

Combustion Synthesis of Metal-Sulfide Cermets: Manufacturing Process, Combustion Characteristics, and Mechanical Properties

by

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August 2014

A thesis submitted to McGill University in partial fulfillment of the requirements for a doctoral degree

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Dedication

To my lovely parents, beautiful sisters, and my beloved Majid For their love and support

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Abstract

Ceramic-metal composites offer unique combinations of hardness and toughness which make them attractive for a variety of applications. Among the ceramic-metal composites (cermets), metal-sulfur compositions may be produced using the Self-propagating High-temperature Synthesis (SHS) technique, a process where the material is created using a self-sustaining combustion reaction. The material studied in the present thesis consists of the product of the reaction between chromium and sulfur powders. The objectives of this study are i) to demonstrate the production of dense chromium-chromium sulfide cermets from the initial reactant powders using combustion synthesis, ii) to investigate the combustion process itself, including a microstructural analysis of the reactants and products, and iii) to evaluate the physical and mechanical properties of the cermets and to correlate them with chemical composition.

We propose a new method for the preparation of the metal-sulfur precursor mixture based on the ability to melt-cast the precursor mixture. This ability, with the properties of the reaction products (i.e., low gas evolution and liquid sulfide products), enables the creation of near-net shape structures and offers the possibility of tuning the microstructure and material properties by changing the composition of the reactant. In order to pursue the combustion synthesis approach to fabricating a Cr-CrS cermet, we began with thermochemical calculations and the phase diagram of the Cr-S reaction with varying equivalence ratios and the pressure at which the synthesis occurs to determine the adiabatic flame temperature and phases of the product at flame conditions using FactSage, a comprehensive multi-phase, multi-component equilibrium database. By modifying the synthesis process, it is found that with an improved manufacturing process, dense Cr-CrS cermet samples without any micro- and macro-cracks, and with porosity about 7% can be produced.

Controlling the final properties of the combustion products is dependent on an understanding of the kinetics and mechanism of structure formation. To develop a better understanding of the Cr-S system, the combustion characteristics of the system were investigated including the quenching thickness, heating zone thickness, flame velocity, and burning rate. The quenching dimension (i.e., the minimum size of sample that can sustain flame propagation with heat losses) in various

geometries was measured and linked to the reaction zone thickness of the flame front. The results obtained illustrate that flames in metal-sulfur compositions are dominated by the reaction zone thickness, in contrast to classical gaseous flames for which the flame thickness is dominated by the preheat zone. The chemical thickness of the front is estimated and it is found that the flame thickness in the present case is dominated by the thickness of the reaction zone. The flame propagation rate affects the heating and cooling rate, which influences the grain growth and other properties of the product. The observation of anomalous propagation modes in which the combustion front appears to lead at the edges of the charge reiterates the importance of differentiating the apparent propagation velocity from the fundamental (normal) burning velocity for SHS systems with liquid products.

To investigate the mechanism of combustion synthesis of Cr-CrS composites, the reactive mixture of Cr and S is used in a combustion front quenching test. The microstructural evolution in the quenched sample is observed by several techniques. Based on these experimental results, a diffusion-dissolution-precipitation mechanism is proposed, and a model corresponding to the mechanism is developed. It is observed that the reaction mechanism depends on the Cr particle size. Finally, an attempt is made to improve the toughness and other mechanical properties of the Cr-CrS cermets by increasing the metal content. The mechanical properties are measured as a function of the Cr:S molar ratio and the results obtained demonstrate that the addition of Cr has a significant influence on the mechanical properties, and leads to an overall improvement in the mechanical properties of the cermets fabricated.

Résumé

Les composites céramiques - métaux (cermets) offrent des combinaisons uniques de dureté et de ténacité qui les rend attrayants pour une variété d'applications. Parmi ces cermets, ceux dont la composition est à base de sulfure de métal peuvent être fabriqués à l'aide d'une technique de synthèse par réaction auto-entretenue à haute température (SHS), un procédé où le matériau est créé par une réaction de combustion qui s'auto-alimente. Le matériau étudié dans cette thèse est composé du produit de réaction de poudres de chrome et de sulfure. Les objectifs de cette étude sont de: i) démontrer la fabrication de cermets denses de sulfure chrome-chrome à partir des réactifs de poudre initiaux au moyen d'une synthèse par combustion, ii) faire l'étude du processus de combustion incluant une analyse microstructurale des réactifs et des produits, iii) évaluer les propriétés physiques et mécaniques des cermets et établir une corrélation avec leur composition chimique.

Nous proposons une nouvelle méthode pour la préparation du mélange précurseur de sulfure de métal basée sur la capacité de faire fondre et de couler le mélange précurseur. Cette capacité, combinée aux propriétés des produits de réaction (c.-à-d. faible dégagement de gaz et produits de sulfure liquides), permet la création de structures de formes extrêmement précise et offre la possibilité d'ajuster la microstructure et les propriétés du matériau en changeant la composition du réactif. Afin de suivre l'approche de synthèse par combustion pour fabriquer un cermet Cr-CrS, nous avons débuté par des calculs thermochimiques et l'élaboration du diagramme de phase de la réaction Cr-S en variant le rapport d'équivalence et la pression à laquelle la synthèse à lieu afin de déterminer la température de la flamme adiabatique et des phases du produit aux conditions de flamme en utilisant Factage, une base de données compréhensive de multiphases et multicomposantes d'équilibre. Il a été constaté qu'un procédé de fabrication modifié permet la fabrication d'échantillons de cermets denses Cr-CrS ne contenant aucune micro- ou macro-fissure et ayant une porosité de 7%.

Le contrôle des propriétés finales des produits de combustion dépend de la compréhension de la cinétique et du mécanisme de formation de la structure. Afin de parvenir à une meilleure compréhension du système Cr-S, les caractéristiques de combustion du système ont été étudiées incluant l'épaisseur de trempe, l'épaisseur de la zone thermique, la vitesse de flamme et le taux

de combustion. Les dimensions de trempe (c.-à-d. dimensions minimales de l'échantillon pouvant maintenir la propagation de la flamme dans des conditions réalistes de pertes de chaleur dans le reacteur) de géométries diverses ont été mesurées et reliées à l'épaisseur de la zone de réaction du front de la flamme. Les résultats obtenus démontrent que les flammes dans les compositions de sulfure de métal sont dominées par l'épaisseur de la zone de réaction, par constraste aux flammes gazeuses classiques qui sont dominées par l'épaisseur de la zone de préchauffage. L'épaisseur chimique du front a été estimée et il a été trouvé que l'épaisseur de la flamme dans le cas présent est dominée par l'épaisseur de la zone de réaction. Le taux de propagation de la flamme détermine le taux de chauffage et de refroidissement ce qui influence la croissance des grains ainsi que d'autres propriétés du produit. L'observation de modes de propagation anormaux mené par lefront de combustion aux bords de la charge réitère l'importance de différencier entre la vitesse de propagation apparente et la vitesse de combustion (normale) dans les systèmes SHS avec des produits liquides.

Afin d'étudier le mécanisme de synthèse par combustion d'un composite Cr-CrS, un mélange réactif de Cr et S est utilisé dans un essai au choc thermique de front de combustion (CFQ). L'évolution microstructurale dans l'échantillon trempé est observée à l'aide de plusieurs techniques de caractérisation. Un mécanisme de diffusion-dissolution-précipitation est proposé basé sur les résultats expérimentaux obtenus et un modèle correspondant à ce mécanisme développé. Il est constaté que le mécanisme de réaction est fonction de la taille des particules de Cr. Enfin, une tentative visant à améliorer la ténacité ainsi que d'autres propriétés mécaniques des cermets Cr-CrS est effectuée en augmentant la teneur en métal. Les propriétés mécaniques ont été mesurées en fonction du rapport molaire Cr:S et les résultats obtenus démontre que l'ajout de Cr a mène une amélioration générale des propriétés mécaniques des cermets fabriqués.

Acknowledgments

First and Foremost, I would like to express my deepest gratitude and appreciation to my research supervisors, Professor David L. Frost and Professor François Barthelat for their excellent guidance, consistence support, invaluable suggestions and supervision throughout this study. This project would have never been accomplished without their continuous support and generous advice.

I also would like to extend this gratitude to other members of my PhD advisory committee: Professor Andrew J. Higgins and Professor Pascal Hubert for their useful insights and suggestions. I would also like to extend special thanks to Dr. Sam Goroshin for his support, insight, and scientific advice. I am indebted to Professor In-Ho Jung who helped me in using FactSage and for his contributions to the thermochemical calculations using FactSage.

I truly thank the Faculty of Engineering at McGill University, and the Natural Sciences and Engineering Research Council of Canada for their collaborative financial support for this project.

Special thanks to the technical staff of the machine shops in Mechanical and Electrical Engineering department, and Materials and Characterization Lab in Materials Engineering Department, particularly Gary Savard, Andreas Hofmann, Donald Pavlasek, Mathieu Beauchesne, Dr. Florence Paray, Monique Riendeau, and Line Mongeon. I would like to thank Jean-Philippe Dionne and Clint Hedge at Allen Vanguard Company for their collaboration in ballistic tests.

I would like to express a heartfelt thank you to my friends and colleagues who continuously supported me during this study, particularly Jihane Ajaja, Mercedes shiue, Mohammad Mirkhalaf, Ravi Kiran Chintapalli, Dr. Ahmad Khayer Dastjerdi, Lawrence Szewciw, Dr. Deju Zhu, Sacha Cavelier, Dr. Reza Rabiei, Alexander Capozzi, Philippe Julien, Michael Soo, Jan Palecka, Jason Loiseau, Anthony Devito, Amir Farzadfar, and Mehdi Sanjari.

Last but not least, I would like to say my deepest thanks to my loving parents and sisters for their incredible support and encouragement throughout the years, and to my beloved Majid for his endless love, extreme patience and sincere encouragement.

Chapter 1 Introduction

Chapter 1: Introduction

This chapter presents a brief introduction to engineering ceramics and their potential use in personal ballistic armor systems. From a mechanics perspective, the shortcomings of ceramic materials and the benefits of ceramic-metal composite (cermet) materials in the context of ballistic performance are discussed. Metal-sulfide cermets are chosen specifically for study in the present work due to the possibility of producing these cermets directly with a chemical synthesis process and also the ability to systematically vary the properties of the cermet. The synthesis process, denoted self-propagating high temperature synthesis (SHS), permits net-shape manufacturing of the metal-sulfide cermet. The significance of studying the combustion properties of this reactive system, and analyzing the mechanism of structure formation during the combustion reaction itself are explained. Finally the objectives and structure of the thesis are presented.

1.1 Ceramic-metal composites as personal ballistic armors

The performance of metallic materials in armor systems is adequate in general and the cost is reasonable but the high density of metals is a drawback. The development of lightweight ceramics for armor applications dates back to early 1960's. Ceramic materials have been considered for lightweight armor because of their low density, high compressive strength and hardness [1-3]. In addition, engineering ceramics possess several desirable properties other than those mentioned above, including high melting temperatures, and good corrosion resistance. These outstanding features of ceramics make them attractive for different purposes. However, the widespread use of ceramics in applications is still limited by their brittleness, fragility and lack of toughness, which may lead to premature failure of the material in service. One possible approach to improve the properties of a ceramic is to add a ductile metal phase as a bonding agent to toughen the ceramic. Such ceramics with the toughness and ductility of metals [4-7]. In fact, the primary objective of producing cermets is to incorporate the desirable properties of ceramics and metals, and preferably suppress the undesirable properties of each. Therefore, ceramic composite armor ideally combines the ductility of metals with the light weight and high

hardness of ceramics. As a result, ceramic metal armor is significantly lighter than an equivalent metallic armor which would provide similar protection against a projectile [1-3, 8, 9].

1.2 Metal-sulfide cermets

Among the metal ceramic composites (cermets), metal-sulfur compositions offer the option of producing the composite material via a reactive wave. Thermodynamic calculations indicate that the adiabatic flame temperature of many metal-sulfur reactions may be sufficiently high to support a self-propagating flame front leading to the direct synthesis of the final metal-sulfide product. Equilibrium thermodynamic calculations demonstrate that Mg, Si, Ti, Cr, Mn, Zn, and Mo can all react with sulfur and potentially produce high-purity metal-sulfide compounds with combustion synthesis. Metal-sulfur combustion is a promising process for a wide range of practical applications because of the high flame temperature, low ignition temperature and large energy release [10, 11]. Among all the metal sulfur systems, three systems of Cr-S, Fe-S and Y-S are predicted to be gasless from equilibrium calculations and hence the amount of pores in the final product is expected to be minimal, depending on the purity of the reactant powders [12]. Also, the thermodynamic analyses predict a 100% yield of the final condensed product for the two systems Cr-S and In-S. These two elements are predicted to react with sulfur without the formation of gaseous products at normal pressure and produce a liquid flame [12].

Metal-sulfide composites are in high demand in the chemical, metallurgical, and electrical industries because of their valuable characteristics such as hardness, semi-conductivity, photo-, cathodo- x-ray-, and electro-luminescence, infrared transparency, catalytic properties, as well as optical and magnetic properties [13-24]. Currently, sulfide ceramics are used for cathodes in batteries, as an additive in steel production, as high-temperature lubricants, as a catalytic material for the catalytic hydrodesulfurization (HDS) process, as electrodes for hydrogen fuel cells, and in systems that convert solar energy into electrical and chemical energy [14, 25-31]. For the specific case of chromium sulfide, there is currently no bulk production and apparently the only application for CrS in the literature is as a solid lubricant [32].

1.3 Current manufacturing methods for metal-sulfides

Current manufacturing methods for metal sulfides usually involve one of two different principal methods, including i) a complex multistage wet chemical process involving the precipitation of the corresponding salts from an aqueous solution with hydrogen sulfide, or ii) hot sintering of the respective elemental reactant powders in a resistive furnace in a high-pressure inert or hydrogensulfide atmosphere [10, 12, 21]. In more detail, chromium sulfide has been synthesized by precipitation of a solution of CrCl₂ + (NH₄)₂S, and also by sintering the chromium and sulfur powders for up to 3 hours at temperatures ranging from 1400–1900 °C [14]. These methods have some disadvantages, e.g., using the wet process for production of metal sulfides has a detrimental environmental impact. The sintering process is quite expensive in terms of external energy requirements and also because of the high sintering temperature, it is difficult to avoid the loss of sulfur and crystal growth [10]. These conventional methods for synthesizing ceramic metal composites are complex, time- and energy-consuming, not suitable for the manufacture of articles with a complex shape, and environmentally harmful. Hence, in order to address these shortcomings, the self-propagating high temperature synthesis (SHS) process was considered as an alternative method for manufacturing the metal-sulfides which offers significant advantages over the traditional ceramic-metal composite manufacturing methods [4].

1.4 Self-propagating high temperature synthesis (SHS)

The term self-propagating high temperature synthesis was first coined by the Russian scientists Borovinskaya, Skiniro and Merzhanov in 1967 [33]. The use of a combustion reaction to synthesize a refractory material was first considered by Walton and Poulos who produced cermet materials using thermite reactions [34]. The SHS process has been used extensively over the past fifty years to synthesize more than 500 materials including the following classes of materials: intermetallics, ceramics, carbides, borides, silicides, nitrides, sulfides, aluminides, carbonitrides, hydrides, binary compounds, complex composites, and functional gradient materials [35-41]. SHS or more generally combustion synthesis utilizes an exothermic chemical reaction to sustain the propagation of a reactive wave. After initiation, the propagation of the reactive front serves to convert the reactants into products [4, 36, 42-44]. Based on empirical observations, the following conditions are necessary for the SHS reactions to be self-sustained:

$$T_{a} \geq 1800 \text{K}$$
 (1-1)
 $\frac{\Delta H_{f}^{0}}{C_{p}} \geq 2000 \text{K}$ (1-2)

where H_{f298}^{0} is the enthalpy of product formation, _{ad} is the adiabatic temperature, and Cp₂₉₈ is the molar heat capacity of the products at the temperature of 298K [43]. The SHS process typically leads to the formation of products with a high purity, because the high reaction temperature causes impurities to volatilize.

Two primary modes of this process have been recognized, namely a plane wave propagation mode and a thermal explosion mode. In the plane wave propagation mode, the reactants ignite by rapid heating at one end of the green sample. In this mode, the reaction zone propagates as a wavefront through the sample, driven by the exothermicity of the reaction. The thermal explosion mode involves heating the green sample using a rapid heating rate in a furnace until the reaction is initiated uniformly throughout the whole sample [37, 42].

The chemical reactions associated with SHS are typically completed in a fraction of a second (reaction time ~0.1 s for the metal-sulfur reactions studied in the current work [12]), leading to the formation of the condensed product. The high reaction rates, large thermal gradients, and relatively rapid cooling in the SHS process can avoid undesirable grain growth in the products which usually occurs in the conventional sintering method, and also can give rise to metastable or new non-equilibrium phases [4, 7, 40, 45]. Joining of metals to ceramics presents some difficulties due to the differences in mechanical, thermal and physical properties of these materials. The SHS process can lead to strong adhesion between the metal and ceramic phases, as the ceramic phase may grow inside the liquid metal during combustion synthesis [36, 37, 46].

A major drawback of materials produced with the SHS process is their porosity, which results from several sources, including the porosity in the original reactants, adsorbed gases present on the reactant powders, as well as gas evolution, molar change and thermal migration during the reaction process itself [39, 47-49]. The traditional method for sample preparation with the SHS technique is to compact the reactant powder mixture in a steel die with a press to attain a typical density of about 80% of the theoretical maximum density, prior to igniting the mixture. This

method requires a large compression force to increase the density of the reactive mixture and to minimize any pores in the green compact [50, 51].

