant difference between the actual and predicted values of mass transfer coefficients and dissolution times suggests that the terminal velocity theory developed for aqueous media is inadequate for the high temperature liquid metal systems studied in the present work. It would appear that a simple extension of this theory to metallic systems may be flawed. This conclusion is reinforced by the fact that much better agreement would be obtained between the present data and predictions based upon Kolmogoroff's theory of turbulence for modelling dissolution processes. This will be presented in detail in Chapter 4 of this work.

However, if someone insists in analysing the results for dissolution of iron and manganese particles in a stirred liquid aluminum via terminal velocity, he can correlate the results via the following proposed correlations given in Table 3.7.

 Table 3.7 Proposed correlations for dissolution of iron and manganese in stirred liquid aluminum in case of fully suspended particles.

Eq. No	Element	Proposed correlation	R*	Figure
3.33	Mn	$Sh = 2 + 0.02 \text{ Re}^{0.83} \cdot Sc^{0.33}$	0.958	3.13
3.34	Fe	$Sh = 2 + 0.01 \text{ Re}^{0.9} \cdot Sc^{0.33}$	0.955	3.12
3.35	Mn	$Sh = 0.1 \ Re^{0.513} \cdot Sc^{0.33}$	0.999	3.13
3.36	Fe	$Sh = 0.1 \ Re^{0.505} \cdot Sc^{0.33}$	0.999	3.12

*: R is correlation coefficient obtained via the method of least squares analysis, R = 1 indicates a perfect fit, see appendix 4.

As seen from Table 3.7, Eqs [3.33] and [3.34], having a form similar to those equations proposed by proponents of the "terminal velocity theory", show poor fits, (with substantial scattering) of the data around the equations. Neglecting the diffusion term in the Sherwood correlation (=2), and regressing the data, Eqs [3.35] and [3.36] can also be obtained. These equations fit extremely well with no any scattering in the data, (see Figures 3.12 and 3.13).

Moreover, as Figure 3.14 indicates, using Eqs [3.35] and [3.36] for terminal velocity theory, actual dissolution times of manganese and iron particles in molten metal can be predicted satisfactorily, with standard errors of 10 and 8.5, respectively, (or correlation coefficients of 0.999), see appendix 4.

3.6 Conclusions

Since the kinetics of dissolution of alloying particles is controlled by mass transfer through a concentration boundary layer, mass transfer coefficients can be greatly affected by relative velocities of the particles in the system. On the other hand, due to irregular motion of fine particles in highly turbulent flows, the relative velocity of the particles with respect to the fluid's motion is extremely difficult to describe. This difficulty has lead cold model researchers to suggest two approaches, the first being the terminal velocity theory, the second, Kolmogoroff's theory of local isotropy.

In this chapter the applicability of the terminal velocity theory has been investigated. The results obtained revealed that the terminal velocity approach along with correlations developed for aqueous models, could not be applied to the present high temperature system *i.e.* the dissolution of iron and manganese particles in turbulently stirred liquid aluminium.

It has been proposed by previous researchers that, during full suspension of particles in stirred aqueous systems, the terminal settling velocity of particles in stagnant baths can be considered as being representative of the relative velocity between solid particles and liquid. Substituting terminal velocities in relevant correlations, minimum mass transfer coefficients are obtained.

In the present study, water modelling experiments in conjunction with dimensional analysis of the link between water models and high temperature systems, allowed that suspension behaviour of alloying particles in molten aluminum to be studied. Then, through sampling of melt continuously, mass transfer coefficients of suspended iron and manganese particle classified in the range of $90 < d_p < 550 \ \mu m$ have been measured. The results obtained have shown significant differences between theoretical and measured values.

Terminal velocity examiners remarked that terminal velocity theory yields only minimum mass transfer coefficients. In order to justify the theoretical results with experimental values, modification (or increment) factors, have been recommended. In the present study, even without applying any enhancement factor, the theoretical mass transfer coefficients were much higher than those deduced from the experimental results. In the other words, the experimental results were only in the order of 13 to maximum 33 pct of the predicted values.

Finally, applying the "terminal velocity theory" in accompaniment with the Sherwood correlations suggested by cold model researchers, to the molten metal systems lead to serious errors in terms of the mass transfer coefficients predicted. However, if one insists in applying the terminal velocity theory for dissolution of alloying particles in turbulent molten aluminum system, a correlation in the form of:

$$Sh = 0.1 Re^{0.5}, Sc^{0.33}$$
 (3-33)

with a correlation coefficient of 0.999 can be useful, even though the general form of the equation is quite different from equations suggested, previously.

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3.7 Nomenclature

Α	constant in Sherwood correlation
C,	maximum solubility of solute in the aluminum melt
Сь	bulk concentration of solute at time $t = C_t$
C。	initial concentration of solute at $t=0$
C _D	drag coefficient
C _f	final concentration of solute in the aluminum melt
dR/dt	rate of change of particle radius
D	solute diffusivity
d _P	particle diameter
d _{Fe}	iron particle diameter
d _{Mn}	manganese particle diameter
Dv	vessel diameter
DI	impeller diameter
E	dimensionless mass transfer coefficient, (K _j /K _t)
F _B	buoyancy force
F _D	drag force
Fg	gravity force
g	gravitational constant
K _m	mass transfer coefficient
K _j	justified mass transfer coefficient
Κ	theoretical mass transfer coefficient
Ko	frequency factor in Arrhenius equation
J	flux of material
L	dimension of length in dimensional analysis
Μ	dimension of mass in dimensional analysis
Ns	critical rotational speed of impeller

- N rotational speed of impeller
- P input power in the system
- P_N power number (= $P/\rho_L.N^3.D_I^5$)
- Q activation energy in Arrhenius equation
- R particle radius
- R_o initial radius of particle
- R_t radius of particle at time t after addition
- R gas constant in Arrhenius equation
- Re particle Reynolds number $(U_t.d_p/v)$
- S.D standard deviation
- S surface of the disk
- Sc Schmidt number (=v/D)
- Sh Sherwood number (= $K_m.d_p/D$)
- t_D required time for complete dissolution
- t time after addition
- T dimension of time in dimensional analysis
- T temperature in Arrhenius equation
- U relative velocity
- U_t terminal settling velocity
- V volume of the melt
- W apparent weight of the solid particles in the liquid
- W_d uncertainty in diameter of particles, (99.5% confidence limits)
- W_{Km} uncertainty in mass transfer coefficients, (99.5% confidence limits)
- X concentration of solid ir liquid (dimensionless)
- ω angular speed of rotation of disk
- ε rate of input mixing energy
- ρ_L liquid density
- $\rho_{\rm p}$ particle density
- $\Delta \rho$ solid and liquid density difference
- v liquid kinematic viscosity
- μ liquid viscosity
- π_i dimensionless group numbers, (i=1, 2, 3, 4)

3.8 References

1. R.J. O'Malley, C.E. Dremann and D. Apelian, "Alloying of Molten Aluminum by Manganese Powder Injection", *Journal of Metals*, Feb., 1979, pp.14-19.

2. T. Pedersen, E. Myrbostad, "Refining and Alloying of Aluminum by Injection", *Light Metals*, 1986, pp. 759-765.

3. T.A. Engh, "Alloy Addition to Aluminium by Pneumatic Injection", *Aluminium Melt Refining and Alloying, Theory and Practice*, 1989, The University of Melbourne, 1989, July 10-12, pp. H1-H15.

4. N. Tunca, G.W. Delamore, and R.W. Smith, "Corrosion of Mo, Nb, Cr and Y in Molten Aluminium", *Metallurgical Transactions A*, 1990, vol. 21A, pp. 2919-2928.

5. V.N. Yeremenko, Ya. V. Natanzon, V.I. Dybkov, "Interaction of the Refractory Metals With Liquid Aluminum", *Journal of the Less-Common Metals*, 1976, vol. 50, pp. 29-48.

6. V.N. Eremenko, Ya. V. Natanzon and V.P. Titov, "Kinetics of Chromium Dissolution in Aluminium at 700-900°C", *Russian Metallurgy (Metally)*, 1980, pp. 193-197.

7. G.S. Ershov, A.A. Kasatkin and A.A. Golubev, "Dissolution and Diffusion of Alloying Elements in Liquid Aluminium", *Russian Metallurgy (Metally)*, 1979,

no. 2, pp. 62-64.

8. J.B. Darby, D.B. Jugle and O.J. Kleppa, "The Rate of Solution of Some Transition Elements in Liquid Aluminium", *Transactions of the Metallurgical Society of AIME*, 1963, vol. 227, pp. 179-185.

9. M. Niinomi, Y. Suzuki and Y. Ueda, "The Dissolution of Ferrous Alloys into Molten Aluminium under the Forced Flow", *Journal of the Japan Institute of Metals*, 1981, vol. 45, pp. 416-424.

10. L.N. Shibanova, A.A. Vostryakov and B.M. Lepinskikh, "Dissolution of Iron and Titanium in Metal Melts", *Russian Metallurgy (Metally)*, 1990, pp. 519-521.

11. V.N. Eremenko, Ya.V. Natanzon and V.P. Titov, "Dissolution Kinetics of Cobalt and Iron in Liquid Aluminium", *Russian Metallurgy (Metally)*, 1977, No.2, pp. 77-81.

V.N. Yeremenko, Ya.V. Natanzon and V.I. Dybkov, "The Effect of Dissolution on the Growth of the Fe₂Al₅ Interlayer in the Solid Iron-Liquid Aluminium System", *Journal of Materials Science*, 1981, vol. 16, pp. 1748-1756.
 V.N. Eremenko, Ya.V. Natanzon, V.P. Titov and A.G. Tsydulko, "Kinetics of Nickel Dissolution in Liquid Aluminium", *Russian Metallurgy (Metally)*, 1975, no. 1, pp. 55-57.

14. V.I. Dybkov, "Interaction of Iron-Nickel Alloys with Liquid Aluminium", Journal of Materials Science, 1993, vol. 28, pp. 6371-6380.

V.G. Levich, *Physicochemical Hydrodynamics*, 1962, Prentice-Hall, N.J., p.
 69.

16. V.I. Dybkov, "Interaction of 18Cr-10Ni Stainless Steel with Liquid Aluminium", Journal of Materials Science, 1990, vol. 25, pp. 3615-3633.

17. G.A. Hughmark, "Mass and Heat Transfer from Rigid Spheres", AIChE Journal, 1967, vol. 13, pp. 1219-1221.

18. G.A. Hughmark, "Mass Transfer for Suspended Solid Particles in Agitated

Liquids", Chemical Engineering Science, 1969, vol. 24, pp. 291-297.

19. P. Harriott, "Mass Transfer to Particles: Part 1. Suspended in Agitated Tanks", AIChE Journal, 1962, vol. 8, pp. 93-102.

