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The Analysis and Minimization of Oxygen Contamination in the
Powder Processing of Molybdenum Disilicide

by

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
Molybdenum Disilicide as a Future Engineering Material	1
LITERATURE SEARCH	4
Current Powder Processing Techniques	4
Oxygen Contamination in the Molybdenum Disilicide System	9
The "pesting" phenomena of molybdenum disilicide	9
Silica formation in molybdenum disilicide	11
Oxygen Control	15
Self-Heating High Temperature Synthesis	16
OBJECTIVES OF RESEARCH	18
MATERIALS AND METHODS	20
Powders Used	20
Powder Characterization Techniques	22
Powder size analysis	22
Powder surface area analysis	22
Light microscopy	23
Scanning Electron Microscope (SEM)	23
Oxygen analysis	24

Auger Electron Spectroscopy (AES) and Energy Dispersive Spectroscopy (EDS)	25
Auger Electron Spectroscopy Depth Profiling	26
X-Ray Diffraction	26
Density Testing	26
Processing Methods	27
Cold Isostatic Pressing	27
Hot Isostatic Pressing	28
RESULTS AND DISCUSSION	30
Initial Powder Characterization	30
Oxygen analysis	30
X-Ray Diffraction	32
Powder size analysis	33
Powder surface area analysis	34
Imaging of the powders	35
Auger Electron Spectroscopy and Energy Dispersive Spectroscopy (EDS) analysis of powders	42
Significance	46
Processing of Fully-Dense Compacts	51
Analysis of Specimens with Varying Amounts of Oxygen Contamination	61
Production of Powders with a Lower Relative Amount of Oxygen	80
Reduction of the Powders	80
Self-Heating High Temperature Synthesis	84

SUMMARY	95
FUTURE RESEARCH POSSIBILITIES	98
BIBLIOGRAPHY	99

INTRODUCTION

Molybdenum disilicide (MoSi_2) has been known as a high melting (2030°C) intermetallic compound for almost eighty years. It has found application as a heating element material due to its metal-like conduction and excellent oxidation and corrosion resistance at temperatures up to 1650°C (1). This oxidation resistance is due to the formation of a self-healing, protective silica (SiO_2) layer. It also has a moderate density (6.24 g/cm^3). These properties make MoSi_2 an attractive candidate for structural use in high-temperature, oxidizing atmospheres such as turbine blades. However, its brittleness below 1000°C , low creep resistance, and the occurrence of a "pest" oxidation around 550°C have previously denied its use.

Molybdenum Disilicide as a Future Engineering Material

Turbine engine efficiency is directly related to how high a temperature the turbine section can maintain. Titanium and nickel-based super-alloys have been engineered to their maximum abilities. Any progress in high-temperature structural materials involve a new base material (2). New materials, primarily intermetallics, that will maintain structural integrity in this high temperature regime (above

1300°C) are being researched. MoSi_2 has a low enough ductile to brittle transition temperature ($\approx 900^\circ\text{C}$) that it has toughness in the regime of use for turbine blades, unlike ceramic materials such as silicon carbide. MoSi_2 exhibits good heat conduction, which is required in turbine blades, to allow for heat transfer from the blades. However, with higher temperature use, oxidation also becomes a serious threat to most materials. Thus, MoSi_2 is a prime candidate for this application if its pest oxidation, brittleness below 1000°C , and high temperature creep can be overcome.

A solution to these problems is being thoroughly pursued, predominantly by using MoSi_2 as a matrix for various composites (3-26). These efforts seem premature due to the minimal understanding of the monolithic material and the lack of suitable synthesis and processing techniques (27). The role that oxygen contamination (and thereby silica) plays in the ductile to brittle transition, low temperature fracture toughness, creep resistance, and pest phenomena has been questioned and needs to be thoroughly researched prior to further application engineering (28-34). The focus of this research will be the development of an improved powder processing method using a glass can, the understanding the role of oxygen contamination in the system and the procedures required to make compacts with minimal contamination. The

mechanical property effects of this contamination will be left for future research.

LITERATURE SEARCH

The literature search was limited to types of processing whose final product would be used in a structural application. The production of fully-dense molybdenum disilicide compacts is done using powder processing. Since surface contamination can be significant in powder processing an investigation into the effects and manner of oxygen contamination in the molybdenum disilicide system was then completed. A method of producing cleaner molybdenum disilicide was then researched.

Current Powder Processing Techniques

Powder metallurgy is necessary in the processing of MoSi_2 fully dense compacts used for mechanical testing and structures. Due to MoSi_2 's high melting temperature (2030°C), it is not feasible to melt the material for processing due to containment, contamination, and other problems inherent in high temperature processing. The phase diagram for the Molybdenum-Silicon system is shown in Figure 1.