1.5 Characterization of combustion synthesis parameters

It is accepted that controlling the final properties and characteristics of the synthesized product is dependent on an understanding of the kinetics and mechanism of structure formation. The reaction mechanism may involve several intermediate steps during the synthesis reaction during which intermediate products may form. Information regarding the mechanism of structure formation during the reaction may be obtained by measuring the properties of the propagating combustion front as well as by rapidly quenching the reaction and carrying out post-test material analysis of the products [52].

One analysis technique is based on direct electron-microscopic observation of the interaction between two reactants. In this method, a particle of one reactant is placed on a layer of another reactant, and the reaction is initiated by heating the sample with a high-intensity electron beam from the microscope or with the help of a special attachment. A second analytical technique is time-resolved X-ray diffraction (TRXRD) which provides a direct in-situ observation of the sequence of high-temperature phase transformations, although this technique is often characterized by difficulties in carrying out the experiments and in their interpretation [52, 53]. A third technique is based on rapid quenching of the reaction front during the propagation through the reacting mixture. The so-called combustion front quenching (CFQ) technique may be accomplished, for example, by dropping the sample into liquid argon or using a bulk copper wedge to induce high heat losses [54, 55]. This technique was first developed by Rogachev and co-workers [55-57]. In this method, the flame is extinguished because of the combination of the rapid heat removal by the copper block and the shrinkage of the cross section. The heat loss causes the burning velocity to decrease, and at a critical heat-loss rate the flame extinguishes. In this approach, the microstructure of the reaction products is characterized subject to the different operating conditions, e.g., the reactant particle size, inert content, green density, and so on. Following quenching, the phase composition and microstructure of different zones in the reaction zone can be identified using a layer-by-layer analysis of the quenched regions with a scanning electron microscope (SEM), energy dispersive X-ray (EDX) analysis, or X-ray diffraction (XRD) [58, 59].

1.6 Mechanisms of self-propagating high-temperature synthesis (SHS)

It is of interest to compare different mechanisms that have been proposed to describe the selfpropagating high-temperature synthesis (SHS) process. Three possible interaction mechanisms have been proposed and investigated for metallic systems with a liquid phase, as shown schematically in Fig. 1-1 [60].



Figure 1-1. Schematic of three possible mechanisms for the reaction between two reactants species A and B. The subscripts L and S refer to liquid and solid phases, respectively [60].

The first mechanism involves a dissolution-precipitation process that begins when the lower melting point component B melts. The atoms of the solid component A then start to dissolve in liquid B near the interfacial boundaries. When the melt is saturated, an AB intermetallide precipitates in the melt by means of crystallization. The precipitate is a phase which is in equilibrium with the melt at a given temperature.

The second mechanism is based on a reaction-diffusion model in which the formation of product compound AB is determined by transport of the components by unilateral or bilateral diffusion instead of a dissolution process. This reaction takes place at the particle surface at an infinite rate in the diffusion limit, as is the case for most SHS processes, and proceeds until all of the A particles or the molten B material is consumed.

In the third proposed mechanism atoms of the solid component A dissolve in the liquid B following an increase in the temperature. When the melt is saturated, a solid phase AB' (solid solution or intermetallide) forms inside the liquid, at the interface between A and B. The solute atoms penetrate and diffuse into the solid phase which has a lower melting point compared to component A. This decrease in melting temperature enables the solute atoms to transform into the liquid phase by means of melting. The layer of solid phase formed grows continuously at the interface with the solid component A (A-AB') and transforms into the liquid phase on the opposite boundary (B-AB'). This reaction model has been confirmed by a number of independent methods. Investigation of the interaction and reaction steps is facilitated by the aid of the electron-microscopic technique [60]. Currently, no study is available regarding the details of the mechanisms involved during the combustion synthesis of Cr-S.

1.7 Metal-sulfur reaction

When the metal-sulfur mixture is heated during the combustion process, the volatile component evaporates through the heated layer and reacts with the metal to form a condensed product. The mass loss of the sample and the vapor released are indications of the sulfur evaporation. In metal-sulfur combustion, many parameters over a wide range have been investigated and the results show that the interactions in the wavefront involve both gaseous and liquid sulfur, while the rate of the reaction may be limited by diffusion or kinetics [51, 61]. Below the melting point of sulfur, evaporation can be neglected whereas near the boiling point of sulfur, gasification results in a narrow zone separating the areas containing the liquid and gases. In this situation metal reacts initially with the liquid sulfur and then with the gases formed. Under low external pressures, the reaction occurs in two steps, the first starting when the sulfur melts and the second initiated when the sulfur boils. Under high external pressure and the main reaction is with the liquid. When the amount of sulfur in the mixture is low, the final product is porous and consists of sintered metal particles surrounded by sulfide layers [51, 61].

1.8 Thesis objectives

This thesis is focused on the net-shape manufacturing of chromium-chromium sulfide cermets via combustion synthesis with the study motivated by the production of material with ballistic

protection properties. Objectives of the present work include determining the reaction mechanism and combustion parameters of the Cr-S system, and evaluating the microstructure and mechanical properties of cermet produced. In the context of the present literature, there is currently no bulk production of chromium sulfide, and relatively little research has been performed to characterize the Cr-S system and to investigate its combustion and mechanical properties.

Using a systematic approach by combining various experimental and analytical methods, the specific objectives of this thesis work are:

- Demonstrate the production of chromium-chromium sulfide cermets with the SHS process
- Optimize the manufacturing process to minimize the porosity within the cermet samples
- Characterize the combustion properties, i.e., quenching thickness, reaction zone thickness, propagation velocity, and burning rate
- Investigate the microstructural evolution of the Cr-S mixtures by rapidly quenching the reaction
- Measure the quasi-static mechanical properties of the cermet samples fabricated and evaluate the effect of the improvements applied to the manufacturing process
- Improve the toughness and other mechanical properties of the chromium-chromium sulfide cermets by increasing the metal content

1.9 Thesis organization

The structure of the thesis is based on a collection of four closely related manuscripts. In the current chapter a brief introduction to ceramic and cermet materials has been presented and the self-propagating high temperature synthesis technique has been introduced in the context of metal-sulfur systems which allows for net-shape manufacturing of the cermet product. The objectives of the thesis were then introduced, which include investigating the combustion parameters of the metal-sulfur system and determining the microstructural and mechanical properties of the material.

The bulk of the thesis is contained in chapters 2 - 4, which contain manuscripts that are focused on the following major topics related to the metal-sulfur system: i) manufacturing process (chapter 2), ii) combustion synthesis properties (chapter 3), iii) microstructural evolution (chapter 4), and iv) mechanical properties (chapter 5). The material covered in each chapter is described in more detail below. The author of the present thesis is the lead author on each of the four manuscripts. However, since the manuscripts contain other co-authors that have contributed to the work, the specific contributions of the co-authors is also clarified below.

Chapter 2: "A novel method for net-shape manufacturing of metal-metal sulfide cermets," A. Nabavi, A. Capozzi, S. Goroshin, D.L. Frost, and F. Barthelat. Journal of Materials Science, 2014, in press, DOI 10.1007/s10853-014-8517-4.

Contributions of co-authors: A. Nabavi: carried out all microstructural and SEM analysis of the cermet samples, thermodynamic analysis and wrote the draft of the paper. A. Capozzi, a Masters student: carried out the combustion synthesis tests to prepare the cermet samples. S. Goroshin: provided overall guidance regarding the combustion synthesis process, carried out the DTA tests contained in one figure. D.L. Frost: co-supervisor of thesis work, provided advice on the direction of the work and reviewed the manuscript. F. Barthelat: co-supervisor of thesis work, provided input on the work, particularly regarding the materials analysis; reviewed the manuscript.

In chapter 2, a new method for the preparation of the metal-sulfur precursor mixture based on the ability to melt-cast the precursor mixture is proposed. It shows that how the self-propagating high-temperature synthesis process may be used to produce a chromium-chromium sulfide cermet. Thermodynamic calculations exploit the fact that this mixture of metal and sulfur can support the propagation of reactive waves, without the formation of gaseous products at normal pressure. While the thermochemical calculations predict near-zero gas production for the chromium-sulfur system, the actual cermets show a large amount of porosity (about 70%) when synthesized at atmospheric pressure. The possible sources for porosity are then identified and various improvements to the manufacturing process are applied to bring the porosity down to about 7%.

Chapter 3: "Combustion synthesis of metal sulfide composites", A. Nabavi, A. Capozzi, A.J. Higgins, S. Goroshin, D.L. Frost, and F. Barthelat. Paper manuscript in preparation for submission to the Journal of Self-Propagating High-Temperature Synthesis, 2014.

Contributions of co-authors: The contributions to this paper are similar to the paper in chapter 2, with the addition of Prof. Higgins, who provided input on the design of the combustion experiments as well as on the format of the graphs that present the results.

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Better control over the final properties of the combustion products is dependent on an understanding of the thermodynamics, kinetics, and mechanism of structure formation. The mechanism of structure formation during the combustion reaction may be studied by quenching the combustion wave during the synthesis. In chapter 3, the quenching thickness, or the minimum size of sample that can sustain flame propagation with heat losses, is measured in various geometries. The quenching scale is then linked to the reaction zone thickness of the flame front, and the chemical thickness is directly measured from the reactant-product interface recovered from a quenching experiment. The flame propagation velocity and burning rate are characterized, since the flame propagation speed determines the heating and cooling rate, which influences the grain growth and other properties of the product.

Chapter 4: "Microstructural evolution during the combustion synthesis of Cr-S system," A. Nabavi, D.L. Frost, and F. Barthelat. Manuscript in preparation for journal submission, 2014.

Contributions of co-authors: A. Nabavi carried out all the tests presented in this chapter and wrote the draft of the paper under preparation. Profs. Frost and Barthelat provided input to the direction of the work and also provided comments on the manuscript.

In chapter 4, the mechanism of the combustion synthesis of chromium-chromium sulfide composites is investigated. The microstructural evolution in the quenched samples is observed and analyzed with scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. In addition, the phase constituent of the final product is inspected by X-ray diffraction (XRD). Based on the obtained experimental results, a model for the mechanism of the combustion reaction in Cr-S system is proposed.

Chapter 5: "Mechanical properties of chromium-chromium sulfide cermets fabricated by selfpropagating high-temperature synthesis," A. Nabavi, S. Goroshin, D.L. Frost, and F. Barthelat. Manuscript in preparation for journal submission, 2014.

Contributions of co-authors: A. Nabavi carried out all the tests reported in this chapter and wrote the draft of the manuscript. S. Goroshin, and Profs. Frost and Barthelat provided input on the direction of the work and the latter two also provided suggestions regarding the manuscript.

In chapters 2–4, it was demonstrated that dense cermets with a specific structure may be synthesized. The combustion properties and mechanism of the reaction of the Cr-S system were investigated and defined. It is also important to characterize the mechanical properties of the

cermets that were produced. Therefore, chapter 5 includes a microstructural and mechanical characterization of the fabricated cermets. In this chapter, the mechanical properties of cermets are estimated and the effect on the properties of the improvements to the manufacturing process is evaluated. The effect of increasing the metal content of the cermet is then demonstrated, which leads to an overall improvement of the mechanical properties of the fabricated cermets. Finally, to be able to compare the synthesized Cr-CrS cermets with other materials, the range of the property values for this material are shown on a selection of Ashby charts [62].

In Chapter 6, a summary of the accomplishments of the present work is given and the contributions to original knowledge of this research are outlined. Finally, a few guidelines for future work are given as recommendations.

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Chapter 2

A novel method for net-shape manufacturing of metal-metal sulfide cermets

Chapter 2: A novel method for net-shape manufacturing of metal-metal sulfide cermets

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Journal of Material Science, August 2014, in press

DOI: 10.1007/s10853-014-8517-4

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2.1 Abstract

Ceramic-metal composites (cermets) offer unique combinations of hardness and toughness which make them attractive for a variety of applications. In this study, we propose a new method for the preparation of the metal-sulfur precursor mixture based on the ability to melt-cast the precursor mixture. We have used self-propagating high-temperature synthesis to produce a chromium/chromium sulfide cermet, exploiting the fact that this mixture of metal and sulfur can support the propagation of reactive waves. This ability, together with the properties of the reaction products (low gas evolution and liquid sulfide products), enable the net-shape synthesis of dense, near theoretical density product with a relatively simple and low-cost set-up. While the thermochemical calculations predict near-zero gas production for the chromium-sulfur system, the actual cermets showed a large amount of porosity (about 70%) when synthesized at atmospheric pressure. The possible sources for porosity were identified and the process improved to bring the porosity down to about 7%. We also investigated the physical properties of the produced cermet with optical microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction techniques.

Keywords: Self-propagating high-temperature synthesis; Cermet; Chromium sulfide; Net-shape manufacturing

2.2 Introduction

Metal sulfide composites are in high demand in the chemical, metallurgical, and electrical industries because of attractive characteristics such as hardness, magnetic properties, semiconductivity, electroluminescence, infrared transparency and catalytic properties [1-4]. Current manufacturing methods for metal sulfides usually involve one of two different principal methods, including a complex multistage wet chemical process involving the precipitation of the corresponding salts from an aqueous solution with hydrogen sulfide, or hot sintering of the respective elemental reactant powders in a resistive furnace in a high-pressure inert or hydrogensulfide atmosphere [2]. These conventional methods for synthesizing ceramic metal composites are complex, time and energy consuming, and environmentally harmful. In addition, these methods do not allow the fabrication of articles with complex shapes. Self-propagating hightemperature synthesis (SHS) offers an attractive alternative, with significant improvements over the traditional cermet manufacturing methods [5]. SHS has been used for about 40 years and is an elegant and efficient method for producing a wide range of advanced materials [2, 5, 6]. Based on self-sustained exothermic reaction of the reactants, the method yields materials of high purity, because the high temperatures generated during the reaction cause any impurities to volatilize [2, 7]. Other than an ignition source, SHS does not require an external energy source or complex equipment, as the reaction is self-sustained energetically [7]. In fact, the power requirements of SHS are so low that it is one of the few methods of materials synthesis which is feasible in outer space [8]. In addition, the process is inexpensive and can be used to directly synthesize articles with a desired shape, size and structure [7, 9]. The chemical reactions associated with SHS are typically completed in a few seconds, leading to the formation of the condensed product. Finally, the high reaction rates and relatively rapid cooling in SHS reactions can avoid undesirable grain growth in products which often occurs with conventional sintering methods [5, 7, 10].

A major drawback of materials obtained by SHS is their porosity, which results from several sources, including the porosity in the original reactants, and gas evolution, molar change and thermal migration during the reaction process itself [11, 12]. The traditional method for sample preparation in the SHS technique is to compact the reactant mixture powders to a typical density of about 80% of the theoretical maximum density before igniting the mixture. This method

requires a large compression force to increase the density of the reactive mixture and to minimize any pores in the green compact [2]. To eliminate porosity in the reactants, a new method for the preparation of the precursor charge of a metal-sulfur mixture is proposed in this study, which can be described as melt casting of a reactive mixture, or reactive casting in short. The porosity of the product material was experimentally measured, to verify the thermochemical prediction of low-gas production during reaction and a dense final product. The quenching dimension (minimum size of sample which can sustain flame propagation despite heat losses) was also measured due to its critical importance to the ability to perform net-shape synthesis of complex shapes.

2.3 Thermochemical Predictions

The thermodynamics of the Cr-S reaction (Cr+S \rightarrow CrS) was investigated using FactSage, a multiphase, multicomponent chemical equilibrium software package which includes extensive databases of known chromium sulfur compounds and phases [13]. We computed the adiabatic flame temperature and amount of volumetric gas production (volume of gas at pressure normalized by volume of initial composition, giving an indication of the porosity of the final product) as a function of Cr:S molar ratio at various pressures, as shown in Fig. 2-1 and Fig. 2-2. These calculations predict that the reaction becomes completely gasless when the composition is stoichiometric (Cr:S molar ratio 1), at which point the adiabatic flame temperature peaks at 2333°C. Increasing the Cr content beyond the stoichiometric value reduces the adiabatic flame temperature, while the reaction remains, in theory, gasless.


Figure 2-1. Gas production as a function of Cr:S molar ratio



Figure 2-2. Adiabatic flame temperature as a function of Cr:S molar ratio

The phase diagram of the Cr-S system at a pressure of 1 atm is shown in Fig. 2-3 [14]. This diagram, in combination with the calculation of adiabatic flame temperature, indicates that the products of the synthesis are in the liquid state (prior to cooling and solidification) for the range of chromium-rich compositions studied in this paper ($1.0 \le Cr:S \le 4.0$), which is an advantageous property for net-shape synthesis.



Figure 2-3. Calculated optimized condensed chromium-sulfur phase diagram at a total pressure of 1 bar. Abbreviations; Pyrr stands for high-temperature chromium pyrrhotite, S (orth) for solid pure sulfur with orthorhombic structure, and bcc for the body-centered cubic chromium solution phase [14]

2.4 Experimental procedure

The preparation of the reactive mixture used in this study is straightforward and may be described in a few steps (Fig. 2-7). The chromium powders used in the present work were obtained from Atlantic Equipment Engineers (NJ, USA). Two different Cr powders (99.8% purity) were used: a fine powder with a particle size range given by the supplier of 1-5 μ m (CR-102) and a coarse powder denoted -325 mesh, or nominally <44 μ m (CR-103). Fig. 2-4 shows

SEM images and particle size distributions of the Cr powders, measured with a LA-920 Horiba laser scattering particle size analyzer. Laser diffraction analysis utilizes diffraction patterns of a laser beam passed through the powder and measures the geometrical dimensions of its particle. The CR-102 and CR-103 powders had average particle sizes, based on volume, of 3 μ m and 26 μ m, respectively. Sulfur powder with a purity of 99.5% was obtained from Alfa Aesar (S4981, MA, USA). The average particle size was smaller than 150 μ m (-100 mesh) but did not influence the fabrication process, since the sulfur was always melted to form the reactive mixture.