20. A.W. Nienow, "Dissolution Mass Transfer in a Turbine Agitated Baffled Vessel", *The Canadian Journal of Chemical Engineering*, 1969, vol. 47, pp. 249-285.

21. A.W. Nienow, "Agitated Vessel Particle-Liquid Mass Transfer: A Comparison Between Theories and Data", *The Chemical Engineering of Journal*, 1975, pp. 153-160.

22. D.M. Levins and J.R. Glastonbury, "Particle Liquid Hydrodynamics and Mass Transfer in a Stirred Vessel", *Transactions of the Institute of Chemical Engineers*, 1972, vol. 50, pp. 132-146.

23. R. Conti and S. Sicardi, "Mass Transfer from Freely Suspended Particles in Stirred Tanks", *Chemical Engineering Communications*, 1982, vol. 14, pp. 91-98.

24. P.H. Calderbank and M.B. Moo-Young, "The Continuous Phase Heat and Mass Transfer Properties of Dispersions", *Chemical Engineering Science*, 1961, vol. 16, pp. 39-45.

25. P. Sykes and A. Gomezplata, "Particle Liquid Mass Transfer in Stirred Tanks", *The Canadian Journal of Chemical Engineering*, 1967, vol. 45, pp. 189-196.

26. P.N. Rowe, K.T. Claxton and J.B. Lewis, "Heat and Mass Transfer from a Single Sphere in an Extensive Flowing Fluid", *Transactions of the Institute of Chemical Engineers*, 1965, vol. 43, pp.T14-T31.

27. F. Kneule, "Die Prufung von Ruhrern durch Loslichkeitsbestimmung", *Chemie-Ingenieur-Technik* 1956, vol. 28, pp. 221-225.

28. T.H. Zwietering, "Suspending of Solid Particles in Liquid by Agitators", *Chemical Engineering Science*, 1958, vol. 8, pp. 244-253.

29. K.S. Raghava Rao, V.B. Rewatkar and J.B. Joshi, "Critical Impeller Speed for Solid Suspension in Mechanically Agitated Contactors", *AIChE Journal*, 1988, vol. 34, pp. 1332-1340.

30. G. Baldi, R. Conti and E. Alaria, "Complete Suspended of Particles in Mechanically Agitated Vessels", *Chemical Engineering Science*, 1978, vol. 33, pp. 21-25.

31. C.M. Chapman, A.W. Nienow, M. Cooke and J.C. Middleton, "Particle Gas Liquid Mixing in Stirred Vessels", *Chemical Engineering Research & Design*, 1983, vol. 61, pp. 71-81.

32. P.M. Armenante, Y. Tsang Huang and T.Li, "Determination of the Minimum Agitation Speed to Attain the Just Dispersed State in Solid Liquid Reactors Provided with Multiple Impellers", *Chemical Engineering Science*, 1992, vol. 47, pp. 2865-2870.

33. J.H. Perry, *Chemical Engineers Handbook*, 1950. 3rd Ed., McGraw-Hill, New York, pp. 1019.

34. R.G. Rice and P.J. Jones, "Complete Dissolution of Spherical Particles in Free Fall", *Chemical Engineering Science*, 1979, vol. 34, pp.847-852.

35. P.L.T. Brian and H.b. Hales, "Effects of Transpiration and Changing Diameter on Heat and Mass Transfer to Spheres", *AIChE Journal*, 1969, vol. 15, pp. 419-425.

36. W.E. Ranz and W.R. Marshall, "Evaporation from Drops - I and II", Chemi. Engng Progr., 1952, vol. 48, pp. 141 and 173.

37. N. Frossling, "The Evaporation of Falling Drops", *Beitr. Geophys.*, 1938, vol. 52, pp. 170. (A.E.R.E. Harwell, translation, August 1963), Cited from Ref. 26.

38. R.W. Maxwell and J.A. Storrow, "Mercury Vapour Transfer Studies", *Chemical Engineering Science*, 1957, vol. 6, pp. 204, Cited from Ref. 26.

39. T. Tsubouchi and S. Sato, "Heat Transfer Between Single Particles and Fluids in Relative forced Convection", *Chemical Engineering Progress Symposium Series*, 1960, vol. 56, no. 30, pp. 285. Cited from Ref. 26.

40. T. Yuge, "Experiments on Heat transfer from Spheres Including Combined Natural and Forced Convection", *Trans. Amer. Soc. mech. Engrs*, 1960, vol. 82, Series C, pp. 214, Cited from Ref. 26.

41. L.J. Kudryashev and A. Ya. Ipatenko, "Effect of Free Motion on the Heat Transfer Coefficient for Flow around a Sphere in the Region of Small Reynolds Numbers", *Soviet Physics - Technical Physics*, 1959, vol. 4, pp. 275, Cited from Ref. 26.



Fig. 3.1 Rotational speed as a function of particle diameter for complete suspension in aqueous model.



Fig. 3.2 Predicted speed of rotation as a function of particle diameter for complete suspension of manganese and iron in liquid aluminum.



5 : Tachometer

Fig. 3.3 Schematic of experimental set-up.



Fig. 3.4- Predicted mass transfer coefficients based on terminal velocity theory.



Fig. 3.5 Predicted dissolution times for manganese and iron particles in the fullyentrained condition.



Fig. 3.6 Iron particle diameter as a function of time of immersion in liquid aluminum at 720°C.



Fig. 3.7 Manganese particle diameter as a function of time of immersion in liquid aluminum at 720°C.



Fig. 3.8 A comparison between measured and theoretical mass transfer coefficients as a function of the diameter of iron particles.



Fig. 3.9 A comparison between measured and theoretical mass transfer coefficients as a function of the diameter of manganese particles.



Fig. 3.10 A comparison between predicted and measured dissolution times for iron particles entrained in liquid aluminum at 720 °C.



Fig. 3.11 A comparison between predicted and measured dissolution times for manganese particles entrained in liquid aluminum at 720 °C.



Fig. 3.12 Sherwood-Schmidt correlation as a function of iron particles Reynolds number.



Fig. 3.13 Sherwood-Schmidt correlation as a function of manganese particles Reynolds number.



Fig. 3.14 A comparison between experimental dissolution times of iron and manganese in molten aluminum and theoretical values predicted based on proposed correlations.



DISSOLUTION KINETICS OF Fe AND Mn PARTICLES IN STIRRED LIQUID ALUMINUM

Evaluation of Kolmogoroff's Theory in High Temperature Melts

4.1 Introduction

4.1.1 Mass transfer between rigid particles and a liquid

As mentioned in Chapter 3, mass transfer coefficients for solid particles in a flowing fluid are generally represented by an equation of the form:

$$Sh = 2 + A Re^{m} Sc^{n}$$

$$(4.1)$$

. . ..

According to this equation, in treating mass transfer from or to particles, a knowledge of the particle's Reynolds number, or relative velocity of the particles with respect to the fluid, must be known. In the case of particles entrained in a turbulent liquid in a stirred vessel, this is extremely difficult to clarify. Solid particles as well as liquid both have different gross velocities in direction and magnitude. They move turbulently with various random fluctuations in any direction. As such, the hydrodynamic interactions which control particle-liquid mass transfer in an agitated vessel are highly stochastic and impossible to predict, *ab initio*. However, in aqueous systems, some approaches for treating of mass transfer to or from small particles have been introduced.

In Chapter 3, the terminal velocity approach was introduced. Terminal settling velocity of particles in a stagnant bath has been considered as the relative velocity of the particles in turbulent flow, in calculation of mass transfer. In this chapter, the rate of input mixing energy (*i.e.* dissipation rate of energy) in the system which results from "Kolmogoroff's theory of local isotropy of turbulence" has been employed in another approach to treating mass transfer. In the other words, a dimensionless energy dissipation rate group number in the form of $(\dot{\epsilon}^{1/3}.d_p^{4/3}/\nu)$, has replaced the Reyrolds number in Eq. [4.1] viz;

$$Sh = 2 + A \left(\frac{\dot{\epsilon}^{1/3} d_p^{4/3}}{v}\right)^{\alpha} Sc^{\beta}$$
 (4.2)

where A, α and β are constants, $\dot{\varepsilon}$ and ν are the dissipation rate of energy per unit mass and the kinematic viscosity of fluid, respectively.

4.1.2 Theory of local isotropy of turbulence

Turbulence is always dissipative and requires a continuing supply of energy from the large scale eddies within the bulk flow to feed it. The mechanical energy associated with bulk flow velocities is dissipated by viscous energy losses in the smaller eddies, thereby leading to an increase in the internal energy of the fluid.

In an agitated vessel, the impeller continually produces primary eddies which have a length scale which are similar in magnitude to the dimensions of the main flow. When the Reynolds number of the main flow is high, these large primary eddies are unstable to small disturbances and, through inertial interactions, disintegrate into smaller eddies. These small eddies, in turn, at sufficiently high Reynolds numbers, are unstable. This process is repeated in the form of a cascade until the Reynolds number of the smallest eddies are too small to permit further degeneration.^[1, 2]

The energy which is supplied by an agitator in a stirred vessel for instance, lies chiefly in the main flow and the largest eddies. The nth order of sizes eddies absorb some of the energy from the (n-1)th order eddies and transfer it on partly to the (n+1)th order eddies by means of work done against Reynolds stresses and partly to internal thermal energy. Clearly the amount of energy transferred to higher order eddies will be larger compared with the amount of energy dissipated, for eddies of large dimensions and high velocities. Thus, as the process progresses to higher order eddies with lower characteristic Reynolds numbers, the portion of energy which is dissipated by viscosity will increase and, for the very smallest eddies the motion is entirely laminar. The situation is well summarized in a rhyme which Batchelor^[1] believes is due to L.F. Richardson:

> "Big whorls have little whorls, which feed on their velocity; Little whorls have smaller whorls, and so on unto viscosity."

Since the transfer of energy from large eddies to small eddies occurs in different directions, the directional information of the large eddies is gradually lost. Thus, if a volume of fluid is considered whose dimensions are small compared with the scale of main flow, the magnitudes of fluctuating components of the velocity which are defined by root mean square values of \vec{u}^2 , \vec{v}^2 , \vec{w}^2 , are equal. Thus, *isotropic turbulence* exists, even though the turbulent motions of the larger eddies may be far from isotropic.^[1, 2] Noting that by introducing the concept of local isotropic turbulence, mathematical treatments of turbulent flow, which are considerably complicated, can be resolved.