Figure 1. Molybdenum-Silicon phase diagram

As shown on the graph, MoSi₂ is a quasi-line compound. This means that there is a small range of compositions that will produce MoSi₂. If the system is silicon poor Mo₅Si₃ will be produced. Mo₅Si₃ is not as resistant to high temperature oxidation as the desired MoSi₂. If the system is silicon-rich the presence of excess silicon will be found in the system. This will lead to liquid silicon in the microstructure at temperatures above 1400°C, which would be catastrophic. This excess silicon could also become silica (SiO₂) in the presence of high temperatures and oxygen.

Plasma spraying of MoSi_2 has been used for sputtering, however, it is a "dirty" process due to the inherent presence of high temperatures and large amounts of highly active surface area (35). If a fully-dense compact is to be made from any other type of processing (plasma spraying, mechanical alloying, etc.), the product is reduced to a powder and powder processing is used. The final densification of powder processed MoSi_2 is done in a Hot Isostatic Press (HIP) or a Hot Press (HP) at a temperature below the melting point. For the HIP, a tantalum canning method is most commonly used. Canning of the specimen in tantalum is often difficult to do under a controlled atmosphere, which could lead to silica contamination during the high temperature processing. A compilation of processing conditions that other researchers have used to create near full-density MoSi_2 in the HP and the HIP is given in Table 1.

Table 1. Processing conditions used in the densification of MoSi_2 and MoSi_2 composites prepared from reacted powders

Material	Supplier of Powder	Temp ($^{\circ}\text{C}$)	Pressure (MPa)	Time (hrs)	Ref
<u>Hot Pressing</u>					
MoSi_2	Alfa	1830	"full load"	1	[36]
MoSi_2	Cerac	1700	31		[54]
MoSi_2 (TiC)	Cerac	1700	25	--	[4]
MoSi_2 (SiC)	N/A	1700	30.5	--	[28]
MoSi_2 (SiC)	Materials Research Corp.	1625	41.4	--	[10]
MoSi_2 (PSZ)	Alfa	1700	30	--	[26]
<u>Hot Isostatic Pressing</u>					
MoSi_2	Cerac & Stark	1700	207	4	[50]
MoSi_2	Cerac	1600	310	2	[56]
MoSi_2 (Nb)	Stark	1350	172	3	[9]

However, there is a great deal of variation in how the powders are processed prior to densifying. The most common is to use reacted powders and standard powder handling procedures as shown above in Table 1. Others have started with the elemental powders which allow control of the stoichiometry and purity.

For reacted MoSi_2 powders the press is heated to between 1400 and 1850°C for one to five hours depending on whether the powders included any reinforcements (composites) and what that reinforcement is. This process creates a compact that is near full density.

The elemental powders are reacted to form the intermetallic compound using various techniques. This reaction can be combined with the HIP process. HIPing of the elemental powders is commonly performed at 1400°C for one hour and then followed by a slow cool to room temperature over 12 hours. This produces fully dense compacts (37). Due to the exothermic nature of the reaction, the compact reaches temperatures near 1900°C. Another method being experimented with is mechanical alloying of the powders (38-41). As a way to get ultra-pure MoSi_2 , self-heating high temperature synthesis (SHS) has been used to create MoSi_2 . SHS is of interest in that it can only produce MoSi_2 (i.e. no intermediate compounds) and the reaction volatilizes the oxygen. Both the mechanically alloyed and combustion synthesized samples are milled to powder form and HIPed to make fully dense compacts.

Oxygen Contamination in the Molybdenum Disilicide System

A review of oxygen effects in MoSi_2 , how researchers are dealing with the oxygen contamination, and a potential method of producing relatively clean MoSi_2 is contained in this section. The "pestring" phenomena has been found to catastrophically disintegrate densified MoSi_2 exposed to oxidizing atmospheres around 500°C . The mechanism that causes pestring and how to avoid it will be discussed. Silica formation on MoSi_2 and what effects this may cause are then analyzed. Other researcher's methods of limiting the oxygen contamination are examined and a method able to produce "clean" MoSi_2 is described in the following section.