Figure 2-4. Particle size distributions and SEM images of the Cr powders; fine powder (CR-102, with average particle size of 3 μ m), and coarse powder (CR-103, with average particle size of 26 μ m)

Chromium and sulfur powders were mixed in a roller mill (about 6 hours), in the desired mass ratio. The powder mixture was heated in a mantle up to 160° C which is slightly above the melting temperature for sulfur (temperature > 120° C), but well below the melting temperature of chromium (1907°C). The mixture of the molten sulfur with solid Cr particles was then poured into a mold. No interaction between chromium and sulfur was observed at this step. Upon

cooling of the reactive mixture, the sulfur solidified, forming a matrix of sulfur containing chromium inclusions. Image analysis results show that Cr particles were well-dispersed in sulfur matrix (Fig. 2-5). This reactive mixture was then ignited at ambient pressure by using an electrically-heated tungsten wire embedded in the sample. The self-sustained flame propagated throughout the sample, producing the final metal-sulfide product (Fig. 2-7). Depending on the initial metal/sulfur molar ratio, some unreacted metal may remain in the product, yielding a ceramic-metal composite (cermet), as shown on Fig. 2-8.



Figure 2-5. SEM micrograph of the reactive mixture showing chromium particles (light tone) embedded in solidified sulfur matrix (darker tone). The distribution of the chromium particle was uniform

Differential Thermal Analysis (DTA) using a standard LabsysTM instrument (Setaram Inc, France) was used to analyze the reactivity of chromium-sulfur mixture in the vicinity of the melting point of sulfur and beyond. The samples were prepared in accordance with the method developed in [15]. A small amount (5-12 mg) of ground reactive mixture of Cr-S (using fine Cr powder mixed with S with a stoichiometric ratio) was placed in a heavy-wall quartz capillary tube (2 mm OD, 1 mm ID) which was then flame-sealed from both ends (Fig. 2-6). The tube was wrapped with a thin silver foil that formed a pedestal at the tube end and was placed vertically on the DTA platform. An equivalent, but empty, tube was used as a reference. The DTA instrument recorded the heat flow from the reactive mixture as a function of temperature. As can be seen from Fig. 2-6, the DTA curve for the Cr-S mixture exhibits two peaks; an endothermic reaction

at a temperature of about 117°C, corresponding to the melting point of sulfur, and an exothermic reaction with an onset temperature of about 385° C which is near the ignition temperature of the Cr-S reaction. The reaction onset temperature recorded with the DTA is consistent with the ignition temperature of Cr-S mixture measured in other experiments by Goroshin et al., using samples cast into a small cylindrical container and placed within a fiber heater, which was reported as $423\pm7^{\circ}$ C [16].



Figure 2-6. DTA curve of Cr-S mixture and schematic of the flame-sealed quartz capillary with reactive Cr-S mixture



Figure 2-7. Schematic of the manufacturing process

2.5 Microstructure and composition

Optical microscopy and image analysis were used to examine the microstructure, phase size and distribution of the product samples. Specimens were cut, polished and examined with a scanning electron microscopy (Hitachi S-3000N VP-SEM SEM) and energy dispersive spectroscopy (EDS). The density of the samples, before and after the reaction, was measured. The shape and distribution of the pores within the reacted specimens were determined using image analysis. Results show that the amount of residual Cr-rich phase in the produced cermet changes with the Cr particle size. Fig. 2-8 shows the microstructure of two different samples with a Cr:S molar ratio equal to one, with two different Cr particle sizes. In the sample with coarse Cr particles (26 μ m), there is a significant amount of residual Cr phase in the cermet. In contrast, the sample with similar composition, but finer Cr particles (3 μ m), shows a relatively small amount of residual Cr phase in the cermet. BEE) image of the microstructure of the sample synthesized with coarse Cr powder (26 μ m), with a Cr:S molar ratio equal to 1. The EDX results show that the bright phases are residual Cr-rich phases, and the dark gray matrix is chromium sulfide, as tabulated in Table 2-1.



Figure 2-8. Optical micrographs showing the microstructure of reacted samples with (a) fine Cr particles, and (b) coarse Cr particles, each with Cr:S molar ratio equal to 1. Light regions are residual Cr phase, dark gray regions are chromium sulfide, and black regions correspond to voids



Figure 2-9. BSE image of the microstructure of the sample synthesized with coarse Cr powder (26 μ m), with Cr:S molar ratio equal to 1

Table 2-1. Chemical composition of the matrix and bright phase obtained from EDS point analysis

	Cr (wt%)	S (wt%)	O (wt%)	C (wt%)
Spot 1	86.80	4.75	3.61	4.84
Spot 2	55.20	32.31	2.78	9.72

The X-ray diffraction (XRD) technique was used to determine the nature of the different phases which were formed during the synthesis or post-ignition process. Combustion-synthesized products with a Cr:S molar ratio equal to 1 were ground into fine powders and

analyzed using copper K 1 X-ray radiation to assess the phase constituents. XRD analyses showed Cr and CrS peaks, for both samples made from coarse and fine chromium powders (Fig. 2-10). Their XRD patterns are similar, with a slight difference in intensity of Cr peaks which are higher in the sample with coarse Cr particles compared with the sample with fine Cr particles. Also, according to the XRD patterns, there is sulfur remaining in the samples containing coarse Cr powder. These results indicate that the combustion synthesis is incomplete in the case of coarse Cr powder, as indicated by the residual Cr-rich phase which was detected by XRD and observed with SEM in the final produced cermet. This is discussed in more detail in section 2-6b below.



Figure 2-10. XRD patterns of samples fabricated with fine (1.5 um) and coarse (<44um) Cr powders, both with Cr:S molar ratio equal to 1

2.6 Product Porosity Measurement

Samples synthesized at ambient pressure had generally high porosity (as high as 70%) with a large number of micro and macro cracks. The volumetric porosity was measured using image analysis, based on the ASTM E 562-02 standard test method [17] with the aid of Clemex, an image analysis software. Comparison of porosities before and after reaction indicates that the

pores appeared during the reaction. High porosity represents a significant obstacle to the use of the cermet in structural applications, and we therefore carefully investigated its possible sources in order to suppress it. Potential sources of porosity include impurity-generated porosity, porosity existing within the starting powders and reactive mixture, porosity generated by sulfur vaporization within the flame front, expansion of pre-existing closed pores within the reactive mixture after reaction, and porosity from molar volume changes. The following sections describe how the manufacturing process was modified in order to address these problems and minimize porosity.

a) Vacuum degassing of the melt before ignition: Adsorbed water, low boiling-point impurities, and dissolved hydrogen on the surface of powders prior to SHS, are possible sources for impurity-generated porosity in SHS products. Due to the high combustion temperatures, these impurities are volatilized as the wave propagates through the reactants during the SHS processs [11, 18]. Therefore, the best way to reduce these sources of porosity is to use highly purified initial powders which can eliminate or significantly reduce the formation of impurity-generated porosity, as well as vacuum degassing the molten mixture to remove trapped gases before ignition. By vacuum degassing of the molten mixture, the porosity in the solidified precursor reactive mixture was reduced from around 25% to 3%, eliminating the round, bubble-like pores (gas pores). Fig. 2-11 shows BSE images from reactive mixtures with and without vacuum degassing. The remaining pores in the cermet after degasification appear more elongated, and when observed with SEM, it appears as if the grains were pulled apart during solidification (Fig. 2-12).



Figure 2-11. Backscattered Electron images showing reactive mixture; (a) without vacuum degassing, (b) with vacuum degassing (same composition)



Figure 2-12. Secondary Electron Image showing grain separation during solidification

b) Particle size of reactants: With the use of coarse Cr powder, both the microstructure and the XRD patterns (Figs. 2-8 and 2-10) show that the combustion synthesis was incomplete, because residual Cr-rich phase was detected by XRD and observed with SEM in the final product. The incompleteness of the combustion reaction may be explained by the coarseness of the Cr powder, since a negligible amount of residual Cr-rich phase could be seen in the combustion-synthesized product with fine Cr powder. Smaller reactant particles may lead to the different degree of

completeness of the reaction, because of a higher surface to volume ratio for the powder, with more contact surfaces and shorter distances for the sulfur atoms to diffuse to the chromium particles. If the reaction is incomplete, sulfur will remain unreacted inside the sample. The remaining sulfur might then vaporize because of the high temperature of the reaction and may lead to further porosity generation [19, 20].

Theoretically, there should be no remaining Cr and S when the composition is stoichiometric (Cr:S molar ratio 1). However, the Cr remaining indicates that some of the sulfur has also remained and therefore vaporized during the reaction. Also, in Fig. 2-10 the XRD patterns show there is sulfur remaining in the samples containing coarse Cr powder.

This explains why the cermet produced with coarse Cr powder is more porous than the cermet made with fine Cr powder, with the same composition (Fig. 2-8 in section 2.5). Consequently, finer Cr powders are preferable, but there is a limit imposed by the requirement for the molten composition to be fluid enough to be melt-cast. Large particle sizes produce a fluid-like rheology in the melt, while the very fine Cr particles result in a thick, paste-like composition. It is difficult to remove trapped gases from highly viscous melts by vacuum degassing.

c) Preheating of the mold: In order to fill the mold more easily without producing any pores in the reactive mixture, the mold should be preheated to a temperature near the melting point of sulfur to avoid the sudden solidification of the reactive mixture.

d) Static pressure: The amount of gas products strongly depends on the hydrostatic pressure during the reaction (Fig. 2-1). Higher static pressure of the inert gas atmosphere in which the synthesis is conducted can reduce gas formation by suppressing the vaporization of sulfur and other non-equilibrium processes that may occur within the flame reaction zone. In addition, increased pressure decreases the relative volume occupied by gases that are evolved, further reducing the porosity. Experimentally, the porosity of the product synthesized with a Cr:S molar ratio of 1.15 was measured following synthesis in a high-pressure reactor pressurized with argon and is reported in Fig. 2-13b. The porosity was determined via analysis of the images. Increasing static pressure by increasing the pressure inside the reactor has a visible effect of reducing the

porosity, as shown on Fig. 2-13a. All samples were synthesized with a Cr:S 1.15 molar ratio and with fine Cr powder $(3 \mu m)$.

Increasing the static pressure at which the synthesis occurs to 136 atm leads to a reduction in the porosity of the product to below 14%. However, an additional increase in the pressure above 136 atm does not appear to significantly reduce the porosity further.



(a)



Figure 2-13. (a) Cut samples which were synthesized at 3 different pressures, and (b) Porosity as a function of static pressure at which the synthesis was conducted

e) Vacuum degassing during synthesis: We also investigated the effect of applying vacuum during the synthesis process. For this part of the investigation, the sample was ignited in the molten state, and the samples were synthesized with a Cr:S 1.15 molar ratio and with fine Cr

powder (3 μ m). The samples produced had large pores and were almost as porous as the samples first ignited at ambient pressure (Fig. 2-14). Vacuum degassing during the synthesis process did not appear to decrease the porosity or improve the quality of the final product.



Figure 2-14. Cut sample which was ignited under vacuum

f) Directional solidification: As stated above, there were many micro and macro cracks in the samples produced. In addition, in some samples there were central cracks and voids (Fig. 2-15a). Fig. 2-15b also shows BSE images of the micro and macro cracks in samples which were synthesized under 136 atm with a Cr:S 1.15 molar ratio and with fine Cr powder (3 μ m). These cracks might be a result of thermal shock due to the high cooling rate in SHS (10^3-10^6 °C/min). Most metals and alloys shrink when they change from a liquid to a solid state [21]. As a result, a shrinkage defect will form when the solidification is governed by progressive solidification over directional solidification.







Figure 2-15. (a) Cut samples which show central void and cracks, and (b) BSE image of the micro and macro cracks in produced sample synthesized under 136 atm with Cr:S 1.15 molar ratio and with fine Cr powder (3 μ m)

Directional solidification is achieved by a one-dimensional thermal flux along the sample axis and sufficient heat exchange between the sample and cooling medium. Therefore, in order to prevent cracks and voids from developing, we developed a method to cool the samples slowly and directionally after the reaction. Fig. 2-16 shows a schematic of the directional solidification method in which a jacket of SHS mixture was cast on top of a shallow layer of inert ceramic. This prevented heat loss from the top of the sample, while allowing a small amount of heat to transfer through the inert ceramic, and a greater amount of energy to escape through the base of the steel mold. The solidification front therefore moves in a unidirectional manner from bottom to top. This modification successfully suppressed crack formation (Fig. 2-16).



Figure 2-16. Schematic representation of directional solidification method, and SEM images from a produced sample by directional solidification method in different magnifications

g) *Supercritical sulfur:* Because of the high temperature of the reaction it is possible that some pores may be generated by vaporization of sulfur in the flame front. Also, if sulfur gas was produced rather than consumed during combustion, the existence of sulfur may lead to additional generation of porosity, in a manner similar to the effect of impurity evolution. Since there is no distinction between liquid and gas phases above the critical point, in the next step, we increased the pressure inside the chamber above 275 atm. Since the reaction temperature of Cr-S is 2333° C, after ignition, sulfur would be above its liquid-vapor critical point, such that sulfur as a homogenous supercritical fluid. The critical temperature and pressure for sulfur are 1041°C and 207 atm, respectively. The result was promising, and the porosity of produced cermet decreased to about 7%. Fig. 2-17 show BSE images with different magnifications from a sample produced with the directional solidification method with supercritical sulfur (Cr:S 1.15 molar ratio and with fine Cr powder (3 µm).



Figure 2-17. SEM images from a produced sample by directional solidification method with supercritical sulfur in different magnifications

Thus, in the modified manufacturing process (shown schematically in Fig. 2-18) the particle size of the reactants was considered. Then, the molten mixture of Cr and S powders was degassed in a vacuum chamber (vacuum pressure= 95 kPa) for about 20 minutes and at high temperature to maintain sulfur in a molten state. After that, it was poured into a preheated mold to prevent contact solidification of the melt. The solidified reactive mixture was then placed in a pressurized reactor and ignited in a high-pressure inert gas (Ar) environment, by using an electrically-heated tungsten wire embedded in the sample. By igniting the sample above the liquid-vapor critical point of sulfur, and cooling the samples slowly and directionally after the reaction, the porosity inside the produced cermets was reduced to about 7%, and no cracks were observed inside the cermets (Fig. 2-17).



Figure 2-18. Schematic of the modified manufacturing process

2.7 Combustion front quenching test

As mentioned above, we have introduced and investigated a new method for producing metalsulfide cermets to enable the possibility to perform net-shape synthesis of dense, near theoretical density product. By improving the manufacturing process we were able to produce a dense cermet with no cracks. Then, in the next step we evaluated the possibility of net-shape manufacturing of these cermets by measuring the quenching thickness. Quenching thickness is the minimum size of sample that can sustain flame propagation with heat loss and is one of the fundamental measurements that can be made in a reactive material. Measurement of quenching thickness is of critical importance to the ability to perform net-shape synthesis of complex shapes. Therefore, we measured the quenching thickness of Cr-S mixtures to investigate the lower limit for the thickness of the sample.

To measure the quenching thickness, a rectangular (slab) charge was cast in a brass channel of 1 cm width and a charge thickness that decreased in successive steps as shown in Fig. 2-19. The

flame was initiated in a large reservoir of mixture and then entered the test section, encountering successively smaller charge thicknesses. These tests were performed at ambient pressure (1 atm). The location of quenching was easily identified by melting away the unreacted mixture as well as the visual difference of appearance between the reactant and product upon recovery of the sample.



Figure 2-19. Drawing of the (a) channel (front view), (b) combustion front quenching test (side view)

The results showed that Cr-S mixtures using the fine Cr powder $(3 \ \mu m)$ did not quench in even the smallest channel thickness, successfully propagating in channels as small as 0.6 mm. It was also found that the quenching dimension did not have a strong dependence on the Cr:S ratio. Therefore, it can be concluded that regardless of the chemical composition of the mixture, Cr-S mixtures have very small quenching thicknesses which enables us to perform net-shape synthesis of CrS-Cr cermets with sub-millimeter scale features.

2.8 Conclusions

In this paper we demonstrated the ability of the melt-casting SHS technique to produce near theoretical density chromium/chromium sulfide ceramic metal composite (cermet) articles of a

desired shape. Although thermodynamics predicts that no gas is produced during the reaction for a Cr-rich formulation, synthesis performed at ambient pressure resulted in a product with considerable porosity. The use of a degassed, melt-cast reactive mixture with excess chromium, and performing the synthesis under high pressure has been shown to be the essential requirements to minimize porosity. The ability of the Cr-S system to sustain propagation in small dimension charges, with a quenching distance less than 1 mm with fine Cr powder, implies that the technique developed here can be used for net-shape synthesis of complex shapes with high tolerances. With the various improvements to the manufacturing process, the porosity was reduced from 70% to 7%. This level of porosity obtained is considerably less in comparison to samples produced by other SHS techniques and is comparable to the bulk form of industrially manufactured ceramics [11]. This residual porosity may be attributed to the release of gases evolved by impurities (oxides, moisture, etc.) and the "freezing" of porosity caused by nonequilibrium evolution of gases during the combustion process. Chromium sulfide is also denser than the initial reactive mixture and the liquid sulfide product, which results in shrinkageinduced gaps and pores in the final product. The density of the samples was measured for 8 different samples with a Cr:S molar ratio equal to 1.15, before and after the ignition. The values obtained were 3.78±0.01 g/cc for the reactive precursor mixture compared with 4.04±0.05 g/cc for the cermet produced.