Kolmogoroff concludes therefore that in large Reynolds number flows, all eddies which are much smaller than the primary eddies are completely independent of bulk motion and the details of the agitation device, and in general, also independent of external conditions. The properties of these small eddies are determined solely by the local rate of dissipation of energy per unit mass of fluid, $\dot{\epsilon}$, and the kinematic viscosity of fluid, ν , because these are the only parameters which govern the motions of small eddies. In the other words, the character of the turbulence in this range is determined by $\dot{\epsilon}$ and the other parameter which determined the rate of dissipation, (ν) .^[4]

Following a relatively difficult mathematical and statistical treatment, the energy spectrum of turbulent flow has been formulated in the form:

$$E(k) = C k^4 \exp(-2k^2 v t)$$
(4.3)

where $C = f(\nu, t)$ is a constant, ν is kinematic viscosity, t is time, k (proportional to reciprocal of eddy size) is called the wave number and is related to turbulent frequency n according to the formula $k=2\pi n/U$, where U is time-mean velocity.^[3,4] In Figure 4.1, the energy spectrum function E(k) as a function of wave number, k, has shown. The energy spectrum function increases very rapidly, initially according to k^4 , reaches a maximum value, and decreases monotonously to zero as k increases. By integrating over all wave numbers:

total turbulence kinetic energy =
$$\int_{0}^{\infty} E(k) dk$$
 (4.4)

Given Eqs [4.3] and [4.4], one can establish the rate of change of kinetic energy of turbulent motion, (*i.e.* the dissipation rate of turbulence energy), over all wave numbers as:

$$\dot{\varepsilon} = \frac{\delta \int_{o}^{\infty} E(k) \ dk}{\delta t} = -2\nu \int_{o}^{\infty} k^{2} E(k) \ dk \qquad (4.5)$$

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Meanwhile, the above equation can be obtained from energy equation of the flow using the isotropic turbulence concept^[4]. Also, it is clear from equation that the energy dissipation is selective towards the high wave numbers or small eddies because of the strong effect of the k^2 factor. One notes that for a fluid with high ν , viscous dissipation reduces kinetics energy of turbulent flow effectively.

For this reason, Kolmogoroff assumed that the character of turbulence in the range of high wave numbers (*i.e.* small eddies) is only determined by two parameters, energy dissipation rate ($\dot{\epsilon}$) and kinematic viscosity (ν).

From dimensional reasoning, as first performed by Kolmogoroff, the dissipation rate of turbulence energy and kinematic viscosity can be arranged in such a manner as to give a length scale (Kolmogoroff's length scale, l_k), a time scale and a velocity scale:^[2,4,5,6]

Length scale:
$$l_k = (\frac{v^3}{\dot{\epsilon}})^{1/4}$$
 (4.6)

Time Scale:
$$t = \left(\frac{v}{\varepsilon}\right)^{1/2}$$
 (4.7)

Velocity scale:
$$u = (v\dot{\epsilon})^{1/4}$$
 (4.8)

Thus, the dimension of Kolmogoroff's length scale and velocity scale are such that the Reynolds number with reference to this length and velocity is:

$$Re = \frac{u l_k}{v} = 1 \tag{4.9}$$

Conceptually, the Reynolds number represents a balance of inertial forces to viscous forces. Thus, within the spectrum of eddies sizes, Kolmogoroff's length

scale represents the size where two forces are in balance, *i.e.* $F_i = F_{\mu}$.

Kolmogoroff postulated that if M_1 and M_2 are two points with a distance r in a small volume of turbulent flow, U_1 and U_2 are the velocity components in direction of M_1M_2 at the points of M_1 and M_2 , then a relative velocity between two points U_r , can be defined by: $\overline{U_r^2} = (\overline{U_1 - U_2})^2$. There, $\overline{U_r^2}$ is determined mainly by the small eddies, which are statistically independent of the main flow.^[2, 7]

For $r \ll l_k$, \overline{U}_r^2 can be a function of the local rate of energy dissipation ($\dot{\epsilon}$), distance (r), and kinematic viscosity (ν).^[2,5,7,8] This indicates that the relative velocity (between two point with a distance r inside an eddy with the length scale equal to l_k or smaller) is such that the corresponding Reynolds number will be equal to, or less than, one. As a result, viscous forces will be higher than inertial forces. In this case, \overline{U}_r^2 can be defined by the governing parameters, ν , $\dot{\epsilon}$ and r. From dimensional considerations, one has:

$$\overline{U}_r^2 = C_1 \frac{\dot{\varepsilon}}{v} r^2 \qquad r < l_k \qquad (4.10)$$

while for $l_k \ll r \ll L$, r is still sufficiently small compared to the main flow, however, the picture of the motion is determined by the inertial forces and the influence of viscous forces is unsubstantial; therefore, \overline{U}_r^2 is only a function of $\dot{\epsilon}$ and r.^[2,5,7,8]

$$\bar{U}_r^2 = C_2 \dot{\varepsilon}^{2/3} r^{2/3} \qquad l_k < r < L \tag{4.11}$$

Note that for both Eqs. [4.10] and [4.11], U_r dimension is such that if r is substituted by l_k , then U_r becomes equal to the velocity scale u, defined in Eq. [4.8].

4.1.3 Application of Kolmogoroff's theory to mass transfer

Turbulent flows in the immediate neighbourhood of particles usually affect the particle and any mass, momentum or heat transfer processes around it. When the dissolution process for solid particles in an agitated system is controlled by the thickness of the boundary layers around particles, the effect of the main flow is negligible and mass transfer is largely determined by what occurs in the small volume around the particles. In such cases, Kolmogoroff's theory of local isotropy can be applicable, because it introduces an approximate statistical definition of the flow field in a small volume of turbulent fluid. Here, the average statistical properties of the turbulent flow in the immediate vicinity of the particles involved are determined entirely by the local rate of energy dissipation per unit volume.

By replacing d_P (diameter of particle) with r in Eq. [4.11], Shinner and Church^[7] proposed a correlation between Reynolds number and the dimensionless energy dissipation group number as follows:

$$Re = \frac{\bar{U}_r d_p}{v} = \frac{C_2 \tilde{\epsilon}^{1/3} d_p^{4/3}}{v} \qquad l_k < d_p < L \qquad (4.12)$$

where it was mentioned that U_r should not be taken as representing the real velocity of the particle in the common meaning. It is a statistical parameter describing fluid flow around the particles.

Thus, considering that l_k is too small in turbulent flow versus particle size, a general equation can be presented for mass transfer coefficient in agitated vessels in the form of:

$$Sh = 2 + A \left(\frac{\dot{\epsilon}^{1/3} d_p^{4/3}}{v}\right)^{\alpha} Sc^{\beta}$$
 (4.13)

Using this approach, some cold model researchers were able to analyze their results satisfactorily. In Table 4.1, some of the empirical correlations obtained on this basis are given.

Levins et al. ^[9] , 1972	Sh =2+ $0.5(\dot{\varepsilon}^{1/3}.d_p^{4/3}/\nu)^{0.62}$ Sc ^{1/3}
Sano et al. ^[10] , 1974	Sh = $(2 + 0.4(\dot{\epsilon}^{1/3}.d_p^{4/3}/\nu)^{3/4} \text{ Sc}^{1/3})\phi$
Asai <i>et al.</i> ^[11] , 1988	Sh= $(2^{5.8}+\{0.61(\dot{\varepsilon}^{1/3}.d_p^{4/3}/\nu)^{0.58} \text{ Sc}^{1/3})\}^{5.8})^{1/5.8}$
Kikuchi <i>et al.</i> ^[12] , 1988	Sh =2+ 0.52 $(\dot{\varepsilon}^{1/3}.d_p^{4/3}/\nu)^{0.59}$ Sc ^{1/3}
Ohashi <i>et al.</i> ^[13] , 1981	Sh =2+ 0.59 $(\hat{\epsilon}^{1/3}.d_p^{4/3}/\nu)^{0.57}$ Sc ^{1/3}
Calderbank et al. ^[14] , 1961	$K_{\rm m} \ {\rm Sc}^{2/3} = 0.13 (\dot{\varepsilon}. \nu)^{1/4}$
Brain <i>et al.</i> , ^[15] , 1969	Sh = f($(\dot{\varepsilon}^{1/3}.d_p^{4/3}/\nu)^{1/3}$, Sc ^{1/3})
Sanger et al. ^[16] , 1981	Sh = 2+ 2.31 $(\dot{\varepsilon}.d_p^4/\nu^3)^{0.22}$ Sc ^{0.18}
Conti et al. ^[17] , 1982	Sh = f(($\dot{\varepsilon}^{1/3}$.d _p ^{4/3} / ν) ^{1/3} , Sc ^{1/3})

Table 4.1	Proposed	correlations f	for mass	transfer	based	on	dimensionless
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energy dissipation rate concept.

Therefore, if we assume that the rate of energy supplied in a turbulent system is equal to the average rate of dissipation of energy, the amount of energy supplied to the system is the only important parameter in determining mass transfer coefficients. In this regards, Sano *et al.*^[10] observed that mass transfer coefficients for particles suspended in a vessel agitated by an impeller are almost the same as those for particles in a bubble stirred column, provided the rate of specific energy supplied is the same.

Variations in the dimensions of the agitator, speed of rotation and its position on the vessel only affect the particles mass transfer by changing the local energy dissipation. Levins^[9] found that, there was no systematic scatter in mass transfer coefficient for widely different types of impellers, see Figures 4.2 and 4.3. He also observed that the position of the impeller within the vessel had a

negligible effect on the rate of mass transfer. Sano *et al.*^[10] revealed that the effect of baffles and also variations in diameter of the vessels on mass transfer rate can be represented in terms of corresponding values of $(\dot{\epsilon}^{1/3} d_p^{4/3} / \nu)$.

4.1.4 Limitations of Kolmogoroff's theory

Several objections can be raised against Kolmogoroff's theory. One concerns the choice of an appropriate length dimension for distance (l_k) . The apparently arbitrary assumption that r is identical, or at least proportional, to particle diameter (d_p) is also considered to be another weakness for this approach, and it is quoted that this is far from theory. However the present author suggests that this tenet may be partially justified by theory as follows:

When a laminar flow encounters a fixed particle, it proceeds against a drag force and this results in a reduction in kinetic energy. The reduced kinetic energy per unit mass of the fluid, which is changed to heat as local dissipation of energy per unit mass around the particle, $\dot{\varepsilon}$, can be equated according to:

$$\dot{\epsilon} = -\frac{1}{2} \frac{dU_r^2}{dt}$$
(4.14)

where U_r is relative velocity between fluid and particle. Assuming an encounter time $t=d_p/U_r$, then:

$$\dot{\varepsilon} = \frac{U_r^3}{d_P}$$
 or $U_r = (\dot{\varepsilon} \ d_P)^{\frac{1}{3}}$ (4.15)

Since small particles in a highly turbulent flow encounter small eddies with low Reynolds number, then laminar flow condition may exist around the particles. As a result, Eq. [4.15] obtained has a general form similar to Eq. [4.11] defined by Kolmogoroff and deduced from dimensional analysis. Therefore, r can satisfactorily be replaced by the diameter of the particle, d_{P} .

Any density difference between solid particles and moving liquid media is another important variable which has been neglected in Kolmogoroff's theory. Presumably, particles with different densities in one identical system will exhibit different responses to the fluctuating flow, unless they are so small as to provide no inertial resistance.

4.2 Experimental work

In order to study the effect of the rate of input mixing energy on the rate of mass transfer and kinetics of the alloying process, two different types of impellers were used in the present work; a) a four-bladed graphite impeller, 70 mm diameter, with blades 35 mm high and 10 mm thick, positioned in the centre of the crucible and, b) a six-bladed impeller, of the same diameter and thickness and 40 mm high, placed at the 1/4 diameter position of the crucible. In both configurations, the clearance between the impeller and the bottom of the crucible was selected as 10 mm. The constant speed of rotation desired was readily achieved using a DC motor, and a tachometer installed on top of the motor shaft monitored the speed of rotation during the experiment. The rate of input mixing energy, which was equal to output power of the motor, could be measured by recording the applied current and voltage for each specific RPM. A correction for power losses in the motor was made, motor efficiency being supplied by the manufacturer in the form of graphs for various load conditions. The results obtained were in good agreement with energy values registered by a torque meter that was designed and installed on the shaft of the motor.

Powders of manganese and iron, sieved and classified in the range 212-250 μ m (with an equivalent spherical diameter, $\bar{d}_{o} = 231 \ \mu$ m), were used for this investigation. Further details of the experimental set-up, method of alloying

addition, sampling and analysing methods have been given in Chapter 3.

4.3 Results and discussion

4.3.1 Mass transfer measurement

Based on a literature review, the dissolution of most transition metals in liquid aluminium is mass transfer controlled. The experimental work on the rotating disk technique reveals linear relations between the mass flux of solute, through a boundary layer between the solid and liquid and the square root of the speed of rotation of the disk ($\omega^{1/2}$), (Chapter 3).

Assuming a small control volume at the solid-liquid interface and making a correlation based on a mass balance through the control volume, the rate of change in particle radius (dR/dt) can be related to the mass transfer coefficient, K_m , as:

$$\rho_P \frac{dR}{dt} = -K_m (C_s - C_b) + \frac{\rho_P C_s}{\rho} \frac{dR}{dt}$$
(4.16)

where the first term on the right side involves boundary layer diffusive mass transfer, which is proportional to the difference in solute concentration between bulk liquid C_b and that at the interface, in equilibrium with the solute concentration of the solid C_s , *i.e.* solubility limit. The second term involves a convective mass transfer contribution resulting from the movement of each particle's interface with respect to its boundary layer. This term is only 6 pct of the first term for manganese particles and 4 pct for iron particles.

In dissolving small amounts of alloying elements in the bulk, C_b remains close to zero. In the present series of experiments, the maximum bulk concentration at the end of dissolution was around 0.5-0.6 wt pct, (*i.e.* 12 kg of iron or manganese per cubic meter of liquid aluminum), while the saturation concentrations, determined by the Al-Mn and Fe-Al phase diagrams, are $C_{s,Mn} =$ 140 and $C_{s,Fe} = 90 \text{ kg/m}^3$.^[18] As such, the assumption of zero bulk solute concentrations results in insignificant errors in deduced mass transfer coefficients. However, in order to provide more precision to the final results, C_b was assumed to be equal to the average of the initial and final concentrations of solute within the bulk liquid.

To measure dR/dt for each intensity of mixing, a knowledge of the initial concentration of the solute in the melt before alloying, together with the initial diameters of the particles, is needed. By continuously sampling the melt and measuring increments in solute concentrations within the bulk, the mean sizes of particles at each moment of immersion, (and thence dR/dt), could be calculated, see Appendix [2].

The diameter-time histories of iron and manganese particles, during the dissolution process, for different speeds of rotation of the four-bladed impeller, are shown in Figures 4.4 and 4.5 respectively. In general, increasing the intensity of the stirring moves the time-particle diameter lines towards the origin together with increases in the slopes of the lines. Meanwhile, the existence of plateaux at the beginning of the graphs, suggests a mixed controlled process during the onset dissolution. It would appear that these incubation periods are needed for the dispersion and heating of the particles and also for the removal of any interfacial layers. They involve reactions which conclude within the formation of soluble intermetallic compounds at the solid-liquid interface. Neglecting initial mixed controlled periods, taking the slopes of each curve (dR/dt) and substituting them in Eq. [4.16], mass transfer coefficients can be obtained. The relationship between mass transfer coefficients of iron and manganese particles as a function of speeds of rotation of impeller are shown in Figures 4.6 and 4.7, respectively. The results exhibit rapid increments in the mass transfer coefficients with increasing speeds

In Figure 4.8, dissolution times of iron and manganese particles are shown. As seen, by increasing the speed of rotation of the impeller, particle dissolution times diminished sharply.

Sharp rises in mass transfer coefficients (or rapid decreases in corresponding dissolution times) occurred when the condition of fully suspended condition of particles in the stirred liquid was approached. (For critical speeds of rotation see Chapter 3). However, at higher speeds, further increases in the intensity of mixing had little effect on rates of dissolution. This is in good agreement with the findings of other researchers using aqueous systems.^[14, 19, 20, 21]

In general, in the mixing of solid particles with a liquid, three categories of entrainment of solute particles can be considered, a) On-bottom motion, b) Off-bottom entrainment, and c) Uniform entrainment. As the results indicate, no significant differences appeared in the rate of dissolution when off-bottom conditions moved towards a uniform distribution of particles within the melt.

4.3.2 Measurement of energy dissipation rates

In general, every solid body that has a certain velocity relative to a surrounding fluid, experiences a drag force. To keep this body in its original state, a power P has to supplied to the system. The energy supplied to the liquid, by an impeller rotating in an agitated system, can be calculated from the following equation:^[22, 23, 24]

$$P = P_N \rho_L N^3 D_I^5$$
 (4.17)

where P_N is a dimensionless grouping known as power number, ρ_L is density of the liquid, N is speed of rotation and D_I is diameter of impeller. It is well known that the input power to a stirred system (per unit mass of liquid) is equal to the

average rate of dissipation of energy per unit mass, *i.e.* P/total mass of liquid $=\varepsilon$. In such cases, the average rate of dissipation of energy is usually determined by measuring the torque on the motor. In the current experimental work, the input power for each specific RPM was measured by subtracting the input power of a DC motor, when it rotates in the melt, from the input power when it was essentially unloaded, rotating in air at the same RPM.

In Figure 4.9, the rate of dissipation of energy in the liquid aluminum system as a function of impeller Reynolds numbers and impeller's speed of rotation are shown. The results demonstrated that the six-bladed impeller, placed in an off-centre position, supplied slightly more energy to the system than did the four-bladed impeller placed centrally.

Substituting the rate of input energy measured via the experiments in the system into Eq. [4.17], the power number of the graphite impellers can be calculated. The power number of an impeller is an important parameter in the design of mixing systems. It is reported that within the accuracy of the power measurements, it was revealed that the power number was independent of the size of vessel.^[9] Some research shows that at impeller Reynolds numbers higher than 10^4 , the power number becomes independent of impeller Reynolds number.^[23,25,26] In Figure 4.10, the relation between power numbers obtained and impeller Reynolds numbers rotating in molten aluminum at 720 °C is shown. For the present experimental geometries with $0.9 \times 10^4 < \text{Re}_{impeller} < 13 \times 10^4$, the associated power numbers were approximately independent of impeller Reynolds number. It was found equal to 5.1 for the four-bladed impeller in centre position and 6.2 for the six-bladed impeller in the off-centre position.

4.3.3 Dimensionless energy dissipation rate correlation

In applying Kolmogoroff's theory for the dissolution of solid particles in a stirred system, another point of uncertainty still remains. One may assume that the results obtained just reflect the average rate of energy dissipation over the whole vessel while the theory of mass transfer based on the Kolmogoroff's approach is strictly valid only if the local rate of dissipation of energy is used. However, based on the following explanations, it may be allowable to apply the average rate of dissipation of energy instead of the local rate. First, most recent researchers have analyzed data based on this approach satisfactorily, as seen from Table 4.1. Second, Kikuchi^[12] has found that there is a close agreement between the concept of the local rate of dissipation of energy around a fixed particle and the average rate of dissipation of energy, for suspended particles in stirred tanks.

One should note that, Kolmogoroff proposed two conditions for this approach which frequently apply in stirred reactors: a) a high Reynolds number and, b) a very small length scale of turbulence compared to the scale of the main flow, *i.e.* $l_k \ll L$. For instance, concerning the former condition, at a rate of energy dissipation of 1 W/kg in water at 20 °C, Kolmogoroff's length scale for the smallest eddies l_k is 32 μ m, and for liquid aluminum at 720°C, l_k is 18 μ m. Thus, for an agitator blade with 70 mm diameter (*i.e.* L= 70 mm), $l_K \ll L$. One may conclude that this theory can be applicable to the dissolution of solid particles in agitated turbulent systems.

Measured mass transfer coefficients (from Figure 4.6 and 4.7) and rates of energy dissipation for each specific rotation speed (from Figure 4.9) can be combined together on the basis of Kolmogoroff's approach to find an empirical correlation for mass transfer from or to particles. Similar to Eq. [4.13], the experimental data was plotted in terms of the (Sh-2)Sc^{-1/3} grouping versus the dimensionless rate of dissipation of energy group ($\dot{\epsilon}^{1/3} d_P^{4/3}/\nu$). The results are given in Figures 4.11 and 4.12. Note that the exponent on the Schmidt number in the mass transfer correlation, Eq. [4.13], was selected as 1/3 based on boundary layer theory. At relatively lower rates of input turbulent mixing energy, both sets of results could be satisfactorily correlated by the following equations:

$$Sh = 2 + 0.1 \left(\frac{\dot{\epsilon}^{1/3} d_p^{4/3}}{v}\right)^{0.7} Sc^{1/3}$$
 for Mn particles (4.18)

with a standard error of 0.040, (or a percent relative errors ranging from 4 to 17 pct), and

$$Sh = 2 + 0.13 \left(\frac{\dot{\epsilon}^{1/3} d_p^{4/3}}{v}\right)^{0.6} Sc^{1/3}$$
 for Fe particles (4.19)

with a standard error of 0.041 (5.4 to 14 pct), see appendix 4. Furthermore, the *correlation coefficients* for both present equations, as calculated by the method of least squares, are more than 0.98. As seen from Figures 4.11 and 4.12, at higher rates of input energy, above the point at which particles become freely suspended (entrained), further increases in the rate of mixing produced negligible changes on the Sherwood number. It seems that higher rates of dissipation of energy in the turbulent system around the solute particles have no further effect on the thickness of particle mass transfer boundary layers.