This novel method simplifies the preparation of samples with different shapes, thicknesses, and with a green density close to theoretical density. It also eliminates trapped gases within the reactive mixture, improving the quality of the synthesized product, and homogeneity of the product structure. Cermet samples produced by this method can be used as ballistic armors, heating elements, protective coatings to resist corrosion from liquid metals, and magnetic structures.

2.9 Acknowledgments

This work was supported by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada. Atefeh Nabavi was partially supported by a McGill Engineering Doctoral Award. The authors would like to thank Prof. In-Ho Jung for his contributions to the thermochemical calculations. Input from Prof. Andrew Higgins is also gratefully acknowledged.

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Link between chapter 2 and chapter 3

In the previous chapter, a novel method for manufacturing metal sulfide cermets was introduced and investigated. The manufacturing process was modified in order to minimize cracks and porosity inside the cermet samples. Our findings showed that dense cermets with a specific structure have been obtained. In order to control the properties of the cermets produced, we need a better and clear understanding of the thermodynamics, reaction mechanism, and combustion behavior of the Cr-S system. Therefore, in the next step we investigated the combustion reaction in detail. Thus, the combustion properties were characterized, i.e., the quenching dimensions, reaction zone thickness of the flame front, chemical thickness, flame propagation rate, and burning rate.

Chapter 3

Combustion synthesis of metal sulfide composites

Chapter 3: Combustion synthesis of metal sulfide composites

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3.1 Abstract

Self-propagating high-temperature synthesis of a ceramic metal composite (cermet) consisting of chromium-chromium sulfide is developed. The thermochemical properties and phase diagram of the chromium-sulfur system are investigated using a comprehensive multi-phase, multi-component equilibrium database. Thermodynamic calculations show that some metals such as chromium, iron, and zinc can react with sulfur without the formation of gaseous products at normal pressure and yet demonstrate sufficiently high flame temperatures to support reactive wave propagation. The quenching dimensions (thickness and diameter) are measured in different geometries, and an analysis of the quenched sample enables the chemical thickness of the reactive front to be estimated. The quenching dimension and chemical thickness are found to be on the order of a millimeter and exhibit little dependence on the Cr:S ratio when the reaction is Cr-rich. The velocity of the reactive front is also measured and again appears largely independent of the Cr:S ratio. Visualization of the front highlights the importance of differentiating propagation velocity and fundamental burning velocity.

Keywords: combustion synthesis; SHS; metal-sulfur reaction; quenching, propagation velocity, burning rate, combustion wave quenching

3.2 Introduction

Due to its simplicity and utilization of highly exothermic reactions, self-propagating hightemperature synthesis (SHS) offers a competitive technique to produce advanced materials. In its traditional implementation, however, SHS suffers a disadvantage when utilizing loose powder compacts. Thus, high-pressure, high-temperature sintering is required to produce the nonporous product of a desired shape. Alternatively, SHS can be performed in a high-pressure press to provide sintering simultaneously with combustion synthesis. High-temperature sintering is an expensive and technologically complex procedure, offsetting the advantages of SHS. Hightemperature sintering of metal-sulfides (the material that is the focus of the current study) is even more complicated because it must be performed in an H_2S atmosphere to prevent the loss of sulfur.

In this paper, it is shown that metal-sulfur compositions offer the option of an SHS technique capable of net-shape production with the product at near theoretical density, without resorting to sintering or other post-SHS processing. While other green compositions used in SHS are usually powder compacts of significant porosity, the green mixture of metal-sulfur composition can be cast into nonporous shapes required for the final article. This property derives from the fact that sulfur melts at a relatively low temperature (115 °C), well below the temperature at which significant exothermic reaction begins (usually above 300 °C [1]), enabling the green mixture to be melt cast. Another essential property that permits net-shape processing is the lack of gas production in some metal-sulfur reactions with flame temperatures that are well above the melting point of the final product.

These unique properties of the metal-sulfur SHS system are used in the present paper to develop the background of a technology for net-shape manufacturing of the chromium-chromium-sulfide cermet composites (Cr-CrS), a promising material for ballistic protection. A Cr-CrS cermet has the hardness of stainless steel with only half of the density of steel [2]. Metal-sulfides are also known to have good bonding properties to different metals and other ceramics. Thus, harder inclusions (such as boron carbide or silicon carbide) can be easily imbedded into sulfide ceramics during the SHS process, providing the possibility for producing a functionally-graded material or other advanced material design approaches.

Controlling the final properties of the combustion products is dependent on an understanding of the thermodynamics, kinetics, and mechanism of structure formation. In order to pursue the combustion synthesis approach to fabricating a Cr-CrS cermet, we begin with thermochemical and phase diagram calculations of the Cr+S reaction while varying the equivalence ratio and

pressure at which the synthesis occurs to determine the adiabatic flame temperature and phases of the product at flame conditions. The quenching dimension (minimum size of sample that can sustain flame propagation with heat losses) in various geometries is of critical importance to the ability to perform net-shape synthesis of complex shapes. The quenching dimension is linked to the reaction zone thickness of the flame front, and analysis of the reactant/product interface recovered from a quenching experiment enables the chemical thickness to be directly measured. The flame propagation rate determines the heating and cooling rate, which influences the grain growth and other properties of the product. Characterization of these combustion properties is the aim of this paper.

3.3 Thermochemical and Phase Diagram Calculations

The thermodynamics of the Cr-S reaction were investigated using FactSage, a multiphase, multicomponent chemical equilibrium software package which includes extensive databases (FTmisc and FACT53) of known chromium sulfur compounds and phases [3]. We also calculate the adiabatic flame temperatures of other metal-sulfur systems, including Fe-S and Mn-S. The FactSage package was used to compute the adiabatic flame temperature and volumetric gas production (volume of gas at pressure normalized by volume of initial composition, giving an indication of the porosity of the final product) as a function of Cr:S ratio at various pressures, as shown in Fig. 3-1. These calculations predict that the reaction should become completely gasless as the composition reaches stoichiometric (Cr:S molar ratio 1), at which point the adiabatic flame temperature peaks at 2606 K. Increasing the Cr content beyond the stoichiometric value reduces the adiabatic flame temperature, but the reaction remains gasless.

The phase diagram of the Cr-S system at a pressure of 1 atm is shown in Fig. 3-2 [4]. The phase diagram (in combination with the calculation of adiabatic flame temperature) indicates that the products of the synthesis should be in the liquid state (prior to cooling and solidification) for the range of chromium-rich compositions ($1.0 \le \text{Cr:} \text{S} \le 1.6$) studied in this paper, which is an advantageous property for net-shape synthesis and good adhesion to solid inclusions that might be added to the composition.



Figure 3-1. Adiabatic flame temperature and gas production as a function of Cr:S molar ratio



Figure 3-2. Calculated optimized condensed chromium-sulfur phase diagram at a total pressure of 1 bar. Abbreviations; Pyrr stands for high-temperature chromium pyrrhotite, S (orth) for solid pure sulfur with orthorhombic structure, and bcc for the body-centered cubic chromium solution phase [4]

3.4 Experiment

3.4.1 Materials and manufacturing process

The chromium powders were obtained from Atlantic Equipment Engineers (NJ, USA), with a purity of 99.8%, and with particle size ranges given by the supplier of 1-5 μ m (CR-102) and <44 μ m (CR-103). The particle size distribution of the Cr powders, measured with an LA-920 Horiba laser scattering particle size analyzer shows the CR-102 and CR-103 powders have average particle sizes, based on volume, of 3 μ m and 26 μ m, respectively. Sulfur powder with a purity of 99.5% was obtained from Alfa Aesar (S4981, MA, USA). The average particle size was smaller than 150 μ m (-100 mesh) but did not influence the fabrication process, since the sulfur was always melted to form the reactive mixture.

For some of the experiments in section 3.5, Fe powder was used which was obtained from Atlantic Equipment Engineers with purity of 99.9%, and with a particle size range given by the supplier of <44 μ m. The particle size distribution of the Fe (FE-102) was also measured and shows the FE-102 powder has an average particle size, based on volume, of 34 μ m (Fig. 3-3).



Figure 3-3. Particle size distributions of the Cr and Fe powders; fine Cr powder (CR-102, with average particle size of 3 μ m), coarse Cr powder (CR-103, with average particle size of 26 μ m), and Fe powder (FE-102, with average particle size of 34 μ m)

The preparation of the chromium-chromium sulfide cermets can be explained in few steps (Fig. 3-4). Chromium and sulfur powders were mixed in a roller mill with the desired mass ratio. The powder mixture was then heated in a mantle up to a temperature slightly above the sulfur melting temperature (i.e., temperature > 120° C), but well below the melting temperature of chromium (1907°C). The molten mixture of Cr and S powders was degassed in a vacuum chamber (pressure=95 kPa) for about 20 minutes and at a high temperature to maintain sulfur in the molten state. After that, the mixture was poured into a preheated mold to prevent contact solidification of the melt. Upon cooling of the reactive mixture the sulfur solidified, forming a matrix of sulfur containing well-dispersed chromium inclusions. The solidified reactive mixture was then placed in a pressurized reactor and ignited under a high-pressure inert gas (Ar) environment by using an electrically heated tungsten wire embedded in the sample. By igniting the sample above the liquid-vapor critical point of sulfur and cooling the samples slowly and

directionally after the reaction, the porosity inside the cermets produced was about 7%, and no cracks were formed within the product. The self-sustained flame propagated throughout the sample, producing the final metal-sulfide product. Depending on the initial metal-sulfur molar ratio, the amount of unreacted metal remaining in the product varies, enabling the final product to range from a brittle ceramic to a more ductile metal-like material [5].



Figure 3-4. Schematic of the manufacturing process

3.4.2 Sample Preparation

For the various combustion experiments described in Sections 3.5 and 3.6 below, the molten metal-sulfur mixture was vacuum degassed and then poured into channels which were heated on a heating plate to prevent contact solidification of the melt. The fine Cr powder remained in suspension in molten sulfur while the coarse Cr powder tended to settle in molten sulfur, making preparation of a uniform mixture more difficult. Use of the coarse powder was motivated by the desire to obtain a quenching measurement (Section 3.5) and to increase the Cr content to values

much greater than stoichiometric (Section 3.5 and 3.6), since the large particle size permitted a greater Cr content while still having a fluid-like rheology in the melt, while the fine Cr resulted in a paste-like composition once the Cr:S ratio exceeded approximately 1.3. After gradual solidification, the metal-in-sulfur matrix was hand sanded to remove excess material from exposed surfaces. In select experiments, the mixture was reheated by placing the experimental channel on a heating plate above the melt temperature of sulfur such that the synthesis could be accomplished in the molten state of the green mixture.

3.5 Quenching Thickness and Reaction Zone Thickness Measurements

3.5.1 Quenching Thickness

Measurement of the minimum dimension (thickness of a wide rectangular channel or diameter of a cylindrical tube) that a flame can successfully propagate while experiencing heat loss to the channel walls is one of the fundamental measurements that can be made in a reactive material and has practical relevance to net-shape manufacturing of complex shapes.

To measure the quenching thickness in two different geometries, a cylindrical charge was cast in a series of brass cylinders of decreasing internal diameter (Fig. 3-5a) and a rectangular (slab) charge was cast in a brass channel of 1 cm width and a decreasing thickness in successive steps 0.25 mm of charge thickness (Fig. 3-5b). The flame was initiated in a large reservoir of the mixture and then entered the test section, encountering successively smaller charge dimensions. The quenching location was readily identified by melting and removing the unreacted mixture as well as from the visual difference between the reactants and products upon recovery of the sample.



Figure 3-5. Brass channels used to measure (a) quenching diameter and (b) quenching thickness

Chromium

Mixtures using the fine Cr powder (1-5 μ m) did not quench in even the smallest thicknesses and successfully propagated in channels as small as 0.6 mm. Thus, the coarse Cr powder (<44 μ m) was used in the quenching studies. A summary of the results, showing Go/No-Go results for the flame propagation in the various channels, is shown in Fig. 3-6. These tests were performed at ambient pressure (1 atm). Note that the boundary between successful propagation and quenching was sharp and reproducible. Usually the flame was observed to quench within a few characteristic diameters or thicknesses upon encountering the critical dimension. The quenching dimension did not have a strong dependence on the Cr:S molar ratio, and it is of interest to note that the critical quenching diameter of a cylindrical charge is approximately twice the thickness of the critical thickness of a rectangular slab.



Figure 3-6. Summary of results of quenching diameter and quenching thickness measurements for Cr-S mixtures, in which d_{crit} is critical quenching dimension and t_{crit} is critical quenching thickness

Iron

To measure the quenching thickness in an iron-sulfur system, a reactive mixture of ironsulfur with a molar ratio in the range of $1.0 \le \text{Fe:S} \le 1.6$ was melted and poured into channels with two different geometries, a cylindrical charge and a rectangular (slab) charge, in the same way as for the tests with the Cr-S mixture. These tests were performed at ambient pressure (1 atm). The quenching dimension results are shown in Fig. 3-7 note that the boundary between successful propagation and quenching was once again sharp and reproducible. Results show that the critical quenching diameter of a cylindrical charge in Fe-S mixture is approximately twice the thickness of the critical thickness of a rectangular slab. And also it seems that the quenching dimension did not have a strong dependence on the Fe:S ratio.

Effect of pressure on quenching thickness

To evaluate the effect of pressure on quenching thickness and reaction zone thicknesses, some of the samples were placed in a pressurized reactor and ignited in a high-pressure inert gas (Ar) environment (136 atm). The results obtained show that by increasing the applied pressure from 1 atm to 136 atm, the quenching thickness decreases regardless of either the Cr:S or Fe:S molar ratio (Fig. 3-7).



Figure 3-7. Summary of results of quenching thickness measurements for Cr-S and Fe-S mixtures, ignited at P=1 atm and P=136 atm

3.5.2 Reaction Zone Thickness

The samples recovered from the quenching experiments were effectively "frozen" in their reaction zone structure at the moment of quenching. The samples were sectioned, polished, and

analyzed to investigate the structural changes that occur in the transition zone moving from the reactants to products. Examination of the transition zone also permits the effective chemical thickness of the wave to be determined. The structure within the reaction zone and unreacted section was analyzed using optical microscopy and scanning electron microscopy (SEM). The volume fractions of the different phases were estimated by the aid of image analysis based on the ASTM E 562-02 standard test method [6] with the aid of Clemex, an image analysis software. By analyzing the backscattered images taken with SEM and using a quantification feature of Clemex, the volume fraction of different phases can be extracted as statistical data. Since the atomic masses of chromium, sulfur and chromium sulfide are significantly different from each other, these elements could be easily identified in backscattered images. The change of volume fraction of the different compounds with distance in the reacted and unreacted parts of the sample with a Cr:S molar ratio equal to 1.35 is shown in Fig. 3-8. As expected, by moving from the unreacted to reacted area, the volume fraction of sulfur and chromium decreased, while the volume fraction of chromium sulfide gradually increased until it reached a maximum constant value. The chemical thickness is the length of the transition zone between the completely unreacted and reacted areas, from zero to a constant maximum volume fraction of chromium sulfide. From the results in Fig. 3-8, the chemical thickness appears to be approximately 0.6 mm, and from similar analysis of samples recovered for the different geometries (cylindrical and rectangular) and for varying Cr:S ratios (from 1.0 to 1.6) it was found that the chemical thickness of the flame was approximately constant, and in particular ranged from 0.4 and 0.6 mm.

Effect of pressure on reaction zone thickness

The chemical thickness of samples ignited at ambient pressure was approximately twice the chemical thickness of those samples ignited under high pressure, regardless of the metal-sulfur molar ratio. While varying the Cr:S and Fe:S molar ratios (from 1:1 to 1.3:1), it was found that the chemical thickness of the samples ignited under pressure was approximately constant.



Figure 3-8. Analysis of sample obtained from quenching thickness experiment, showing (a) images of green and reacted mixture and (b) analysis of composition

3.6 Propagation Velocity and Burning Rate Measurement

Flame propagation speed is another important parameter that influences the state of the products and can also give insight into the propagation mechanism and reaction chemistry. While propagation velocities have been widely reported for SHS mixtures, it is important to differentiate between the propagation velocity of a flame (the velocity it appears to move relative to a fixed observer) and the fundamental burning rate (the velocity of material flowing into the combustion front in the normal direction, relative to the wave). Differentiating these quantities necessitates observation of the flame front geometry. For these experiments, the composition was cast into rectangular channels with a U-shaped cross section, leaving the top surface open for direct observation. Early tests showed that burning Cr sparks were violently ejected from the top surface of the burning composition at the flame front, occasionally traveling well ahead of
the flame and igniting the composition, thus leading to inaccurate measurements of the propagation velocity. To suppress this effect, the channels were inserted into a chamber with an argon flow of sufficient velocity opposing the direction of flame propagation to prevent upstream movement of sparks generated within the reaction zone. These tests were performed at ambient pressure (1 atm) and the flame propagation was recorded with a high-speed camera (Casio Exilim Pro EX-F1). Fig. 3-9 shows a schematic of the experimental set-up for observation of the flame propagation. The fine Cr powder (< 5 μ m) was used for these compositions, except for a Cr:S ratio of 1.6, where a 1:4 ratio of coarse to fine Cr was used. A sketch of a typical image of the flame front obtained in these experiments is shown in Fig. 3-10 and photographs of flames propagating in either solid or molten Cr-S mixtures, with various molar fractions, are shown in Fig. 3-11.