In this regard, several arguments can be presented. Alternative possibilities to explain this insensitivity to higher mixing rates, such as the agglomeration of particles or partially rate limiting chemical reactions at the particle melt interface, can be discounted on the basis of experimental observations and previous dissolution studies using rotating disk methods. As seen from Figure 4.13, a thick layer of intermetallic phases can exist around alloying particles during dissolution process, even at high rates of mixing. These showed that the kinetics of dissolution were still dominated by mass transfer at much higher shearing rates than those achieved in the present work. One may therefore conclude that the dissolving particles, being small, resided in micro-eddies within highly turbulent flow fields, moving in harmony with the surrounding liquid, therefore exhibiting no further inertial responses to the moving media. Levins *et. al.*^[27] studied the motion of 80 to 90 μ m iron and aluminium particles in water in a highly stirred system. They found that the ratio of the fluctuating velocity of the particles to that of the liquid was 0.98 for iron particles and 0.99 for aluminium particles. It can be therefore concluded that these particles follow the fluid's motions very closely. That being the case, for alloying particles entrained in turbulent aluminium system, further increases in mass transfer would not be anticipated.

In describing the present phenomena, another approach may be useful. Kolmogoroff defined the size of the eddies in which energy was dissipated as being: $l_k = (v^3/\dot{\epsilon})^{1/4}$, Eq. [4.6].

In Figure 4.14, a plot of l_k versus ε , for aluminum system, is shown. As seen, by increasing the intensity of mixing, l_k decreases sharply. However, at higher rates of mixing, the changes in the size of eddies is very small. One can conclude that by increasing the rate of mixing, initially the number of small eddies which surround the surface of the particles increases, (because the size of the eddies becomes smaller). This, in turn, provides higher mass transfer rates. At higher rates of intensity, however, as the figure shows, no changes in the size of eddies occurs. Consequently, there is no change in the mean number of eddies interacting with the particles. As a result, mass transfer rates exhibit no further increases at higher rates of mixing.

However, the agreement between the results obtained from the two different liquid mixing system geometries, as well as the agreement of cold model studies with the present hot temperature study, suggest that the dimensionless energy dissipation rate group, based on *Kolmogoroff's theory of local isotropic turbulence*,
may be useful as a general parameter in the study of mass transfer phenomena between solid particles and liquid metals. The former can be easily replaced by the Reynolds term in mass transfer correlations. However, in high temperature liquid metal applications, for dissolution of iron and manganese particles in mechanically stirred liquid aluminium, over the critical intensity of mixing, ($\dot{\varepsilon} > 0.5$ W/kg for the experimental system), the theory may not be more useful. Then, clearly, a very high rate of mixing is not suggested.

4.4 Conclusions

Mass transfer from solid iron and manganese particles into turbulent liquid aluminum can be treated by Kolmogoroff's approach. The results obtained indicate that mass transfer coefficients of particles in the range of 212-250 μ m are independent of the methods of stirring (stirrer types and their positions) and can be satisfactorily correlated on the basis of the rate of power input/unit mass. Experimental results showed that mass transfer coefficients of manganese and iron particles are strongly dependent on the intensity mixing, until the particles became fully suspended. Further increases in rates of mixing produced negligible changes in mass transfer coefficients. It would appear that particles stayed in micro-eddies within the turbulent flow field, moving with them, with little further inertial response to the moving fluid. Therefore, from a practical point of view, to improve the kinetics of alloying processes, high intensities of mixing is not recommended, as such measures could promote the loss of liquid metal by oxidation or possibly splashing, as well as unnecessarily wasting stirring energy.

4.5 Nomenclature

A constant in Sherwood correlation

C constant = $f(\nu, t)$

Cs	maximum solubility
C _b	bulk concentration
D	solute diffusivity
d _P	particle diameter
d,	initial average particle diameter
DI	impeller diameter
E(k)	kinetic energy spectrum
F _i	inertial forces
F_{μ}	viscous forces
k	wave number
K _m	mass transfer coefficient
L	scale of the main flow $\approx D_I$
l _k	Kolmogoroff's length scale
n	turbulence frequency
N	rotation speed of impeller
Ρ	rate of input mixing energy per total mass of liquid
$\mathbf{P}_{\mathbf{N}}$	power number = $P/(\rho_L N^3 D_I^5)$
R	particle radius
Re	particle's Reynolds number $= U_r d_P / \nu$
Re _{impeller}	impeller's Reynolds number $= ND_I^2/\nu$
Sc	Schmidt number $=\nu/D$
Sh	Sherwood number $= K_m d_P / D$
t	time scale
u	velocity scale
U	time-average velocity
U,	relative velocity
W	watt

- α constant in Sherwood correlation
- β constant in Sherwood correlation
- ω angular speed of rotation of disk
- $\dot{\epsilon}$ rate of energy dissipation per unit mass of liquid \approx P/total liquid mass
- $\rho_{\rm L}$ liquid density
- ρ_P particle density
- v liquid kinematic viscosity
- μ liquid viscosity
- ϕ Carman's surface factor

4.6 References

 G.K. Batchelor, "Kolmogoroff's Theory of Locally Isotropic Turbulence ", Proceedings of the Cambridge Philosophical Society, 1947, vol. 43, pp. 533-559.
 A.N. Kolmogoroff, Comptes Rendus (Doklady) de l'Academie des Sciences de l'URSS, 1941, vol. 30, pp. 301-305, vol. 31, pp. 538-540 and vol. 32, pp. 16-18.
 R.S. Brodkey, The Phenomena of Fluid Motions, Addison-Wesley Publishing Company, pp. 286-287.

4. J.O. Hinze, Turbulence, An Introduction to Its Mechanism and Theory, 1975, Second Edition, McGraw-Hill, New York, pp. 221-223.

5. S. Panchev, Random Functions and Turbulence, Pergamon Press, Oxford, 1971, PP. 150-151.

6. D.M. Levins and J.R. Glastonbury, "Application of Kolmogoroff's Theory to Particle-Liquid Mass Transfer in Agitated Vessels", *Chemical Engineering Science*, 1972, vol. 27, pp. 537-543.

7. R. Shinnar and J.M. Church, "Predicting Particle Size in Agitated Dispersions ", Industrial and Engineering Chemistry, 1960, vol. 52, pp. 253-256. 8. S. Middleman, "Mass Transfer from Particles in Agitated Systems, Application of Kolmogoroff Theory ", *AIChE Journal*, 1965, vol.11, pp. 750-752 and 760-761.

9. D.M. Levins and J.R. Glastonbury," Particle-Liquid Hydrodynamics and Mass Transfer in a Stirred Vessel, Part II. Mass Transfer ", *Transactions of the Institute* of Chemical Engineers, 1972, vol. 50, pp. 132-146.

10. Y. Sano, N. Yamaguchi and T. Adachi, "Mass Transfer Coefficients for Suspended Particles in Agitated Vessels and Bubble Columns ", *Journal of Chemical Engineering of Japan*, 1974, vol. 7, pp. 255-261.

11. S. Asai, Y. Konishi and Y. Sasaki, "Mass Transfer between Fine Particles and Liquid in Agitated Vessels ", *Journal of Chemical Engineering of Japan*, 1988, vol. 21, pp. 107-112.

12. K.I. Kikuchi, T. Sugawara and H. Ohashi, " Correlation of Liquid Side Mass Transfer Coefficient Based on the New Concept of Specific Group ", *Chemical Engineering Science*, 1988, vol. 43, pp. 2533-2540.

13. H. Ohashi, T. Sugawara, K. Kikuchi and H. Konno, " Correlation of Liquid Side Mass Transfer Coefficient for Single Particles and Fixed Beds ", *Journal of Chemical Engineering of Japan*, 1981, vol. 14, pp. 433-438.

14. P.H. Calderbank and M.B. Moo-Young, " The Continuous Phase Heat and Mass Transfer Properties of Dispersions ", *Chemical Engineering Science*, 1961, vol. 16, pp. 39-54.

15. P.L.T. Brain, H.B. Hales and T.K. Sherwood, "Transport of Heat and Mass Between Liquids and Spherical Particles in an Agitated Tank ", *AIChE Journal*, 1969, vol. 15, pp. 727-732.

16. P. Sanger and W.D. Deckwer," Liquid-Solid Mass Transfer in Aerated Suspension ", *Chemical Engineering Journal*, 1981, vol. 22, pp. 179-186.

17. R. Conti and S. Sicardi, " Mass Transfer from Freely Suspended Particles in

Stirred Tanks ", Chemical Engineering Communications, 1982, vol. 14, pp. 91-98.
18. Selected Values of the Thermodynamics Properties of Binary Alloys, 1973,
American Society for Metals, Metals Park, Ohio, pp. 156-165 and 185-188.

19. A.W. Nienow, "Dissolution Mass Transfer in a Turbine Agitated Baffled Vessel", *The Canadian Journal of Chemical Engineering*, 1969, vol. 47, pp. 248-258.

20. P. Harriott, "Mass Transfer to Particles: Part I. Suspended in Agitated Tanks ", *AIChE Journal*, 1962, vol. 8, pp. 93-102.

21. F. Kneule, "Die Prufung von Ruhrern durch Loslichkeitsbestimmung ", Chemie-Ingenieur-Technik 1956, vol. 28, pp. 221-225.

22. J.Y. Oldshue, *Fluid Mixing Technology*, 1983, McGraw-Hill, New York, p. 51.

23. R.J. McDonough, *Mixing for the Process Industries*, 1992, Van Nostrand Reinhold, New York, p. 42.

24. P.H. Calderbank and M.B. Moo-Young, " The Power Characteristics of Agitators for the Mixing of Newtonian and Non-Newtonian Fluids ", *Transactions of the Institute of Chemical Engineers*, 1961, vol. 39, pp. 337-347.

25. P. Plion, J. Costes and J.P. Couderc, "Study by Laser Doppler Anemometry of the Flow Induced by a Propeller in a Stirred Tank ", *5th European Conference on Mixing*, 1985, Wurzburg, West Germany, 10-12 June, pp. 341-354.

26. N. Harnby, M.F. Edwards and A.W. Nienow, *Mixing in the Process Industries*, Second Edition, 1992, Butterworth-Heinemann, Oxford, p. 140.

27. D.M. Levins and J.R. Glastonbury," Particle-Liquid Hydrodynamics and Mass Transfer in a Stirred Vessel, Part I. Particle-Liquid Motion", *Transactions of the Institute of Chemical Engineers*, 1972, vol. 50, pp. 32-41.



Fig. 4.1 Schematic of turbulent kinetics energy spectrum as a function of wave number, (*i.e.* reciprocal eddy size).



Fig. 4.2 Effect of stirrer to vessel diameter on the mass transfer coefficient.^[9]



Fig. 4.3 Mass transfer coefficient as a function of impeller design.^[9]



Fig. 4.4 Change in mean diameter (μ m) of iron particles during the dissolution process versus the speed of rotation of four-bladed impeller.



Fig. 4.5 Change in mean diameter (μm) of manganese particles during the dissolution process versus speed of rotation of four-bladed impeller.



Fig. 4.6 Mass transfer coefficients for iron particles ($\bar{d}_o = 231 \ \mu m$) as a function of speed of rotation of impeller in aluminum melt.



Fig. 4.7 Mass transfer coefficients for manganese particles ($\vec{d}_0 = 231 \ \mu m$) as a function of speed of rotation of impeller in aluminum melt.



Fig. 4.8 Dissolution times of iron and manganese particles ($\bar{d}_0 = 231 \ \mu m$) as a function of speed of rotation of four-bladed impeller.



Fig. 4.9 The rate of input mixing energy as a function of impeller Reynolds number, ND_1^2/ν .



Fig. 4.10 Power number, $(P_N = P/\rho_L N^3 D_I^5)$ as a function of impeller Reynolds number, $(Re = ND_I^2/\nu)$.



Fig. 4.11 Sherwood-Schmidt correlation as a function of dimensionless rate of energy dissipation for iron particles.



Fig. 4.12 Sherwood-Schmidt correlation as a function of dimensionless rate of energy dissipation for manganese particles.



Fig. 4.13 Intermetallic layer which exists around alloying particles (Mn) during dissolution at high rates of mixing.



Fig. 4.14 The size of energy dissipating eddies in molten aluminum versus the dissipative rate of input energy.

CHAPTER 5

Summary

In general, manganese and iron are two major alloying elements which are added to molten aluminum to improve the mechanical properties of the final products (alloys). These elements, such as the majority of the other transition metals, have higher melting points than the aluminum's melt temperature. As such, when they are added to aluminum, they tend to dissolve rather than melt. At the same time, their rates of dissolution, which is controlled by mass transfer through a boundary layer, are very slow, due to their low solute diffusivities in liquid aluminum. Thus, the kinetics of their dissolution can be improved by mechanical stirring, (*i.e.* creating forced convective mass transfer). Other parameters such as type of alloying agent (pure elements or master alloys), and the method of their addition can also affect the kinetics of the alloying process.

In Chapter 1, through studying the effect of mechanical stirring on dissolution rates, the advantages and disadvantages of commonly used methods of alloying addition in the aluminum industry were described. It seems that among these methods, mixing and compacting powders of high melting point elements and aluminum together, to make briquettes, is the most beneficial and efficient method compared to others. Alloying briquettes not only offered a higher overall dissolution rate as well recovery, but was also convenient in terms of technique of addition.

In Chapter 2, a comprehensive study of the mechanism of a compact briquette's dissolution, together with a comparison between global dissolution times of compact powders and discrete particles has been performed. As a conclusion, a brief summary of the findings are presented here.

A thermal analysis of immersed briquettes of Fe-Al and Mn-Al in molten aluminum indicated that after the aluminum particles in the briquettes melt, exothermic reactions between aluminum and solid particles provide a local accumulation of heat within the briquette. This phenomenon increases the temperature of a briquette sharply, which peaks well above the bath temperature. The high temperature environment within the briquettes accelerates diffusional reactions, which result in the formation of intermetallic rims around particles of alloying elements. It also raises the dissolution rate of intermetallic compounds in the liquid aluminum existing inside the briquette. The dissolution process continues until solute saturation conditions are achieved inside the compact. The thickness of the intermetallic layers then increase rapidly.

Chemical phase analysis of the microstructure of immersed briquettes using the EDS method (Energy Dispersive Spectroscopy) indicated that among four thermodynamically stable intermetallic phases (*viz.* FeAl, FeAl₂, Fe₂Al₅, and FeAl₃), Fe_2Al_5 is the only dominant phase in the Fe-Al system. By contrast, in the Mn-Al system, among the MnAl, MnAl₃ and MnAl₄ intermetallics possible, the only dominant phase was $MnAl_4$. The other intermetallic phases were presumably present only as immeasurably thin layers. It would therefore seem that the diffusion of alloying element atoms (Mn or Fe) and aluminum atoms in Fe₂Al₅ and MnAl₄ phases are much faster than their diffusion in the other layers of intermetallic compounds. For these reasons, MnAl₄ and Fe₂Al₅ phases grow faster. The predominance of one intermetallic phase among several possible intermetallic phases has also been observed in other systems. Similar inter-diffusion experiments in Al-Zr and Al-Ti systems confirm the results of the present work, ZrAl₃ or TiAl₃ being the only phase formed during diffusion.

A theoretical analysis aided by some experimental observations revealed that during the growth kinetics of intermetallic compounds, which obey a parabolic law with time, two behaviours occur. The intermetallic region, MnAl₄, penetrates into the liquid aluminum phase preferentially while the Fe₂Al₅ phase, grows preferentially towards centre of the solid iron particle, (see Figures 2.11 and 2.12). This indicates that the flux of manganese in MnAl₄ is higher than the one quarter of the flux of aluminum, *i.e.* $J_{Mn} > 1/4J_{Al}$, while in the growth of Fe₂Al₅, $J_{Fe} < 2.5J_{Al}$.

During the study of the dissolution of the briquettes, samples withdrawn from the melts demonstrated a swelling in the briquettes, after melting of solid aluminum particles in the briquettes has occurred. Several reasons can cause this expansion. A high solubility of the aluminum phase in the solid iron or manganese phase compared to the solubility of manganese or iron in aluminum is indicative of a relatively unidirectional flow which causes an increase in the volume of the solid particles. As a result, the volume of the briquettes increases. Furthermore, in Al-Fe or Al-Mn systems, the specific volume of intermetallic compounds formed around solid iron or manganese particles is higher than that of pure metals. The total radius of alloying particles increases during the reactions, which in turn, increase the total volume of the briquettes.

Hence, due to the swelling of the briquettes and an increase in buoyancy forces applied on the submerged briquettes, a drop in the total downward force measured by load cell is expected. But, the load cell monitored a constant downward force during expansion of the briquette before disintegration. It transpired that liquid aluminum penetrated into the briquettes and compensated for the buoyancy force. Liquid penetrating into the expanded sample from the bath,

allows continued dissolution of alloying elements to proceed within the briquettes because saturation of the liquid aluminum phase by the manganese or iron is retarded. Moreover, the enhanced temperatures which result from exothermic reactions offer a high driving force for the dissolution of alloying elements within this liquid aluminum present within the compact.

The period that a briquette retains its rigidity in the bath plays an important role in its dissolution performance. During retention of alloying particles within the briquette, the particles are at a higher temperature than the bath. The load cell experiments monitored that manganese briquettes retained their solid skeleton and rigidity for 35 s, and iron briquettes, 25 s. After these retention times, the briquettes collapse in the melt and the dissolution of freely dispersed particles commence. It can be concluded that one main advantage of the briquettes vs powder or master alloy additions relates to the exothermic reactions which occur during this short period of time.

A comparison between the dissolution times of briquettes and the original classified particles used in their fabrication was carried out. The results showed that there was no rise in bulk concentration of solute, prior to disintegration of the briquettes within the melt. However, immediately following the briquette's disintegration, a sharp rise in solute concentration within the bulk metal was achieved. As mentioned before, collapsing briquettes supply some liquid aluminum saturated with solute to the melt. This results in an instant increase in bulk solute concentration. This saturated liquid aluminum was generated by melting 25 wt pct of the solid (i.e. aluminum particles), plus the liquid aluminum which penetrated from the bath into the briquettes during their expansion. In the dissolution of discrete powders, the process is rather different. The process can be broken into two steps. During the first stage, it seems the initial dissolution process is delayed by some physical and chemical reactions (particularly for manganese particles).

Thus, the dissolution rate of particles are initially low. However, in the second period, dissolution is controlled by mass transfer, similar to the dissolution performance of dispersed particles introduced into the melt following collapse of the briquettes. The experimental results indicate that the briquettes were totally dissolved within periods of 420 s (manganese) and 330 s (iron), while the larger sized particles from which they were originally fabricated required a further 150 s, for complete dissolution.

Concluding, the alloying of liquid aluminum using briquettes provides enhanced rates of dissolution, as well as convenience of method, compared to discrete particles.

Following the disintegration of the briquettes and free dispersion of alloying particles into the melt, dissolution rates are controlled by mass transfer from the solid to the liquid phase. Thus, in treating mass transfer rate, a knowledge of the relative velocities between solid particles and the liquid phase is necessary. On the other hand, due to the highly irregular motion of particles (with a complete random fluctuation in three dimension), in a turbulent system, describing the relative velocity of the particles in a stirred vessel is not simple, if not impossible. This difficulty leads the researcher to suggest some approaches in describing of solid-liquid mass transfer phenomena. In Chapters 3 and 4, the theories proposed by cold model researchers; terminal velocity theory and Kolmogoroff's theory, have, for the first time in molten metal systems, been investigated.

The terminal velocity approach suggests that during the full suspension of particles in stirred aqueous systems, the terminal-settling velocity of particles in stagnant baths can be considered as being representative of the relative velocity between solid particles and the liquid.

To evaluate this approach for the dissolution of iron and manganese in molten aluminum, mass transfer coefficients of the particles were first obtained

using theoretical correlations proposed by cold model researchers. In the second step, real values of mass transfer coefficients of alloying particles in molten metal system were measured experimentally. Finally, by comparing theoretical and measured values, the applicability of this theory for the two high temperature alloying systems was assessed.

In general, the movement of solid particles in liquid systems can be influenced by the liquid's drag forces applied to the particles. Thus, the drag coefficient, which is a function of particle Reynolds number, can be related to mass transfer coefficient. In calculation of theoretical mass transfer coefficients, it was found that the motion of the alloying particles (with the size range of 90 < $d_P < 550 \mu m$), in liquid aluminum and the relevant drag force coefficients, are located in the intermediate region (a region between Stokes and Newton's region). Therefore, by substituting the appropriate drag coefficient in terminal velocity correlation and then inserting the terminal velocity deduced in proposed correlations by cold model researchers, the mass transfer coefficients of the particles in a fully entrained condition were predicted.