Figure 3-9. Schematic of the experimental set-up for observation of flame propagation



Direction of propagation

Figure 3-10. Sketch of the shape of the flame propagating in the Cr-S mixture within a channel (viewed from top, observing the open surface of the brass U-channel)



direction of propagation

Figure 3-11. Image of flame propagation (viewed from top, observing open surface of brass Uchannel) for either a solid or molten mixture of Cr-S with molar ratios of Cr:S = 1, 1.3, and 1.6 at ambient temperature and pressure

The measured propagation velocities are shown in Fig. 3-12 and vary from 15 to 70 mm/s, which are significantly greater than previously reported flame speeds in metal-sulfur mixtures in closed

cylindrical channels, which are usually in the range 2 to 10 mm/s and with Cr-S previously being measured at 8 mm/s [1]. The results also show a counterintuitive trend with flame speed increasing with increasing Cr content (above stoichiometric, where adiabatic flame temperature should decrease). However, the photographs in Fig. 3-11 indicate that the large velocities were associated with flames that are "V"-shaped in which the leading edges of the flame are located adjacent to the channel walls. This pattern can be attributed to a forward convective flow of product material occurring at the interface between the mixture and the channel wall. While the melt-casting technique minimized gaps that might be responsible for a convective-driven flow, local melting of the initial composition and expansion of the liquid products is hypothesized to result in a forward convective flow of products at the confining wall. Examination of the high-speed movies also strongly suggested that the flame front on the bottom of the channel (not directly visible) was leading the side wall propagation. Tests performed with three different channel materials (aluminum, brass, steel) did not reveal any significant correlation of propagation speed with confinement material, suggesting that the observed flow is not driven by surface tension.



Figure 3-12. Summary of flame propagation velocity measurements

The triangular shape of the flame front could be suppressed in some cases by reheating the composition past the melting point of the sulfur such that the entire charge was molten prior to propagation. In the case of a stoichiometric composition, the front was approximately parabolic in shape with the region near the center of the charge leading and the propagation speed was only about 15-20 mm/s. The V-shaped front formation reappeared with Cr-rich molten compositions, however, as these compositions had a paste-like consistency and did not exhibit a fluid-like rheology when heated above 120 °C. If the half-angle of the front is measured from the images (Fig. 3-11), then the normal burning velocity can be inferred from the measured propagation velocity, assuming that the leading edge at the wall initiates a sequence of normally propagating

flamelets, such that the half-angle of the front is given by $_{"} = \sin^{-1}\left(\frac{v_{\text{burning}}}{v_{\text{propagation}}}\right)$. If this correction is

applied to the data in Fig. 3-12, then the burning velocity for the various compositions falls within the range of 8 to 12 mm/s, consistent with previous measurements of burning velocity in metal-sulfur mixtures.

3.7 Discussion and Conclusions

This paper has demonstrated the ability of the melt-casting SHS technique developed here to produce near-TMD chromium/chromium sulfide ceramic metal composite (cermet) articles of a desired shape. Although equilibrium thermodynamic calculations predict that no gas evolution will occur for a Cr-rich formulation, synthesis performed at ambient pressure resulted in a product with considerable porosity unless special procedures were invoked. The use of a degassed, melt-cast green mixture with excess chromium and with the synthesis occurring under high pressure (100 atm) has been shown to be the essential requirement for realizing a low porosity product. The ability of the Cr-S system to sustain propagation in very small dimension charges (quenching distance < 1 mm with fine Cr powder) means that the technique developed here is capable of performing net-shape synthesis of complex shapes with high tolerances. To date, an upper limit on the Cr content that permits a self-sustained reaction to occur has not been found. This study stopped at a Cr:S ratio of 1.6 times stoichiometric due to the requirement that the molten composition still be fluid enough to be melt-cast. It is possible that using a bimodal distribution of particle sizes will enable even greater Cr content to be realized, enabling the final product to be "dialed" from a brittle ceramic to a more ductile metal-like material.

The chemical thickness of the front estimated from the microscopy analysis of the quenched samples was found to be approximately 0.5 ± 0.1 mm. Due to the extremely low heat diffusivity of sulfur ($= 10^{-7} \text{ m}^2/\text{s}$) [7], the estimated thickness of the preheat zone is on the order of 0.01 mm ($l_{\text{preheat}} \approx \frac{r}{v_{\text{burning}}} \approx \frac{10^{-7} \text{ m}^2/\text{s}}{10^{-2} \text{ m/s}} \approx 10^{-5} \text{ m}$), i.e., it is much smaller than the chemical reaction zone.

Thus, the flame thickness in the present case is dominated by the thickness of the reaction zone. The quenching diameter and the quenching thickness of the rectangular samples were measured to be 2 mm and 4 mm, respectively. Thus, the ratio of the characteristic quenching sizes to flame thickness was correspondingly four and eight, respectively, for rectangular and cylindrical channels, in good agreement with the qualitative framework of flame quenching theory. This result illustrates that flames in metal-sulfur compositions are dominated by the reaction zone thickness, in contrast to classical gaseous flames for which the flame thickness is dominated by the preheat zone. Finally, the observation of anomalous propagation modes in which the combustion front appears to lead at the edges of the charge reiterates the importance of

differentiating the apparent propagation velocity from the fundamental (normal) burning velocity for SHS systems with liquid products.

3.8 Acknowledgments

This project was supported under NSERC Strategic Grant "Design and Net-shape Manufacturing of Hybrid Composites for Ballistic Protection" with Francois Barthelat serving as principal investigator. The authors would like to thank Prof. In-Ho Jung for his contribution to the thermochemical calculations.

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Link between chapter 3 and chapter 4

In the previous chapter, the combustion parameters of the Cr-S system were studied. It is understood that controlling the final properties and characteristics of the combustion products is dependent on an understanding of the mechanism of structure formation. Investigating the reaction mechanism means we must determine the steps of the synthesis reaction as well as the intermediate products. Therefore, the next chapter is dedicated to a better understanding of the mechanism of the Cr-S reaction and the evolution of the microstructure of the CrS during the SHS reaction. In this respect, the mechanism of structure formation during the combustion reaction is studied by following the propagation of the combustion front. The microstructural evolution in the quenched specimen is observed and analyzed with SEM and energy dispersive X-ray (EDX) spectroscopy. The constituent phases of the combustion-reacted product are inspected with XRD. Based on the experimental results obtained, a mechanism for the combustion reaction is proposed, and a model corresponding to the mechanism is drawn.

Chapter 4

Microstructural evolution during the combustion synthesis of chromium sulfide

Chapter 4: Microstructural evolution during the combustion synthesis of chromium sulfide

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4.1 Abstract

To investigate the mechanism of the combustion synthesis of a chromium-chromium sulfide composite, a combustion front quenching test is carried out with a reactive mixture of chromium and sulfur. The microstructural evolution in the quenched sample is observed with scanning electron microscopy and analyzed with energy dispersive X-ray spectroscopy. In addition, the constituent phases of the final product are inspected with X-ray diffraction. Based on the experimental results, a diffusion-dissolution-precipitation mechanism is proposed to describe the conversion of the initial reactants consisting of chromium particles embedded in a sulfur matrix to the final chromium sulfide compound. It is observed that the reaction mechanism depends on the chromium particle size. In the case of small particles, the final structure consists of chromium sulfide, whereas with large particles the chromium does not completely dissolve and the final product consists of unreacted chromium particles surrounded by chromium sulfide.

Keywords: Microstructural evolution; chromium sulfide; combustion synthesis

4.2 Introduction

It is generally accepted that controlling the final properties and characteristics of a material produced by combustion synthesis is dependent on an understanding of the kinetics of the reaction and the mechanism of structure formation. To elucidate the reaction mechanism it is necessary to determine the intermediate steps during reaction synthesis as well as identify the intermediate products. The mechanism of structure formation during the combustion reaction can

be studied by various techniques including quenching the combustion wave during synthesis and carrying out post-test analysis of the sample [1].

One analysis technique is based on direct electron-microscopic observation of the interaction between two reactants. In this method, a particle of one reactant is placed on a layer of a second reactant, and the reaction is initiated by heating the sample with the aid of a high-intensity electron beam from the microscope. A second technique is time-resolved X-ray diffraction (TRXRD) which provides a direct in-situ observation of the sequence of high-temperature phase transformations. This experimental technique is challenging to achieve and is also characterized by difficulties in the interpretation of the results [1, 2]. A third technique is based on rapid quenching of the reaction front during its propagation through the reacting mixture. Combustion front quenching (CFQ) may be accomplished, for example, by dropping the sample into liquid argon (Deevi and Munir, 1990) or using a bulk copper wedge to induce high heat losses to quench the reaction (Merzhanov et al., 1990). The flame is extinguished due to the combination of the rapid heat loss to the copper block and the shrinkage of the cross section. This approach allows the investigator to relate the microstructure of the end products with the different experimental conditions including the reactant particle size, inert content, green density and so on. Following reaction quenching, the phase composition and microstructure of the different zones associated with the combustion wave can be identified using a layer-by-layer analysis of the quenched regions by scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD). If the quenched sample is investigated without any grinding or polishing, only the structure of the surface shape may be observed. Therefore, to observe the internal microstructural evolution of the reactant particles, it is conventional to grind and polish the quenched samples prior to examining them with the various analytical techniques [3, 4].

It is of interest to review some of the different reaction mechanisms that have been proposed to occur during self-propagating high-temperature synthesis of metallic systems with a liquid phase. Three such mechanisms are shown schematically in Fig. 4-1. The first one is a dissolution-precipitation mechanism in which the reaction between the reactant species A and B starts when the component with the lower melting point melts (in this case component B). The atoms of the solid component A start to dissolve in liquid B near the interfacial boundaries. When the melt is saturated, an AB intermetallide precipitates in the melt by means of crystallization. The

precipitate may remain in equilibrium with the melt at a given temperature. The second mechanism is based on a reaction diffusion model in which the formation of the product compound AB is determined by the transport of the components by unilateral or bilateral diffusion instead of a dissolution process. This reaction takes place at the particle surface at an infinite rate in the diffusion limit, as is the case for most SHS processes, and proceeds until all the A particles or the molten B component is consumed. In the third proposed mechanism, atoms of the solid component A dissolve in the liquid B following an increase in the temperature. When the melt is saturated, a solid phase AB (solid solution or intermetallide) forms inside the liquid, at the interface of A and B. The solute atoms penetrate and diffuse into the solid phase which has a lower melting point compared to component A. The decrease in melting temperature enables the solute atoms to transform into the liquid phase by means of melting. The layer of the solid phase formed grows continuously at the interface with solid component A (A-AB') and transforms into the liquid phase on the opposite boundary (B-AB'). This reaction model has been confirmed by a number of independent methods some of which with the aid of electron-microscopic visualization [5].



Figure 4-1. Schematic of three possible mechanisms of interaction in an SHS reaction between a solid component and a liquid phase [5]

To the best of our knowledge, no detailed study on the combustion synthesis of Cr-S has been reported to date. In the present work, the microstructural evolution during the combustion reaction of Cr-S mixtures is studied using the combustion front quenching approach. Coarse Cr powders are used in the tests, and the microstructural evolution in the quenched specimen is observed and analyzed with SEM and energy dispersive X-ray spectroscopy. The constituent

phases of the combustion-reacted product are inspected with XRD. Based on the experimental results, a diffusion-dissolution-precipitation mechanism for the combustion reaction is proposed.

Prior to describing the experiments fabricating a Cr-CrS cermet sample, we first consider some equilibrium thermodynamic calculations of the Cr-S reaction with varying equivalence ratio at atmospheric pressure, to determine the adiabatic flame temperature of the product at the flame conditions.

4.3 Thermodynamic Prediction

The thermodynamics of the Cr-S reaction were investigated using FactSage, a multiphase, multicomponent chemical equilibrium software package which includes extensive databases of known chromium sulfur compounds and phases [6]. The FactSage package was used to compute the adiabatic flame temperature as a function of the Cr:S ratio at ambient pressure, shown in Fig. 4-2, to determine if the Cr-S mixture is expected to support self-sustained flame propagation. The empirically established flame temperature limit in SHS systems at which a self-sustained combustion wave is typically observed is about 1800 K [7]. These calculations predict that the adiabatic flame temperature peaks at 2606 K, as the composition reaches stoichiometric (Cr:S molar ratio 1). Increasing or decreasing the Cr content beyond the stoichiometric value reduces the adiabatic flame temperature.



Figure 4-2. Adiabatic flame temperature as a function of Cr:S molar ratio

4.4 Mixture Procedure

The chromium powders used in the present work were obtained from Atlantic Equipment Engineers (NJ, USA). Two different Cr powders (99.8% purity) were used: a fine particle with an average particle size of 1-5 μ m and a coarse powder of <44 μ m (-325 mesh). Fig. 4-3 shows SEM images of the fine and coarse Cr powders. The sulfur was obtained from Alfa Aesar with a purity of 99.5%. The average particle size of the sulfur powder was smaller than 150 μ m (-100 mesh), however, in all experiments the sulfur was melted, so the initial particle size has no influence on the experimental results.



Figure 4-3. SEM images of Cr powder (a) fine powder (1-5 μ m), and (b) coarse powder (<44 μ m)

The chromium and sulfur powders were combined in the desired ratio via a mass balance and then mixed in a roller mill prior to being carefully heated in a heating mantel to the molten state of the sulfur (temperature > 120 °C). The molten mixture was then poured into a channel which was heated on a heating plate to prevent contact solidification of the melt. A tungsten wire embedded in the samples was electrically heated to ignite the mixture.

4.5 Combustion front quenching

In this study, combustion flame quenching experiments were performed in a rectangular three piece channel of 1 cm width and a decreasing thickness in successive steps of charge thickness as shown in Fig. 4-4a. The melted reactant mixture was poured into the assembled preheated mould from the top. The flame was initiated in a large reservoir of the mixture and then propagated into the test section, encountering successively smaller charge dimensions. The reaction was conducted at ambient pressure. Ignition was initiated by electrical heating of a tungsten coil which is inserted at the top of the sample as the melted mixture solidifies (Fig. 4-4b).



Figure 4-4. Schematic of (a) Brass channel used for combustion front quenching test, (b) the combustion front quenching test set up and, (c) the prepared sample for microscopic investigation

As mentioned, the flame will be extinguished at some point where the heat loss to the brass mould is such that the propagation cannot be sustained. The quenching location is easily identified by melting the remaining unreacted mixture as well as directly from the visual difference between the reactants and products upon recovery of the sample.

Following the flame quenching experiments, the three parts of the mould were separated. The sample was then sectioned longitudinally and fixed in epoxy (Fig. 4-4c). Samples were polished and then cleaned with ethanol. The structure within the reacted, reacting and unreacted zones was then analyzed with an optical microscope and SEM. Fig. 4-5 shows the back-scattered electron images of the microstructure of the various zones of the sample synthesized with <44 μ m Cr powder, with a Cr:S molar ratio equal to 1.

The volume fractions of the different phases were estimated by the aid of image analysis, based on the ASTM E 562-02 standard test method with the aid of the image analysis software Clemex [8]. By analyzing the backscattered images taken by SEM and using a quantification feature of Clemex, the volume fraction of the different phases can be extracted as statistical data. The change of volume fraction of the different compounds with distance in the different parts of the sample can then be determined. Moving from the unreacted to reacted area, the volume fraction of sulfur and chromium decreased, while the volume fraction of chromium sulfide gradually increased until it reached a maximum constant value. The length of the transition zone corresponds to the distance between the totally unreacted and reacted areas, from zero to a constant maximum volume fraction of chromium sulfide.



Figure 4-5. BSE images of the microstructure of (I) reacted zone, (II) reacting zone, and (III) unreacted zone corresponding to apparatus in Fig. 4-4 (c) of the sample synthesized with <44 μ m Cr powder, with a Cr:S molar ratio equal to 1.

Mixtures using the fine Cr powder (1-5 μ m) did not quench in even the smallest thicknesses and successfully propagated in channels as small as 0.6 mm. Therefore the coarse Cr powder (< 44 μ m) was used in the flame quenching tests. In addition, the length of the transition zone for the samples with a Cr:S molar ratio equal to one appears to be approximately 0.5 mm, and while varying the Cr:S ratio the length of the transition zone was found to be not strongly dependent on the Cr:S molar ratio.

The sectioned samples after quenching test were inspected layer by layer by X-ray diffraction (XRD; Cu K) to study the phase constituent. XRD phase composition analysis of the quenched Cr-S mixtures confirmed that the CrS compound forms during the reaction. The XRD patterns of the reacted, reacting and unreacted areas (I, II and III), as shown in Fig. 4-6, indicate that the reacted part is composed of CrS as the major phase with a small residual amount of Cr and S present. By moving from the reacted area (a) to the unreacted area (e), the amount of CrS decreases while the amount of Cr and S increases.

The XRD patterns of the five zones around the frozen combustion wave in Fig. 4-6 show that the unreacted zone (e) is a mixture of elemental Cr and S. The quenched reactant front or reacting area (d) is a mixture of elemental Cr, S and a small amount of CrS. The reacted zones (c) and (b) are composed of CrS with some unreacted elements Cr and S, with an increase in the CrS content. The product or reacted zone (a) is contains abundant CrS with a small amount of Cr and S as residual phases. From Fig. 4-6, it can be seen that by moving from zone (e) to (a), the peak intensities of Cr and S decrease gradually, whereas that of CrS increases gradually. The results also indicate that the CrS compound was directly synthesized with the Cr and S mixture, and no intermediate components appear during the combustion process.



Figure 4-6. Diffraction patterns to represent the stages of the reaction of Cr-S

4.6 Microstructural evolution

Fig. 4-7 shows an SEM image of the initial reactants in the unreacted zone of the quenched specimen. The bright particles are Cr, and the darker gray matrix consists of S, as indicated by EDS.