In measuring actual mass transfer coefficient experimentally, it was necessary to determinate the critical speed of rotation of the impeller in the melt, required to raise the alloying element particles off the furnace bottom. However, a uniform distribution of entrained particles within the whole vessel was not required. Due to the inherent opaqueness of the melt, the evaluation of the degree of suspension (on-bottom or off-bottom condition) of the particles was not easy. However, water modelling experiments in conjunction with dimensionless analysis between cold and hot model systems were used to resolve this problem. Defining five dimensionless π group numbers, and designing the systems such as to have equal corresponding dimensionless numbers, a correlation between the critical speed of rotation of the impeller in the (visible) water model system and the (opaque) molten metal system was obtained. Using this correlation, the critical speed of rotation of impeller required to suspend manganese and iron particles in molten aluminum could be predicted.

Through the sampling of the melt and measuring the changes in the initial sizes of alloying particles entrained into the turbulent molten aluminum, the actual mass transfer of classified particles with specific sizes in the range of 90 to 550 μ m have been obtained. A comparison between measured mass transfer coefficients and predicted values indicates a significant difference. It was observed that for manganese particles, the measured values are only in the order of 13 to 15 pct of the theoretical values, while for iron particles they were as small as 14 to 16 pct of the theoretical values, (when A=0.72). The theoretical dissolution times of the particles were also only 13 to 16 pct of the actual results. However, in order to reduce any uncertainty in the final conclusion, other proposed correlations for mass transfer in aqueous systems, were investigated. For all cases, the differences between experimental and predicted values were significant.

It should be mentioned that in the terminal velocity approach, by substituting terminal velocity into the relevant correlations, only the minimum mass transfer coefficients will be obtained. The minimum mass transfer coefficients are then multiplied by a modification factor, to align theoretical mass transfer coefficients with experimental results. However, for the present study, even without applying this correction factor (which is infact an enhancement factor), the theoretical mass transfer coefficients were much higher than the measured results. Accordingly, it can be concluded that the terminal velocity approach, developed for aqueous models, cannot certainly be used for the dissolution of iron and manganese particles in stirred liquid aluminium. Employing this theory in accompaniment with the Sherwood correlations suggested by aqueous model researchers would be flawed. Nonetheless, if one wishes to retain terminalsettling velocity as the relative velocity of entrained alloying particles in a turbulent melt, a correlation obtained in the form of:

$$Sh = 0.1 \ Re^{0.5} \ Sc^{0.33}$$
 (5.1)

with a *correlation coefficient* more than 0.999 is recommended. One will note that the general form of this equation is quite different from previous correlations proposed in cold models. However, it can be used to determine the actual mass transfer coefficients of iron and manganese particles in liquid aluminum satisfactorily.

Besides the terminal velocity theory, another approach for treating mass transfer in aqueous stirred systems was introduced. In Chapter 4, for the first time, the applicability of the Kolmogoroff's approach in high temperature has been investigated. In this model, the relative velocity of the particles can be replaced by the rate of dissipation of energy in the system around entrained particles. In other words, a dimensionless energy group number in the form of $\dot{\epsilon}^{1/3} d_{P}^{4/3} / \nu$ is substituted for the Reynolds number in the relevant Sherwood correlations, where $\dot{\varepsilon}$ is the rate of energy dissipation, d_p is the particle diameter and ν is the kinematic viscosity of liquid. Therefore, by measuring the rate of input mixing energy into the system, *i.e.* the rate of dissipation of energy in the system, mass transfer coefficients of particles can be predicted. The results obtained from this approach indicate that mass transfer coefficients of manganese and iron particles (with an equivalent spherical diameter, $\overline{d_n} = 231 \ \mu m$) were independent of the methods of stirring (stirrer types and their positions) and could be satisfactorily correlated as a function of the rate of power input per unit mass. At relatively lower rates of input turbulent mixing energy, the experimental data *i.e.* measured mass transfer coefficients and energy dissipation rate at each specific rotation

speed, could be plotted in terms of the (Sh-2)Sc^{-1/3} grouping versus the dimensionless rate of dissipation of the energy group, $\dot{\epsilon}^{1/3} d_P^{4/3} / \nu$, (with correlation coefficients of more than 0.98) in the form of:

$$Sh = 2 + 0.1 \left(\frac{\dot{\varepsilon}^{1/3} d_p^{4/3}}{v}\right)^{0.7} Sc^{1/3}$$
 for Mn particles (5.2)

$$Sh = 2 + 0.13 \left(\frac{\dot{\epsilon}^{1/3} d_p^{4/3}}{v}\right)^{0.6} Sc^{1/3}$$
 for Fe particles (5.3)

The results demonstrate that mass transfer coefficients increase when the intensity of the mixing is increased. However, at higher rates of energy input, above the point at which particles become freely entrained in flow field, the further increases in the rate of mixing produced negligible changes in mass transfer coefficients (or Sherwood number). One may therefore conclude that the dissolving particles, being small, resided in micro-eddies within highly turbulent flow fields, moving in harmony with the surrounding liquid and therefore exhibited no further inertial responses to the moving media. However, agreement between the results obtained from the two different liquid mixing system geometries as well as the agreement of cold model studies with the present hot temperature study, suggest that the dimensionless energy dissipation rate group, based on *Kolmogoroff's theory of local isotropic turbulence*, may be useful as a general parameter in the study of mass transfer phenomena between solid particles and liquid metals. The former can easily replace the Reynolds term in the mass transfer correlations.

Concluding, in high temperature liquid metal applications, the dissolution of iron and manganese particles in mechanically stirred molten aluminium revealed that beyond the rate of intensity needed for just completely suspending dispersed solid particles, the theory may not be of further relevance. Over that critical intensity of mixing, ($\dot{\varepsilon} > 0.5$ W/kg for the experimental system) the rate of

dissolution was found to be almost independent of the rate of mixing. Therefore, from a practical point of view, in order to improve the kinetics dissolution of alloying particles in the melt, a very high intensity of mixing is not recommended, such measures could promote the loss of liquid metal by oxidation or possibly splashing, as well as unnecessarily wasting stirring energy.

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Contribution to knowledge

1. The kinetics of dissolution of compact briquettes of alloying elements and aluminum particles in turbulent molten aluminum have been investigated.

2. A comparison between dissolution behaviour of compact briquettes of alloying particles and discrete particles revealed that exothermic reactions inside the briquettes improve the dissolution rates of the briquettes .

3. Mass transfer coefficients and the dissolution times of particles entrained within a turbulent field of liquid media as a function of the intensity of mixing and particle size have been measured.

4. Proposed models in aqueous systems for the dissolution of fine particles in a turbulently stirred liquid have been studied in molten aluminium.

- Terminal velocity theory in conjunction with proposed correlations was found to be inapplicable to the high temperature system studied. However, a new correlation for treating mass transfer coefficients and dissolution times of suspended iron and manganese particles in stirred turbulent liquid aluminum has been derived.

- Kolmogoroff's theory of local isotropy is applicable to high temperature before full entrainment of the particles in the melt is reached. In this regard, respective correlation has been proposed. Using this correlation, mass transfer coefficients of fine particles as a function of input mixing energy can be predicted satisfactorily.

5. Mass transfer rates of iron and manganese into liquid aluminum melt are strongly dependent on the intensity of the mixing. However, from a practical point of view, very high rates of mixing is not recommended.

Future work

1. The author believes that the dissolution of other high melting alloying particle in molten metals, which is controlled by mass transfer through a boundary layer, will demonstrate the same trend, (*i.e.* will not obey the terminal velocity theory or show limited agreement with Kolmogoroff's theory). This needs further investigation.

2. Similarity between equations obtained for iron and manganese particles suggested that an equation with a general form and very close to these equations may be used for dissolution of particles of other transition metals in molten aluminum, which again calls for more investigation.

3. The particle size range used in the present experiments is selected such as to be suitable for measurement using the LiMCA technique. However, the dissolution of other particle's sizes located in Stoke's region or Newton's region can be investigated.

4. In the study of the Kolmogoroff's theory in high temperature, only two geometrical systems for mixing were used. However, the investigation in other geometrical systems such as mixing by an inert gas, (and measuring the input energy by plume of gas), or a combined system of gas and impeller may be required.

Appendix 1

Application of the rotational disk technique to the calculation of diffusion coefficients

Diffusion coefficients of high melting point additives in liquid aluminum play an important role in determining rates of alloying dissolution. In general, the diffusion coefficient is a function of chemical composition and temperature. During the dissolution of most transition metals in liquid aluminum, saturation concentrations are relatively low, so that the influence of concentration on diffusion coefficients can be considered negligible. The temperature dependence of the diffusion coefficient can be described using Arrhenius equation as:

$$D_T = D_o \exp(-\frac{E_D}{RT}) \tag{1}$$

where D_T is the diffusion coefficient of alloying atoms passing through a concentration boundary layer (m²s⁻¹), D_o is a frequency factor (m²s⁻¹), E_D is the activation energy for diffusion (Jmole⁻¹), R is universal gas constant (=8.314 Jmole⁻¹K⁻¹), and T represents absolute temperature (°K).

Using the rotational disk technique, D_o and E_D can easily be measured. At first, via running the experiment at different rotational speed and using Eqs [3.1] to [3.4] (given in Chapter 3), mass transfer coefficient and then diffusion

Appendix 1

coefficient, for a given temperature can be obtained. Then the experiments will continue for different temperatures. An appropriate linear relation between lnD and 1/T is obtained, indicating that the dissolution of solid alloying metals in a liquid can be analyzed in the form of an Arrehenus equation. In Table 1, Arrhenius parameters, and the diffusion coefficients of several transition metals in liquid aluminum at T=720°C (including manganese and iron), using the rotation disk method, are shown.

Alloying element	D _o (10 ⁻⁴) (m ² s ⁻¹)	E _D (10 ³) (Jmole ⁻¹)	D _{720°C} (10 ⁻⁹) (m ² s ⁻¹)
Mn	2.15	102.67	0.85
Fe	168.7	131.88	1.95
Cr	24.22	134.99	0.19
Ti	21.82	158.93	0.0095
Cu	0.341	82.85	1.49
Ni	2.273	93.40	2.77
Nb	0.0015	36.9	1.72
Ta	0.0026	41.2	1.78
Мо	0.0028	40.2	2.16
W	0.0035	41.9	2.21

Table 1. Diffusion coefficients of some alloying elementsin liquid aluminum

Appendix 2

Calculation of change in a particle's size during dissolution via measured changes in the bulk concentration

To calculate of the change in particle radius during dissolution, the initial solute concentration (before alloying addition), together with the number of such addition particles should be known. Assuming spherical particles with an equivalent initial radius R_0 , the number of particles (N) in total mass, m, of alloying elements added to liquid aluminum, can be calculated via the equation:

$$N = \frac{m}{4/3 \pi R_o^3 \rho_p}$$
(2)

where ρ_p and m are density and total mass of alloying elements, respectively.