Figure 4-7. BSE image of the microstructure of unreacted zone - zone III in Fig. 4-4c of the sample synthesized with <44 μ m Cr powder, with a Cr:S molar ratio equal to 1

4.6.1 Solid-state diffusion between Cr particles and S

The first change that took place in the reacting zone, i.e., zone II in Fig. 4-4c, of the quenched specimen was the solid-state diffusion reaction between the Cr particles in contact with S, as shown in Fig. 4-8. Fig. 4-8a shows the Cr particle contacted with the S matrix. The microstructure of this region "F" in Fig. 4-8a is shown in Fig. 4-8b, and two diffusion layers denoted "E" and "F" were observed. The EDX results showed that the layer "F" (61 wt% Cr) was CrS, and the layer "E" (94 wt% Cr) was a Cr-matrix solid solution. The region "C" corresponds to a Cr particle and the region "D" is sulfur in Fig. 4-8a. The two red plus signs in Fig. 4-8a indicate the positions at which the EDS point analyis was carried out.

It is important to note that the shape and size of the reacting Cr particles, as shown in Fig. 4-8, do not change remarkably when compared with those of the initial Cr particles. It is still possible to observe the sharp edges of the Cr particles. These results therefore suggest that the diffusion between the Cr particles and S had occurred prior to the melting of the S, in the solid state, and the reaction started at the surface layer and gradually propagated into the interior.



Figure 4-8. SEM photographs showing the solid-state diffusion between Cr and S: (a) CrS diffusion layer forming on the surfaces of Cr particles, and (b) the microstructure of region "F" in (a).

4.6.2 Melting of S, dissolving of Cr particle and precipitating of CrS particles

In Fig. 4-9a, the gray layer denoted as "G" appeared on the surface of the Cr particle "F" was shown. As can be seen, the Cr particle "F" was wholly coated with the gray layer "G". The EDS analyses of the gray layer "G" in Fig. 4-9a indicate that the coating layer "G" contained both Cr and S atoms. These results imply that S had melted and Cr particle was gradually coated with the liquid S, at the same time, the Cr particle had started dissolving into the S melt, and this led to the formation of the Cr-S melt surrounding the Cr particle.

The microstructure of the gray layer "G" is shown enlarged in Fig. 4-9b, with the points "J" and "K" indicating the points at which the EDX analysis was carried out. According to the EDX results (shown in table 4-1), the matrix point "K" is Cr-S melt (92 wt.% Cr), whereas the particle at point "J" corresponds to CrS (62 wt.% Cr). Therefore, these results suggest that the continued dissolution of the Cr particles into the Cr-S melt led to the precipitation of CrS particles in the Cr-S melt when it became saturated. Moreover, the Cr-matrix solid solution located at the point "I" (94 wt.% Cr) had also formed at the surface of the Cr particle.



Figure 4-9. BSE images showing: (a) Cr particle being wholly coated with the gray layer; (b) microstructure of the gray layer around the Cr particle; (c) X-ray dot mapping for element Cr in (a); (d) X-ray dot mapping for element S in (a); and (e) The elemental distribution along line in image (b)

The EDX results for the different regions in the CrS particles in Fig. 4-9b showed that the Cr content in the CrS particle near the Cr particle is significantly higher than for the one far from the Cr particle. This is also confirmed by the results shown in Figs. 4-9c, 4-9d. Figs. 4-9c and 4-9d show the distribution of elements Cr and S along the line shown in the Fig. 4-9b.

Table 4-1. Chemical composition of the matrix and bright phase in Fig. 4-9b obtained from EDS point analysis

	Cr (wt%)	S (wt%)
Spot J	62	38
Spot K	92	8

4.6.3 Dissolution of Cr particles and precipitation of CrS particles

With continued dissolution of the Cr particles, the size of the undissolved Cr particles became progressively smaller. Simultaneously, the CrS particles gradually precipitated more and more in the saturated Cr–S melt, and the coating layers surrounding the Cr particles became thicker and thicker, as shown in Fig. 4-10a. Fig. 4-10b shows a Cr particle "L" totally coated with the CrS particles "M" in the Cr–S melt.



Figure 4-10. SEM images showing: (a) coating layer surrounding the Cr particle became thicker and thicker in transition zone; (b) more CrS particles precipitating in the Cr-S melt around Cr particle

4.6.4 Combustion-reacted product

Fig. 4-11 shows an SEM image of the combustion-reacted product at lower magnification, and many pores such as "O" can be found. In addition, there were still some dissolution-incomplete Cr particles such as "N" in Fig. 4-11.



Figure 4-11. SEM image of the microstructure of the product in the combustion-reacted product

For the samples with a Cr:S molar ratio equal to 1.3, there is remaining Cr embedded in the CrS matrix around the Cr particle inside the reacted zone in the combustion-reacted product, indicating that the mechanism of the reaction is the solution precipitation mechanism (Fig. 4-12).



Figure 4-12. Remaining Cr (indicated with arrows) embedded in the CrS matrix around the Cr particle inside reacted part in the combustion-reacted product

4.7 Discussion

4.7.1 Combustion reaction mechanism

From the microstructural evolution during the combustion reaction of the Cr-S mixture observed above, it can be seen that the combustion reaction between the Cr particles and S started with solid-state diffusion between the Cr particles and S, and continued with melting of sulfur followed by a dissolution-precipitation mechanism. A schematic showing the steps associated with the dissolution-precipitation mechanism is shown in Fig. 4-13. As the temperature reaches the melting point of S, the sulfur around the Cr particles melts. Then the Cr particles start to dissolve into the liquid S, and these results in an increase of Cr content in the S melt. CrS particles then precipitate out in the Cr-S melt when the saturation point is reached, and the precipitation of the CrS particles occurs continuously with the dissolution of the Cr particles.



Figure 4-13. Schematic of the steps corresponding to the dissolution-precipitation mechanism

As mentioned, in the dissolution-precipitation mechanism, the solid phase which is precipitating in this process must be the phase which is in equilibrium with the melt at a given temperature. Based on the Cr-S phase diagram (Fig. 4-14), CrS is the only phase that can be in equilibrium with the melt. For the samples with a Cr:S molar ratio equal to 1.3, there is Cr remaining around the Cr particle inside the reacted part of the combustion-reacted product, which indicates that the mechanism of the reaction corresponds to a solution-precipitation mechanism (Fig. 4-12).

Due to the presence of the solid solution, the reaction mechanism between the Cr and S could not correspond to the second mechanism described earlier (see Fig. 4-1) which is based on a reaction diffusion model. In the diffusion mechanism no solid solution should be observed. Due to the fact that there is no intermediate product and only one phase (CrS) formed during the reaction and existing as the final product, it may be concluded that the reaction mechanism also does not correspond to the third mechanism discussed in section 4.2.



Figure 4-14. Calculated optimized condensed chromium-sulfur phase diagram at a total pressure of 1 bar. Abbreviations; Pyrr stands for high-temperature chromium pyrrhotite, S (orth) for solid pure sulfur with orthorhombic structure, and bcc for the body-centered cubic chromium solution phase [9]

4.7.2 Degree of completeness of the combustion reaction

Both the microstructure and the XRD patterns show that the combustion synthesis was incomplete because residual phases, the dissolution-incomplete Cr particles and the S solid solution, were detected by XRD and also observed with SEM in the final product. This incompleteness of the combustion reaction is likely due to the coarse scale of Cr powder, in contrast with the fine Cr powder in which virtually no residual Cr particles were observed in the combustion-synthesized product. Therefore, it is suggested that the different size of the reactant particles can lead to a different degree of diffusion of the S into the dissolving Cr particles. Not surprisingly, the finer the reactant particle size, the shorter the diffusion distance needed for the S atoms to penetrate the Cr particles.

4.8 Conclusions

In the present investigation, a Cr-S mixture was ignited and quenched, and then the combustionreacted product was inspected by XRD, while the microstructural evolution of the reaction in the quenched sample was analyzed with SEM and EDX. Based on the experimental results, a mechanism for the combustion reaction has been proposed with the following stages. The combustion reaction between the Cr particles and S starts with solid-state diffusion between the Cr particles and S, and continues with the melting of sulfur. The atoms of Cr then start to dissolve in the liquid sulfur near the interfacial boundaries. The melting of the S leads to the dissolution of the Cr particles into the S melt, and then CrS particles precipitate in the saturated Cr–S melt. The completeness of the combustion reaction was a function of the Cr particle size, with the highest completion occurring with the finest (1-5 um) Cr powder, resulting in a negligible amount of residual phases within the combustion-synthesized samples in contrast with coarser Cr particles which did not fully react.

4.9 Acknowledgments

The authors would like to Prof. In-Ho Jung for his contribution in thermodynamic calculations with FactSage.

4.10 References

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Link between chapter 4 and chapter 5

In last 3 chapters, it was shown that the method developed can be successfully used to manufacture chromium-chromium sulfide cermets. Knowledge of the properties of the cermets produced is critical for understanding the mechanics of these composite materials. Therefore, in the next stage, microstructural characterization of the material is performed and the mechanical properties are evaluated. We first estimate the mechanical properties of the fabricated cermets and evaluate the effect of the improvements applied to the combustion manufacturing process. We then attempt to improve the toughness and other mechanical properties of the Cr-CrS cermets by increasing the metal content. The mechanical properties are therefore measured as a function of the Cr:S molar ratio. Results obtained from quasi-static properties demonstrate the role of chromium addition, which leads to an overall improvement of the mechanical properties of the cr-CrS cermets are added to a selection of Ashby charts, and based on them some applications for this cermet are proposed.

Chapter 5

Mechanical properties of chromiumchromium sulfide cermets fabricated by self-propagating high-temperature synthesis

Chapter 5: Mechanical properties of chromium-chromium sulfide cermets fabricated by self-propagating hightemperature synthesis

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5.1 Abstract

Metal sulfides are widely used in a variety of applications requiring high hardness, toughness, infrared transparency or catalytic properties among them, pure CrS has a significant hardness, but its toughness is insufficient for tool applications. In this study, the microstructure and mechanical properties of chromium-chromium sulfide cermets are investigated. The chromiumchromium sulfide cermet is manufactured using self-propagating high-temperature synthesis, a process in which the material is created using a self-sustaining combustion reaction between the chromium and sulfur. This type of synthesis allows the creation of near-net shape structures and offers the possibility of tuning the microstructure and material properties by changing the composition of the reactants. In this work dense cermets with specific microstructures are fabricated. Microstructural characterization is performed using optical microscopy, scanning electron microscopy, and energy dispersive spectroscopy. The mechanical properties of the cermet (e.g., Young's modulus, fracture toughness, flexural strength and microhardness) are also measured and related to the morphology and chemical composition of the samples. We find that the addition of Cr leads to an overall improvement in the mechanical properties, i.e., the flexural strength and hardness of the cermet are improved by 60% and almost 38%, respectively. We also find that the density and fracture toughness of the cermets increase with the addition of Cr.

Keywords: Mechanical properties; Self-propagating high-temperature synthesis; Cermet; Chromium sulfide; Ashby charts

5.2 Introduction

Engineering ceramics are attractive materials because of their low density, high compressive strength and hardness. However, their use in actual applications is currently limited by their brittleness, fragility and poor toughness. A possible approach to toughen ceramics is the inclusions of a metallic ductile phase. Such ceramic-metal compounds, called cermets, combine the hardness and stiffness of ceramics with the toughness and ductility of metals [1-5]. Among cermets, metal sulfide composites are in high demand in the chemical, metallurgical, and electrical industries because of their valuable characteristics such as hardness, semi-conductivity, electroluminescence, infrared transparency, catalytic and magnetic properties [6-9]. Currently, metal sulfides are used for cathodes in batteries, additives in steel production, high temperature lubricants, catalytic material for the hydro-desulfurization, electrodes for hydrogen fuel cells, and solar energy conversion into electric and chemical energy [7, 10-16]. There is currently no bulk production of chromium sulfide, however, we know from the literature that chromium sulfide has magnetic properties, and already is used as a catalyst in chemical processes, and as a solid lubricant [7, 17-19]. Metal-sulfur compositions, such as Cr-S are attractive in that they offer the possibility of fabrication using the self-propagating high-temperature synthesis (SHS) technique.

In a previous study, we used a new method for the preparation of the metal-sulfur precursor charge based on the ability to melt-cast the precursor mixture [20]. We used SHS to produce a chromium-chromium sulfide cermet, using the ability of the metal-sulfur mixture to support the propagation of reactive waves. This ability, with the properties of the reaction products (i.e., low gas evolution and liquid sulfide products), enable the possibility to perform net-shape synthesis of dense, near theoretical density product with a relatively simple and low-cost set-up [20]. This novel method simplifies the preparation of samples with different shapes, thicknesses, and with a green density close to the theoretical density. It also improves the quality of the synthesized product, and homogeneity of the product structure [1, 7, 21, 22].

While the thermochemical calculations predict near-zero gas production for the chromium-sulfur system, the actual cermets exhibited a large amount of porosity (about 70%) when synthesized at

atmospheric pressure. With the various improvements to the manufacturing process, the porosity was reduced by an order of magnitude from 70% to 7% [20]. The level of porosity obtained (approximately 7% for the best samples) is considerably less in comparison to samples produced by other SHS techniques and is comparable to the bulk form of industrially manufactured ceramics [23].

In the present study, we first estimate the mechanical properties of the fabricated cermets and evaluate the effect of the improvements applied to the combustion manufacturing process (section 5.10). Then, we attempt to improve the toughness and other mechanical properties of the Cr-CrS cermets by increasing the metal content. The mechanical properties are measured as a function of Cr:S molar ratio and the results obtained demonstrate that the addition of Cr has a significant influence on the mechanical properties.

One of the advantages of this type of synthesis is that it offers the possibility of tuning material properties and material behavior by changing the reactant composition. In particular, it is in theory possible, by systematically increasing the Cr content in the precursor mixture, to tune the final product from a brittle ceramic to a more ductile metal-like material. In other words, the ductility of the Cr-CrS cermet can be controlled through the variation of the Cr:S molar ratio in the reactive mixture, enabling the cermet to contain an excess of chromium in the final product to increase ductility. Although equilibrium thermodynamic calculations predict that 200% excess Cr is the upper limit on the Cr content for a self-sustained reaction to occur [24], this study stopped at a Cr:S ratio of 4 times stoichiometric in order to find the maximum Cr content that could be added to the produced cermet. All thermodynamic calculations were carried out using the FactSage thermochemical software [25].

5.3 Materials and manufacturing process

The preparation of the reactive mixture used in this study is straight forward and is shown schematically in Fig. 5-1. The chromium powders were obtained from Atlantic Equipment Engineers (NJ, USA), with a purity of 99.8%, and with particle size ranges given by the supplier of 1-5 μ m (CR-102) and <44 μ m (CR-103). The particle size distribution of the Cr powders, measured with an LA-920 Horiba laser scattering particle size analyzer shows the CR-102 and CR-103 powders had average particle sizes, based on volume, of 3 μ m and 26 μ m, respectively.

Sulfur powder with a purity of 99.5% was obtained from Alfa Aesar (S4981, MA, USA). The average particle size was smaller than 150 μ m (-100 mesh) but did not influence the fabrication process, since the sulfur was always melted to form the reactive mixture. As a first step, samples were synthesized at atmospheric pressure. These fabricated samples generally had high porosity, including both micro- and macro-cracks. To reduce the porosity and number of cracks that form in the product, a modified manufacturing process was used, which is described below.

Chromium and sulfur powders were mixed in a roller mill with in the desired mass ratio. The powder mixture was then heated in a mantle up to a temperature slightly above the melting temperature for sulfur (i.e., temperature > 120° C), but well below the melting temperature of chromium (1907°C). The molten mixture of Cr and S powders was degassed in a vacuum chamber (pressure = 95 kPa) for about 20 minutes and at high temperature to maintain sulfur in the molten state. After that, the mixture was poured into a preheated mold to prevent contact solidification of the melt. Upon cooling of the reactive mixture the sulfur solidified, forming a matrix of sulfur containing well-dispersed chromium inclusions. The solidified reactive mixture was then placed in a pressurized reactor and ignited under a high-pressure inert gas (Ar) environment, by using an electrically heated tungsten wire embedded in the sample. By igniting the sample above the liquid-vapor critical point of sulfur and cooling the samples slowly and directionally after the reaction the porosity inside the produced cermets was about 7%, and no cracks were formed within the product. The self-sustained flame propagated throughout the sample, producing the final metal-sulfide product. Depending on the initial metal/sulfur molar ratio, the amount of unreacted metal remaining in the product varies, enabling the final product to range from a brittle ceramic to a more ductile metal-like material (Fig. 5-2a, 5-2b).



Figure 5-1. Schematic of the modified manufacturing process

5.4 Structural and microstructural characterization

To investigate the microstructure of the samples produced, including the morphology, size, distribution and composition of the different phases, the specimens were cut, polished and examined with scanning electron microscopy (Hitachi S-3000N VP-SEM), optical microscopy and energy dispersive spectroscopy (EDS). The volume fractions of voids and the different phases within the specimens were estimated by performing image analysis on backscattered electron images (BSE) and optical microscopic images, based on the ASTM E 562-02 standard test method for determining volume fraction by systematic manual point count [26]. By analyzing the backscattered images taken by SEM and using a quantification feature in the Clemex image analysis software package, the volume fractions of different phases were extracted as statistical data. The atomic masses of chromium, sulfur and chromium sulfide are
significantly different from each other, and therefore these elements could be easily identified in backscattered images.

X-ray diffraction (XRD) was used to determine the nature of the different phases which were formed during the synthesis or post-ignition process. Combustion-synthesized products with a Cr:S molar ratio 1:1.3 were ground into fine powders and analyzed using copper K 1 X-ray radiation to assess the phase constituents. XRD analyses showed Cr and CrS peaks (Fig. 5-2c).





Figure 5-2. Backscattered images of produced samples each with Cr:S molar ratio equal to; (a) 1.15:1, and (b) 4:1 sample. Light regions are residual Cr phase, dark gray regions are chromium sulfide, and black regions correspond to voids; (c) XRD pattern of samples fabricated with Cr:S molar ratio 1:1.3

5.5 Density

The density of the samples after the reaction was measured. The relative density of the Cr-CrS cermets, obtained by the Archimedes method, varied between 83 and 110% of the theoretical density of CrS, for an initial Cr:S molar ratio of 1.15:1 to 4:1, respectively. Additionally, the pores were small and uniformly distributed throughout the cermets produced. The density of Cr is higher than that of CrS and Cr_2S_3 and, as expected, cermet density increases from 4.04±0.05 to 5.37±0.04 g/cm³ as the Cr content was increased from 115% to 400%, respectively (see Fig. 5-3).



Cr:S Molar Ratio

Figure 5-3. Density of cermets produced as a function of Cr:S molar ratio

5.6 Microhardness

In order to measure the micro-hardness of the synthesized samples, the samples were cut and fixed in epoxy, then polished with a 3-µm diamond paste and then cleaned with ethanol. Micro-hardness measurements of the matrix of the cermets produced were made using a BUEHLER 2101 Vickers microhardometer, and the hardness test was performed under an indentation load

of 50 gf for 20 s. Analysis points were sufficiently spaced to eliminate the effect of neighboring indentations. Indents were made on the porosity-free areas, and any distorted indents indicating entrapped pores were discarded from the measurements. An average of 10 indentations was performed on each sample cross-section and the values are reported in Fig. 5-4.



Cr:S Molar Ratio

Figure 5-4. Hardness of cermets produced as a function of Cr:S molar ratio

Fig. 5-4 shows that the microhardness increases with increasing Cr content within the reactive mixture. Based on the Cr-S phase diagram [27] and XRD results, the chromium solute content (solid solution) of these cermets can contribute to the hardness improvement. One-way ANOVA exhibited a significant difference (p<0.005) among the tested cermet materials for the mean values of microhardness. As can be seen in Fig. 5-4, the hardness is measured to range from 221±18 HV to 305±8 HV, for Cr:S 1.15:1 and 4:1 molar ratios, respectively. For comparison, the hardness of annealed chromium at 1100°C is 110 HV, chromium that is extruded, annealed, and rolled at 400 °C is 160 HV, 304 stainless steel is 183 HV, and 316 stainless steel is 220 HV [3].

5.7 Three-point bending

For the three-point bending test, specimens were prepared by cutting the fabricated cermet into small sized beam-type prisms with a length of 20 mm and rectangular cross section of 4×4 mm and 2×4 mm, using a high precision diamond saw (Fig. 5-5a). The quasi-static mechanical tests were performed using a three-point bending fixture mounted on a miniature loading stage as shown in Fig. 5-5b (Ernest F. Fullam Inc., Latham, NY). The loading stage and sample were placed under an optical microscope (BX-51M, Olympus, Markham, Canada) equipped with a CCD camera (RETIGA 2000R, Qimaging, Surrey, Canada) to capture crack propagation, as shown in Fig. 5-5c. The specimens were loaded at a rate of 0.0025 mm/s up to complete failure. For each composition, six different test samples were used. One-way ANOVA showed that flexural strength was significantly affected by Cr content in fabricated cermets (p<0.01). As can be seen from Fig. 5-6, the flexural strength increases from 444 to 727 as the Cr:S molar ratio increases from 1.15:1 to 4:1, respectively. The Young's modulus also increases with increasing Cr content in the cermet with Cr:S 4:1 molar ratio (Fig. 5-7).





(c) Figure 5-5. (a) Samples for three-point bending test, (b) photograph of test setup, and (c) crack propagation along the cermet sample



Figure 5-6. Flexural strength of produced cermets as a function of Cr:S molar ratio



Figure 5-7. Young's modulus of produced cermets as a function of Cr:S molar ratio

5.8 Fracture toughness

Fracture toughness tests were performed using a three-point bending fixture with a span of 16 mm, mounted on a miniature loading stage (Ernest F. Fullam Inc., Latham, NY). The specimens were loaded at a rate of 0.0025 mm/s up to complete failure. Samples were prepared by cutting the cermet specimen into small beam-shaped pieces with a length of 20 mm and a rectangular cross section of 2×4 mm, using a high precision diamond saw. The samples were then prenotched using the diamond saw. One side of the specimen was polished and the notch was deepened and sharpened with a razor blade. The notch depth was about 2.0 mm, which was within 0.45-0.55 of the width in order to comply with the ASTM E1820-01 standard test method for measurement of fracture toughness, as shown in Fig. 5-8b. For each composition, 6 different test samples were used.

One-way ANOVA revealed a significant influence of the Cr:S molar ratio on the fracture toughness values of the cermets produced (p < 0.05). Fig. 5-8a shows that increasing the Cr content from a Cr:S molar ratio 1.15:1 to 4:1 improved the fracture toughness of the cermet by almost 75%.



Cr:S Molar Ratio

Figure 5-8. (a) Fracture toughness of synthesized cermets as a function of Cr:S molar ratio, and (b) Samples for fracture test

5.9 Fracture surfaces

Fig. 5-10 shows the fractured surfaces of the flexural samples. The microstructure of the specimens was examined using SEM on fresh fractured surfaces, containing the remaining Cr particles and the chromium sulfide phase. Secondary electron (SE) and backscattered electron (BSE) images of each surface are shown in Fig. 5-10. The combination of these two imaging modes provides valuable and complementary information, i.e., the SE mode focuses on image topography, and the SE image has relatively good resolution and provides more detail regarding the surface morphology. In contrast, in the backscattered electron image of the same fracture surface, the surface texture is less obvious. However, a difference in contrast is now visible between the Cr and CrS phases. Since the intensity of the BSE signal is strongly dependent on the mean atomic number of the compound, BSE images contain compositional information, and because heavier elements with a high mean atomic number backscatter more efficiently, they appear brighter than lighter elements in a BSE image [28]. Therefore, the white phase in the BSE images corresponds to areas of Cr which has the highest atomic number, and whereas the phase with a gray appearance would be CrS which has a lower atomic number.

From an examination of Fig. 5-9, which shows a fracture path in a 4:1 Cr:S molar ratio cermet, it is apparent that the fracture path passes directly through the Cr particles. A few secondary cracks can be seen in some Cr particles and these are indicative of the brittle nature of the Cr particles. The interface plays an important role in the fracture behavior of cermets. If the fracture strength of the matrix is greater than that of the Cr particles, as in this case, the Cr particles crack when the magnitude of the local stress exceeds the particle fracture strength. This points to the fact that particle breakage has taken place during the fracture process and is characteristic of a strong Cr particle-CrS matrix bond.



Figure 5-9. Fracture path in a synthesized cermet with a Cr:S molar ratio of 4:1

From a physical point of view, a certain amount of ductility in the reinforcement can cause a significant improvement in the toughness of brittle matrix composites. It has also been recognized that for achieving an improvement in the fracture toughness, the matrix–reinforcement interfacial strength is as important as the ductility of the reinforcing phase, and the ductility of the reinforcing phase alone is not sufficient. For example, if the interface is very strong, a high degree of constraint can lead to a triaxial state of stress, resulting in a brittle failure of the ductile reinforcement. As a result, under these circumstances there would not be a significant increase in the composite toughness [29].

SE images show relatively featureless, flat surfaces suggesting little or no plastic deformation. Brittle or non-ductile (also called semi-brittle) fracture involves little or no appreciable plastic deformation prior to failure. As can be observed, the major toughening mechanism is the partial plastic deformation of chromium particles.

Fig. 5-10 shows typical features of brittle fracture surfaces. In this case, the origin of fracture is usually a surface defect i.e., porosity, microcracks, inclusions, angular-shaped constituent particles, etc. A surface defect will act as a point of stress concentration within the material. Presence of such points of high stress concentrations will greatly increase the possibility of brittle failure. Specially, ceramics and glasses have very high yield strengths, and thus very little

plastic deformation takes place at crack tips in these materials. Even allowing for a small degree of crack blunting, the local stress at the crack tip is still in excess of the ideal strength and is thus large enough to literally break apart the interatomic bonds there; the crack then spreads between a pair of atomic planes giving rise to an atomically flat surface by cleavage. In the vicinity of regions in these Figs., brittle cleavage fracture modes were observed. The fracture surface has a faceted morphology because of the different orientations of cleavage planes in the grains. Cleavage fracture occurs by separation along certain crystallographic planes having low Miller indices [29, 30].



Figure 5-10. Fracture surface in a synthesized cermet with a Cr:S molar ratio of 4:1; (a) SE image, and (b) BSE image

5.10 Effect of manufacturing process

Samples synthesized at ambient pressure generally had high porosity (as high as 70%) with a large number of micro- and macro-cracks. The possible sources of the porosity were considered and as a result the manufacturing process was modified in order to address these issues and

minimize the porosity [20]. In the modified manufacturing process the particle size of the reactants was considered. Then, the molten mixture of Cr and S powders was degassed in a vacuum chamber (vacuum pressure= 95 kPa) for about 20 minutes and at high temperature to maintain sulfur in a molten state. After that, it was poured into a preheated mold to prevent contact solidification of the melt. The solidified reactive mixture was then placed in a pressurized reactor and ignited in a high-pressure inert gas (Ar) environment, by using an electrically-heated tungsten wire embedded in the sample. By igniting the sample above the liquid-vapor critical point of sulfur, and cooling the samples slowly and directionally after the reaction, the porosity inside the produced cermets was reduced to about 7%, and no cracks were observed inside the cermets.

To demonstrate the effect of these improvements in the manufacturing process, we tested one primary sample, which had 18.6% porosity and contained thermal cracks, as well as one of our final samples produced which had 7% porosity with no cracks, but with the same composition (i.e., a Cr:S molar ratio of 1.15:1). As can be seen from Fig. 5-11, the cermets which were fabricated with a Cr:S molar ratio of 1.15:1 and had 18.6% porosity and thermal cracks, were brittle with a flexural strain less than 1%, and a flexural strength of 64.55 ± 2.72 MPa. In comparison, the cermets fabricated with the same Cr:S molar ratio, but under the modified manufacturing process, had a flexural strain of around 2%, and a flexural strength of 444.75 ± 160.5 MPa.



Figure 5-11. Flexural strength of synthesized cermets with the same Cr:S molar ratio but a different porosity and presence of cracks (or not) within the cermet

Like the flexural strength test, the same two different samples were tested to measure fracture toughness, i.e., the first cermet sample had 18.6% porosity with thermal cracks and the second cermet sample had 7% porosity with no cracks, each with the same Cr:S molar ratio. According to the ASTM standard E1820-01, the fracture toughness of the cermets was determined to be 1.61 ± 0.44 MPa·m^{1/2} and 2.36 ± 0.35 MPa·m^{1/2}, respectively (Fig. 5-12). All the load-deflection curves indicated that the samples behaved linearly near the beginning of the test up to peak values, followed by catastrophic brittle fracture of the samples.



Figure 5-12. Fracture toughness of synthesized cermets with the same Cr:S molar ratio but different porosity and cracks within the cermet

The results obtained show that the modified manufacturing process improved the flexural strength and fracture toughness of the two synthesized cermets with same composition, by 640% and 45%, respectively. The common products of SHS usually have thermal cracks and at least 20% porosity. Therefore, it shows these results would be a proof of efficiency of the modified manufacturing method.

5.11 Ashby diagrams

Application of a component usually depends on a combination (or several combinations) of its properties. To facilitate the selection of materials for particular applications, Ashby suggested the idea of plotting one property against another, or in other words, mapping the property fields, showing the range of parameters occupied by each class of materials. Since each property of an engineering material has a wide range of values, the ranges of the axes are chosen to include all materials. In these charts, the data for a given class of materials can be enclosed together by heavy lines like an envelope. Some of the mechanical properties of materials are of primary importance, in engineering design and also in characterizing the material. These include the material density, strength, modulus, and toughness [31]. The Ashby charts are useful in several

ways. They condense a huge amount of information into a compact but easy accessible form, they display relations between material properties which helps in estimating and checking data, and they can adopt a technique that is useful for performance-optimization technique. Therefore, to be able to compare the synthesized Cr-CrS cermets with other materials, the ranges of the property values for this material have been added to some of the Ashby charts. The extension of the bubble-shaped region for Cr-CrS cermets reflects its range of property values, obtained by varying the Cr content.

Many applications and designs look for strength and stiffness at minimum weight. Therefore, one of the most useful of all the charts is shown in Fig. 5-13, which shows E/... plotted against $\dagger_f/...$. In this chart, the word "strength" refers to *yield* strength for metals and polymers, *tear* strength for elastomers, *tensile* strength for composites and woods, and *flexural* strength (modulus of rupture) for ceramics. For all of them, the symbol \dagger_f is used. These are measures of "mechanical efficiency", which means the use of the least mass of material to do the most structural work. Composites lie at the upper right. They emerge as the material class with the most attractive specific properties which is one of the reasons for their increasing use. Ceramics have high stiffness and strength per unit weight, but their brittleness excludes them from much structural use. Metals are penalized because of their relatively high densities. Cr-CrS cermets fall on the overlap area between composites and metals which prove that they may perform better than many metals and ceramics in structural applications.



Figure 5-13. Specific modulus E/... plotted against specific strength $\dagger_f/...$ [31]

Fig. 5-14 shows another Ashby chart, in which the fracture toughness is plotted against strength. In this chart, the qualifications for "strength" are the same as before. The diagram has applications in selecting materials for the safe design of load bearing structures. Materials toward the top left have high toughness and low strength. Thus, they yield before they fracture. Materials toward the bottom right do the opposite – they fracture before they yield. Cr-CrS cermets lie on the overlap area between technical ceramics and composites which shows they behave similarly to CFRP, SiC, Al_2O_3 , WC, B_4C , etc. in these applications.



Figure 5-14. Fracture toughness K1c plotted against strength [31]

Considering these Ashby charts for material selection, it can be concluded that cermets produced in this study can be used in a variety of applications. They can be used as ballistic armors, e.g., composite armor, tank armor, bulletproof vests, and with a metal they can perform as hybrid composite armors. They have the ability to be used in a very wide range of service temperatures, especially at high temperatures since the melting point of chromium and chromium sulfide is higher than 1000°C. Thus, another application of them is as a refractory material which can be used as a heating elements and in high-temperature kilns.

The cermets produced in the present study can also perform well in a corrosive environment since Cr corrosion resistance is very good. Therefore, Cr-CrS cermets can be used in all applications which involve exposure to seawater or heavy water, such as for parts of ships or naval structures. They can perform as protective coatings to resist corrosion from liquid metals. Therefore, they can replace stainless steel, Ni alloys, and Ti alloys, and furthermore the

manufacturing cost of the cermet is lower than these materials. These cermets can be used in the petroleum industry as pipes for natural gas extraction since there the H_2S gas in natural gas is very corrosive but does not degrade the Cr-CrS cermets. As a result, they can be used in any industry that involves the use of H_2S , such as in facilities for the separation of heavy water from normal water, wastewater treatment plants, and so on. By adding additional metal to the composition, the fracture toughness may be increased. In this case Cr-CrS cermets can be replace Al alloys and steels used in many applications such as the aerospace and automobile industries. The Cr-CrS cermets have the added attraction of having similar properties to steel, but about half the density.

Fig. 5-15 shows the relative cost of different materials based on the latest version of Ashby diagram [31]. The estimated cost of raw materials for producing 1 kg of cermet in the laboratory is about \$5-9/kg, with the range in the cost due to differences in the Cr content.



Figure 5-15. The approximate price/kg of materials. Commodity materials cost about \$ 1/kg, special materials cost much more [31]

5.12 Conclusions

The aim of this work was to demonstrate the production of dense cermets from original starting powders, to evaluate their physical and mechanical properties and to correlate them with the chemical composition. This paper has demonstrated the ability of the melt-casting SHS technique developed here to produce near theoretical density chromium/chromium sulfide ceramic metal composite (cermet) articles of a desired shape. Dense specimens with Cr particles embedded in a chromium sulfide network were obtained.

The microstructure, mechanical properties, and fracture surfaces of CrS-based cermets have been investigated and clearly observed. Also, the influence of Cr addition on the microstructure and mechanical properties of Cr-CrS cermets has been investigated. Although thermodynamics predicts that 200% excess Cr is the upper limit on the Cr content that permits a self-sustained reaction to occur, in this study the synthesis of the cermets was demonstrated to be possible for a Cr:S molar ratio of up to 4 times the stoichiometric value.

Mechanical properties were measured as a function of Cr:S molar ratio. Quasi-static properties demonstrate the role of chromium addition, which leads to an overall improvement of the mechanical properties of the fabricated cermets. Statistical analysis was performed using one-way ANOVA. P values less than 0.05 were considered to be statistically significant in all tests. The differences in means of each group were analyzed by analysis of variance (ANOVA) with micro-hardness, flexural strength and fracture toughness as the dependent variables, and the Cr:S molar ratio (chromium content) as the independent factor. ANOVA exhibited highly significant differences among the tested composite materials for the mean values of micro-hardness (p < 0.005), flexural strength (p < 0.01), and fracture toughness (p < 0.05).

According to the manufacturing process of Cr-CrS cermets that we conducted and described here, it is possible to make these cermets as functionally graded materials, because they can be cast layer by layer with different compositions (various Cr contents) in a mold with desirable final shape of the article. Harder inclusions with different geometries and volumes (such as boron carbide or silicon carbide) also can be embedded into sulfide ceramics during the SHS process making a hybrid composite with applications as a material for ballistic armor.

5.13 Acknowledgement

This project was supported under NSERC Strategic Grant "Design and Net-shape Manufacturing of Hybrid Composites for Ballistic Protection" with Francois Barthelat serving as principal investigator. The authors would like to thank Deju Zhu for his contributions in mechanical characterization methods. The authors also appreciate the effort of Alexander Capozzi for his input regarding the synthesis of chromium sulfide samples.