The decrease in the total mass of N particles exposed to dissolution, at time t after addition is can be related to the increase in solute concentration via:

$$C_{t} = C_{o} + \frac{N\left(\frac{4}{3}\pi R_{o}^{3} \rho_{p} - \frac{4}{3}\pi R_{t}^{3} \rho_{p}\right)}{M} \times 100$$
(3)

where

 C_{o} =initial concentration of alloying elements in liquid aluminum (wt pct)

 C_t = concentration of alloying elements in liquid aluminum at time t after addition (wt pct)

M = The total weight of (liquid aluminum + alloying particles)

 \mathbf{R}_{t} = radius of alloying particles at time t after additions

When R_t is close to zero (end of dissolution), C_t reaches its final concentration, C_f :

$$C_{f} = C_{o} + \frac{N \frac{4}{3} \pi R_{o}^{3} \rho_{p}}{M} \times 100$$
(4)

After dividing Eq. [3] by Eq. [4], the relation between size of the particles at each moment of dissolution and measured solute concentration is:

$$R_{t} = R_{o} \left(1 - \frac{C_{t} - C_{o}}{C_{f} - C_{o}} \right)^{\frac{1}{3}}$$
(5)

Appendix 3

Uncertainty analysis

In general, several types of errors may cause uncertainty in the experimental measurements. First, gross blunders in instrument or apparatus construction may invalidate the data. Second, fixed errors (or systematic errors), that remain roughly the same from one reading to another, may exist. Third are random types of error. These errors can be caused by personal fluctuations, random electronic fluctuations in apparatus or instruments, various influences of friction, etc.. In many instances, it is not easy to distinguish between fixed errors and random errors.

However, a very careful recent calibration, with standards of high precision, can be useful in lowering the uncertainty in readings. This is much better than performing measurements with an instrument of unknown calibration history.

Now, suppose a set of measurements with specified uncertainties is made and these measurements are then used to calculate some desired results of the measurements. How can one estimate the amount of uncertainty in the calculated results from the uncertainties in primary measurements? If the result R is a function of independent measured variables $x_1, x_2, x_3, ..., x_n$, with particular uncertainties, then:

$$R = R(x_1, x_2, x_3, ..., x_n)$$
(6)
At first, one may suggest the combination of all the errors in the result R, in the most detrimental case in order to estimate the maximum error in R, but this is quite unlikely. For instance in the calculation of the electrical power of a motor (power = volt x amps), when the voltmeter reads an extreme "high value", there is no reason why the ammeter would also simultaneously read an extreme "high value". Therefore, this combination is most unlikely.

A more precise method of estimating uncertainty in the experimental results has been suggested as:

$$w_{R} = \left[\left(\frac{\partial R}{\partial x_{1}}w_{1}\right)^{2} + \left(\frac{\partial R}{\partial x_{2}}w_{2}\right)^{2} + \dots + \left(\frac{\partial R}{\partial x_{n}}w_{n}\right)^{2}\right]^{1/2}$$
(7)

where, w_R is the uncertainty in the result and w_1 , w_2 , ..., w_n are the amount uncertainties in independents variables x_1 , x_2 , ..., x_n , respectively.

Calculation of uncertainties in particles size (W_{R}) :

Initial particles size (R_o), the measured concentration of dissolving particles at time t (C_t), initial concentration (C_o) and final concentration obtained (C_f) can be correlated to calculate the particles size in each moment of dissolution (R_t) as follows:

$$R_{t} = R_{o} \left(1 - \frac{C_{t} - C_{o}}{C_{f} - C_{o}} \right)^{1/3}$$
(8)

Taking the partial derivatives of R_t in relation to the variables R_o , C_t , C_o and C_f respectively and substituting the products of sensitivity of each variable and its uncertainty, *i.e.* [($\partial R_t/\partial R_o$).w_R], [($\partial R_t/\partial C_o$).w_C], [($\partial R_t/\partial C_f$).w_{Cl}] and [($\partial R_t/\partial C_t$).w_{Cl}],

into Eq. [7], then, the uncertainty in R, can be expressed as:

$$w_{R_{t}} = \left[A^{-1} w_{R_{o}}^{2} + \frac{R_{o}^{2}A^{2}}{9(C_{f} - C_{o})^{4}} (w_{C_{t}}^{2}(C_{f} - C_{o})^{2} + w_{C_{o}}^{2}(C_{f} - C_{t})^{2} + w_{C_{f}}^{2}(C_{t} - C_{o})^{2})\right]^{1/2}$$
(9)

where

$$A = \left(\frac{C_f - C_i}{C_f - C_o}\right)^{-2/3}$$
(10)

In following tables, the amount of uncertainties W_{Rt} in some calculated sizes of iron and manganese particles are given, noting that W_{Ct} , W_{Co} and W_{Ct} vary in the range of 0.002 to 0.006 wt pct, depending on the concentration of the solute in bulk.

Fe particles

 $R_o = 545 \ \mu m$, $C_o = 0.095 \ wt \ pct$, $C_f = 0.6051 \ wt \ pct$

Time (s)	C _t (wt pct)	$R_t \pm$ uncertainty (μ m)
0	0.0946	545 ± 47
50	0.1141	538 ± 46.4
100	0.1985	505 ± 43.6
150	0.2752	471 ± 40.6
200	0.4470	369 ± 31.8
250	0.4703	350 ± 30.2
300	0.5651	233 ± 20.3
350	0.5902	168 ± 15.4
425	0.6026	91 ± 10.1
485	0.6051	0

Fe particles

Time (s)	C _t (wt pct)	$R_t \pm$ uncertainty (μ m)
0	0.113	361 ± 62
50	0.135	356 ± 61.1
100	0.201	341 ± 58.3
150	0.478	250 ± 42.9
200	0.652	210 ± 36.1
230	0.631	135 ± 23.3
260	0.651	88 ± 16.2
305	0.657	59 ± 7.4
345	0.661	0

 $R_0=361 \ \mu m$, $C_0=0.113 \ wt \ pct$. $C_1=0.661 \ wt \ pct$

Mn particles

Time (s)	C _t (wt pct)	$R_t \pm$ uncertainty (μ m)	
0	0.004	463 <u>+</u> 37	
50	0.015	460 ± 36.7	
100	0.056	450 ± 35.9	
150	0.258	391 ± 31.3	
200	0.352	357 ± 28.5	
250	0.453	310 ± 24.8	
300	0.567	230 ± 18.4	
350	0.6138	171 ± 13.9	
400	0.6412	90 ± 11.4	
440	0.644	68 ± 8.3	
475	0.647	0	

$R_{o} = 463 \ \mu m$,	$C_0 = 0.004 \text{ wt pct},$	$C_{f} = 0.647$	wt pct
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Mn particles

Time (s)	C _t (wt pct)	$R_t \pm$ uncertainty (μ m)
0	0.0151	181 ± 31
30	0.0256	180 <u>+</u> : 30.8
65	0.044	178 ± 30.5
90	0.187	162 ± 27.7
120	0.248	154 <u>+</u> 26.4
150	0.4453	120 ± 20.5
180	0.535	95 ± 16.3
210	0.6175	37 ± 7.2
240	0.6230	0

 $R_o = 181 \ \mu m$, $C_o = 0.0151 \ wt \ pct$, $C_f = 0.6230 \ wt \ pct$

Uncertainties in dR/dt and mass transfer coefficients

In following tables, the uncertainties in measured dR/dt and also K_m for different sizes of iron and manganese particles are presented.

Particle diameter (μm)	Correlation coefficient*	$\frac{dR/dt \pm W_{dR/dt}}{(\mu m/s)}$	$\begin{array}{c} K_{m} \pm W_{Km} \\ (\mu m/s) \end{array}$
538±46	0.986	-0.644± 0.074	59.4± 6.2
457±36	0.980	-0.636± 0.074	59.0± 6.2
356± 61	0.980	-0.6415 ± 0.163	59.7± 13.6
245± 42	0.982	-0.6065± 0.158	56.4± 13.2
177±30	0.973	-0.586± 0.162	53.3± 13.5
126±22	0.994	-0.5725± 0.167	52.8± 13.9
87 <u>±</u> 14	0.978	-0.5705± 0.163	52.6 <u>±</u> 13.6

Fe particles

* Noting that a correlation coefficient equal to one indicates a perfect fit of the lines with respect to the data.

<u>Mn</u>	particles

Particle diameter (μm)	Correlation coefficient	$\frac{dR/dt \pm W_{dP/dt}}{(\mu m/s)}$	$\frac{K_{m} + \tilde{W}_{Km}}{(\mu m/s)}$
540±47	0.984	-0.573± 0.058	29.7±2.8
460± 37	0.982	-0.562± 0.059	29.2±2.9
358± 61	0.977	-0.546± 0.132	28.3± 6.5
250± 43	0.981	-0.550± 0.126	28.5± 6.2
178± 30	0.950	-0.512± 0.134	26.6± 6.6
124±22	0.956	-0.513 ± 0.142	26.7± 6.9
89±15	0.911	-0.470± 0.124	24.2 ± 6.1



Calculation of standard error

Assume we have two variables, X (independent) and Y (dependent), which are measured over a range of values, (such as times of immersion of particles in the melt and times of complete dissolution, or the rates of input energy in the system and mass transfer coefficients measured). We may be able to obtain an analytical expression of Y as a function of X. In this case, the standard error of Y, $\sigma_{Y,X}$, for the data is:

$$\sigma_{Y,X} = \left(\frac{\sum (Y_i - Y_{iC})^2}{n - 2} \right)^{1/2}$$
(11)

where Y_i are the actual value of Y measured by experiment and Y_{iC} are the values computed from analytical expression obtained for the same value of X. Also by dividing of 100 $\sigma_{Y,X}$ by Y_i , the percent relative errors in Y_i can be deduced.

Calculation of correlation coefficient

If one can find a suitable correlation between X and Y by either least square analysis or graphical curve fitting, then, by calculation of the correlation coefficient, r, one can know how good this fit is. This parameter is defined as:

$$r = \left(1 - \frac{\sigma_{Y,X}^2}{\sigma_Y^2}\right)^{1/2}$$
(12)

where $\sigma_{Y,X}$ is defined above and

$$\sigma_{Y} = \left(\frac{\sum (Y_{i} - Y_{m})^{2}}{n - 1} \right)^{1/2}$$
(13)

while

$$Y_m = \frac{1}{n} \sum_{i=1}^n Y_i$$
 (14)

If r is equal to one, it indicates that there are no deviations between data and the values obtained from correlation, *(i.e.* $\sigma_{Y,X}$ is equal to zero). If not unity, the smaller the value of r, the poorer is the fit of data to the curve.