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Chapter 6 Conclusions

Chapter 6: Conclusions

6.1 Summary of accomplishments

The essential rationale for producing ceramic-metal composites is to incorporate the desirable properties of ceramics and metal, while suppressing the undesirable properties of both. Cermets therefore offer unique combinations of hardness and toughness which make them attractive for a variety of applications. Among the metal-ceramic cermets, metal-sulfur compositions offer the possibility of production with a combustion synthesis technique, which provided the motivation to study the manufacturing process and further investigate the combustion behavior and mechanical properties of the product cermet. In this context, the present work provides the following new insights regarding the manufacturing process and characterization of chromium-chromium sulfide cermets:

• A new method for the preparation of the metal-sulfur precursor mixture was introduced based on the ability to melt-cast the precursor mixture. Self-propagating high-temperature synthesis was used to produce a chromium-chromium sulfide cermet, exploiting the fact that this mixture of metal and sulfur can support the propagation of reactive waves. In summary, we demonstrated the ability of the melt-casting SHS technique to produce near theoretical density chromium-chromium sulfide cermet articles.

• Although equilibrium thermodynamic calculations predict that no gas is produced during the reaction for a Cr-rich formulation, performing the synthesis at ambient pressure resulted in a product with considerable porosity (as high as 70%). The high porosity represents a significant obstacle to the use of the cermet in structural applications, and we therefore carefully investigated its possible sources in order to suppress it. The use of a degassed, melt-cast reactive mixture with excess chromium, and performing the synthesis under high pressure are the essential requirements to minimize porosity. With the various improvements to the manufacturing process, the porosity was reduced to about 7%, which may be attributed to the release of gases evolved from impurities (oxides, moisture, etc.) and the subsequent "freezing" of the porosity caused by the non-equilibrium evolution of gases during the combustion process.

• To demonstrate the effect of these improvements on the manufacturing process, we tested one primary sample as well as one of our final samples produced with the same composition.

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The results obtained show that the modified manufacturing process improved the flexural strength and fracture toughness of the two synthesized cermets, by 640% and 45%, respectively.

• The ability of the Cr-S system to sustain propagation in small dimension charges (quenching distance smaller than 1 mm with fine Cr powder), together with the properties of the reaction products (low gas evolution and liquid sulfide products) demonstrate that the manufacturing technique developed here is able to produce cermet samples with complex shapes with high tolerances.

• Measurement of the minimum dimension (thickness of a wide rectangular channel or diameter of a cylindrical tube) that a flame can successfully propagate while experiencing heat loss to the channel walls is one of the fundamental measurements that can be made in a reactive material and has practical relevance to net-shape manufacturing of complex shapes. Therefore, the quenching diameter and the quenching thickness of the Cr-S mixure were measured. We found that the quenching dimension did not have a strong dependence on the Cr:S molar ratio, and it is of interest to note that the critical quenching diameter of a cylindrical charge is approximately twice the thickness of the critical thickness of a rectangular slab. The results from quenched samples that were reacted up high ambient pressure (136 atm) demonstrate that the quenching thickness and quenching diameter are smaller for the samples ignited under high pressure, regardless of the Cr:S molar ratio.

• The chemical thickness is the length of the transition zone between the totally unreacted and reacted areas, i.e., from zero volume fraction of chromium sulfide to near zero volume fraction of sulfur. The chemical thickness was measured to be approximately 0.5 ± 0.1 mm, and similar analysis of samples recovered from different geometries (cylindrical and rectangular) and for varying Cr:S ratios (from 1.0 to 1.6) found the chemical thickness of the flame to be approximately constant. The chemical thickness of samples ignited at ambient pressure is approximately twice the chemical thickness of those samples ignited under high pressure, regardless of the metal-sulfur molar ratio. Even with a variation in the Cr:S molar ratio (from 1:1 to 1.3:1), the chemical thickness of the samples ignited under pressure was approximately constant.

• As noted above, the chemical thickness of the front estimated from the microscopy analysis of the quenched samples was found to be approximately 0.5 ± 0.1 mm. Due to the extremely low heat diffusivity of sulfur (= 10^{-7} m²/s), the estimated thickness of the preheat zone is on the

order of 0.01 mm, i.e., much smaller than the chemical reaction zone. Thus, the flame thickness in the present case is dominated by the thickness of the reaction zone.

• The quenching diameter and the quenching thickness of the rectangular samples were measured to be 2 mm and 4 mm, respectively. Thus, the ratio of the characteristic quenching sizes to flame thickness was correspondingly four and eight, respectively, for rectangular and cylindrical channels, in good agreement with the qualitative framework of flame quenching theory. This result illustrates that flames in metal-sulfur compositions are dominated by the reaction zone thickness, in contrast to classical gaseous flames for which the flame thickness is dominated by the preheat zone.

The flame propagation speed is another important parameter that influences the state of the product and can also give insight into the propagation mechanism and reaction chemistry. While propagation velocities have been widely reported for SHS mixtures, it is important to differentiate between the propagation velocity of a flame (the velocity it appears to move relative to a fixed observer) and the fundamental burning rate (the velocity of material flowing into the combustion front in the normal direction, relative to the wave). Differentiating these necessitates observation of the flame front geometry. For these experiments, the composition was cast into rectangular channels with a U-shaped cross section, leaving the top surface open for direct observation. The results also show a counterintuitive trend with flame speed increasing with increasing Cr content (above stoichiometric, where the adiabatic flame temperature is expected to decrease). However, the results obtained indicate that the large velocities were associated with flames that are "V" shaped where the leading edges of the flame were located at the channel walls. This pattern can be attributed to a forward convective flow of product material occurring at the interface between the composition and the channel wall. While the melt-casting technique minimized gaps that might be responsible for a convective-driven flow, local melting of the initial composition and expansion of the liquid products is hypothesized to result in a forward convective flow of product at the confining wall. Observation of the high speed movies also strongly suggested that the flame front at the bottom of the channel (not directly visible) was leading the side wall propagation.

• Tests performed with three different channel materials (aluminum, brass, steel) did not reveal any significant correlation of propagation speed with confinement material, suggesting that the observed flow was not driven by surface tension.

• The observation of anomalous propagation modes in which the combustion front appears to lead at the edges of the charge reiterates the importance of differentiating the apparent propagation velocity from the fundamental (normal) burning velocity for SHS systems with liquid products.

• The forward convective propagation phenomenon could be partially suppressed by reheating the composition past the melting point of the sulfur such that the entire charge was molten prior to propagation. In this case, for a stoichiometric composition the front was approximately parabolic in shape with the region near the center of the charge leading and the propagation speed was only 15-20 mm/s. This technique did not suppress the V-front formation with Cr-rich molten compositions, however, as these compositions remained paste-like and did not exhibit a fluid-like rheology when heated above 120 °C. The burning velocity for the various compositions falls within the range of 8 to 12 mm/s, consistent with previous measurements of burning velocity in metal-sulfur mixtures.

• To investigate the mechanism of combustion synthesis of the chromium-chromium sulfide composite, the reactive mixture of Cr and S was used for a combustion front quenching test. The Cr-S mixture was ignited and quenched, the combustion-reacted product was inspected by XRD, and the microstructural evolution of the reaction in the quenched sample was analyzed with SEM and EDX. Based on these experimental results, the mechanism of the combustion reaction was discussed. From the microstructural evolution during the combustion reaction of Cr-S mixture, it was concluded that the combustion reaction between Cr and S starts with solid-state diffusion between the Cr particles and S, and continues with the melting of sulfur. Atoms of Cr then start to dissolve into the liquid sulfur near the interfacial boundaries. The melting of the S particles results in the Cr particles dissolving into the S melt, and then the CrS particles precipitate in the saturated Cr–S melt. Also a model corresponding to the solid phase diffusion-dissolution-precipitation mechanism of the self-propagating combustion synthesis has been developed.

• It was observed that the reaction mechanism depends on the Cr particle size. For the case of small particles, the final structure consists of chromium sulfide, but coarse Cr particles do not completely dissolve and remain unreacted, surrounded by chromium sulfide. Both the microstructure and the XRD patterns show that the combustion synthesis was incomplete in the case of coarse Cr powder. Apparently the different reactant particle size lead to different degrees of diffusion of S into the dissolving Cr particles, which follows from the obvious statement that

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the finer the reactant particle size, the smaller the diffusion distance for S atoms to move into the Cr particles.

• In the present study, we first estimated the mechanical properties of the fabricated cermets and then attempted to improve the toughness and other mechanical properties of the Cr-CrS cermets by increasing the metal content. Although thermodynamics predicts that 200% excess Cr is the upper limit on the Cr content to permit a self-sustained reaction to occur, this study continued investigation of cermets up to a Cr:S molar ratio of 4 times the stoichiometric value. Dense specimens with Cr particles embedded in a chromium sulfide network were obtained. The microstructure, mechanical properties, and fracture surfaces of the CrS-based cermets have been investigated and clearly observed.

• Mechanical properties were measured as a function of Cr:S molar ratio. Quasi-static properties demonstrate the role of chromium addition, which leads to an overall improvement of the mechanical properties of the fabricated cermets. Statistical analysis was performed using one-way ANOVA. P values less than 0.05 were considered to be statistically significant in all tests. The differences in means of each group were analyzed by analysis of variance (ANOVA) with micro-hardness, flexural strength and fracture toughness as the dependent variables, and the Cr:S molar ratio (chromium content) as the independent factor. ANOVA exhibited highly significant differences among the tested composite materials for the mean values of micro-hardness (p < 0.005), flexural strength (p < 0.01), and fracture toughness (p < 0.05).

6.2 Thesis contributions to original knowledge

The following list summarizes the main contributions to original knowledge in the present study:

- Demonstrated the combustion synthesis of a new cermet (chromium-chromium sulfide)
- Developed a novel manufacturing technique to synthesize metal-sulfide cermets, which was optimized to minimize the porosity of the product
- Evaluated the microstructure and mechanical properties of the fabricated cermet and correlating them with the chemical composition
- Proposed a model based on the solid phase diffusion-dissolution-precipitation mechanism for combustion synthesis of the chromium-sulfur system
- Determined the combustion parameters, i.e., quenching thickness and diameter, chemical thickness, heating zone thickness, flame propagation speed, and burning rate

- Demonstrated an improvement in the mechanical properties of Cr-CrS cermets by increasing the metal content in the product
- Plotted the material properties on Ashby diagrams which is useful for finding new applications for the fabricated cermets based on its density and properties

6.3 Future work

During the course of this research, a method for net-shape manufacturing of chromiumchromium sulfide cermets was developed and the combustion behavior and microstructure evolution in the Cr-S system were studied. The mechanical properties were investigated and based on them, new applications for the cermet were proposed. These studies and methods provide a platform for further exploring the full potential of the metal-sulfur composites, and the following guidelines are proposed as a continuation to this work:

• According to the manufacturing process of Cr-CrS cermets that we conducted and described here, it is possible to make these cermets as functionally graded materials, because they can be cast layer by layer with different compositions (various Cr contents) in a mold with the desirable final shape of the article. The ability to generate a sample with a continuous variation in properties is attractive for many applications and could be explored in further work.

• It is possible to make a hybrid composite by adding hard ceramics inclusion to the fabricated cermet. Harder inclusions with different geometries and volumes (such as boron carbide or silicon carbide) can be easily imbedded into the reactive mixture and remain in the cermet after the SHS synthesis. The mechanical and ballistic properties of hybrid composites produced in this way could then be investigated. The size, volume and geometry of the embedded ceramic elements can be optimized based on modeling results.

• The manufacturing method developed is simple and low-cost and can be used to fabricate other metal-sulfur systems, e.g., iron-sulfur, manganese-sulfur, etc. It is also possible to make hybrid composites by using a ternary system such as Cr-Fe-S.

• In-situ manufacturing of a hybrid composite (sulfide cermet with ceramic inclusions) can be studied based on the exothermic reaction below:

 $Cr_2O_3+(X)Cr+2 Al + S = CrS + Al_2O_3 + (1+X) Cr$

According to the thermodynamic calculations, this reaction can occur in the SHS mode since it satisfies both empirical conditions for self-sustained reactions (equation 1-1 and 1-2 in chapter 1). Thermodynamic calculations indicate that we can add 600% excess Cr to this reaction and a self-sustained reaction is still expected to occur (X=6). Based on the improvement to the properties of the Cr-S system with added Cr in the present work, it is expected that the mechanical properties of this hybrid composite with high Cr content would be quite attractive for a variety of applications.

6.4 Publications from the present work

6.4.1 Referred journals

- A. Nabavi, A. Capozzi, S. Goroshin, D. Frost, F. Barthelat, "A novel method for net-shape manufacturing of metal-metal sulfide cermets", Journal of Materials Science, 2014, in press.
- A. Nabavi, S. Goroshin, D. Frost, F. Barthelat, "Mechanical properties of chromiumchromium sulfide cermets fabricated by self-propagating high-temperature synthesis"
- A. Nabavi, D. Frost, F. Barthelat, "Microstructural evolution during the combustion synthesis of Cr-S system"
- A. Nabavi, A. Capozzi, A. J. Higgins, S. Goroshin, D. Frost, F. Barthelat, " Combustion synthesis of metal sulfide composites"
- J. Loiseau, A. Nabavi, A. Capozzi, A. J. Higgins, D. Frost, F. Barthelat, "Ballistic Impact Response of Chromium-Sulfur Composite Ceramics"

6.4.2 Conference papers

- A. Nabavi, A. Capozzi, S. Goroshin, D. Frost and F. Barthelat, "Net-shape Manufacturing of Metal-Metal Sulfide Cermets by SHS", SHS 2013, XII International symposium on selfpropagating high temperature synthesis, South Padre Island, TX, USA, Oct 2013.
- J. Loiseau, A. Capozzi, A. Nabavi, O. Petel, A. Devito, S. Goroshin, A. J. Higgins, D. Frost, "Ballistic Impact Response of Chromium-Sulfur Composite Ceramics", International Ballistics Society (IBS) conference, Germany, April 2013.

- A. Nabavi, A. Capozzi, A. Higgins, S. Goroshin, D. Frost, F. Barthelat, "Combustion Synthesis of Chromium Sulfide Metal-Ceramic Composites for Ballistic Protection", ISICP, Quebec city, Canada, July 2012.
- A. Nabavi, A. Capozzi, A. Higgins, D. Frost, S. Goroshin, F. Barthelat, "Combustion Synthesis of a Chromium/Chromium Sulfide Ceramic-Metal Composite", Combustion Institute–Canadian Section, Spring Technical Meeting, University of Toronto, May 2012.
- A. Nabavi, A. Capozzi, S. Goroshin, D. Frost, F. Barthelat, "Net-shape manufacturing of a novel cermet using self-propagating high temperature synthesis", The Minerals, Metals and Materials Society (TMS) annual meeting, US, Florida, Feb 2012.

Appendix I: Cr-CrS cermet properties plotted on Ashby charts

Fig. I-1 shows a Young's modulus-density chart. An important use of this chart is in material selection for applications in which mass must be minimized. Guidelines corresponding to three common geometries of loading are shown on the chart. They are used to select materials for elastic design at minimum weight. As expected, Cr-CrS cermets extend along the overlap area between metals and ceramics and have a combination of properties of both groups. This chart gives an indication of the possible applications of this new cermet through a comparison with existing materials. For example, Cr-CrS cermets exhibit a total overlap with Ti alloys. They also provide the same Young's modulus as Cu alloys with a much lower density. The Young's modulus of Cr-CrS cermet is close to that of steel while its density is about a half of steel. Moreover, they have a higher Young's modulus and lower density than Zinc alloys. Therefore, they can be considered to replace these materials in specific applications because of their low-cost and relatively convenient manufacturing process, which leads to a lower final price for the production of these cermets.



Figure I-1. Young's modulus E plotted against density \cdot . The heavy envelopes enclose data for a given class of material. The diagonal contours show the longitudinal wave velocity. The guide lines of constant E/ , E1/2/ , and E1/3/ allow selection of materials for minimum weight, deflection-limited, design [1]

A chart showing material strength versus density is shown in Fig. I-2. In this chart, the word "strength" refers to *yield* strength for metals and polymers, *tear* strength for elastomers, *tensile* strength for composites and woods, and *flexural* strength (modulus of rupture) for ceramics. For all of them, the symbol σ_f is used. This charts helps in materials selection in lightweight plastic design. Guidelines are drawn on the chart for materials selection for the minimum weight design of ties, beams and plates, columns, and for yield-limited design of moving components in which inertial forces are important. According to this chart, Cr-CrS cermets have the same range of strength with Al₂O₃, SiC, and Si₃N₄. Its strength is higher than GFRP, Al, Mg, zinc and lead alloys. It also has overlap with Ti alloys and steels. These cermets are much lighter than tungsten carbide, although they have a similar strength.



Figure I-2. Strength $_{\rm f}$ plotted against density (yield strength for metals and polymers, compressive strength for ceramics, tear strength for elastomers, and tensile strength for composites). The guide lines of constants f/, 2/3 f/, and 1/2 f/ are used in minimum weight, yield-limited, design [1]

One of the most useful of all the charts is shown in Fig. I-3, which plots Young's modulus against strength. In this chart, the qualifications for "strength" are the same as before. The design guidelines help with the selection of materials for springs, knife-edges, pivots, diaphragms, and hinges. Contours of fracture strain or yield strain (σ_f/E) - the strain at which the material ceases to be linearly elastic- appear as a series of parallel lines. Cr-CrS cermets lie on the 0.01 contour, as good as composites, woods, and the best metals.



Figure I-3. Young's modulus, E, plotted against strength, f [1]

References

1. Ashby, M.F., *Chapter 4 - Material Property Charts*, in *Materials Selection in Mechanical Design (Fourth Edition)*, M.F. Ashby, Editor. 2011, Butterworth-Heinemann: Oxford. p. 57-96.