The "pestring" phenomena of molybdenum disilicide

MoSi_2 is known for its excellent oxidation resistance. However, around 500°C it is known to catastrophically oxidize and this was described first in 1955 by Fitzer as the "pest" phenomena (42). This pestring has been found to be a function of molybdenum oxide (MoO_3) volatility. MoO_3 has a melting temperature of 795°C and therefore does not volatilize rapidly below 600°C . The unsublimed MoO_3 interferes with the cross-linking of the slow-growing SiO_2 structure and causes the formation of SiO_2 particles instead of a continuous SiO_2 layer. The pest oxide is found to be composed of a mixture of

small MoO_3 crystals and small "islands" of silica (43). Catastrophic pesting is due to voluminous oxide formation in pre-existing cracks, a volume increase of 340% occurs when MoO_3 is formed, and when SiO_2 is formed an increase of about 180% is incurred (44). Around 500°C , where little MoO_3 volatilization occurs, these voluminous oxides form in pre-existing cracks and pores. The stresses caused by the oxide formation combined with the residual stresses due to cooling of the anisotropic crystal structure lead to crack propagation. A schematics of this process is shown in

Figure 2.

Figure 2. Schematic of the "pesting" phenomena

In MoSi_2 samples of less than 98% theoretical density, exposure to these temperatures for several days causes complete disintegration of the sample. Catastrophic pesting never occurs in fully dense MoSi_2 , due to the lack of oxide nucleation sites and easy diffusion pathways through the cracks (45,46). However, even the presence of microcracks in MoSi_2 composites due to the difference in the coefficient of

thermal expansion between the matrix and the fibers is enough to allow pesting to occur. Therefore, the pest phenomena is not a material property, but is a function of microstructure (47). Another way to prevent pesting is to pre-oxidize at high temperatures (around 1200°C). Above 1000°C, the MoO_3 sublimates rapidly and allows the formation of a continuous SiO_2 layer. This leads to the oxidation resistance that MoSi_2 is known for (48-53).

Silica formation in molybdenum disilicide

Other researchers have stated that even at room temperature, the attraction of MoSi_2 to oxygen leads to contamination problems. This could be a significant problem when using powder processing due to the large amount of exposed surface area (54). The oxidation reaction is shown below.

Since SiO_2 has a relatively high heat of formation, it is assumed that oxidation would occur if not for a thin adherent film of oxide. The available information on the oxidation kinetics of silicon has been reviewed and graph of the

kinetics of this oxidation reaction extrapolated to room temperature is shown in Figure 3.

Figure 3. Kinetics of the oxidation of pure silicon extrapolated to room temperature where the amount of oxygen consumed = $k \log(1+0.4t)$ [55]

The oxidation rate constant, k , which is graphed on the vertical axis, defines the rate at which the oxidation proceeds. A smaller value for the rate constant would signify slower kinetics for the oxidation reaction. Therefore, using the ideal extrapolation shown in Figure 3, it would seem that the kinetics of MoSi_2 oxidation at room temperature would be extremely slow. If the activation energy of the oxidation

reaction remained constant over the temperature range the ideal extrapolation would be warranted. However, this is not the case. The activation energy required for the oxidation reaction can be reduced significantly by a change in the diffusion method or by the effects of tunneling in thin oxide layers. At high temperatures lattice diffusion is the dominant method of anion and cation transport through the oxide scale. However, at low temperatures grain boundary diffusion becomes significant, which is much easier than lattice diffusion at low temperatures and would reduce the required activation energy. In electron tunneling, a constant electric field is created across the oxide layer, which reduces the activation energy required for cation migration. These changes in the required activation energy can lead to a kinetics curve that looks more like the non-ideal curve shown in Figure 3. Thus, it is possible that room temperature oxidation of the powders could occur, even if only enough to create a thin protective scale that passivates the surface. Therefore, determining the state of oxygen on or in the powder when exposed to the atmosphere, and how this contamination occurs is key to this research.

How oxygen contamination in the powder state affects the properties of fully dense MoSi_2 is not fully understood. It has been proposed by other researchers that a fully dense MoSi_2 compact with a minimal amount of oxygen (less than

6500 ppm) would have a ductile to brittle transition temperature between 1300-1400°C instead of the previously reported 1000°C. The discrepancy between these two reported values is most likely due to the presence of silica in the grain boundaries, which would contribute to viscous sliding of grains above 1000°C (56). This ductile behavior in the high purity MoSi_2 above 1300°C is shown in Figure 4.

Figure 4. Stress-strain curves for high purity MoSi_2 deformed in a four-point flexure at various temperatures [56]

Other problems may be related to the silica contamination of the microstructure as well. The observed high temperature creep of MoSi_2 could also be due to the wetting of the grain boundaries by the silica, leading to viscous sliding of grains during deformation at temperatures above 1000°C. It has also

been found that grain growth is limited by larger amounts of silica content (57).

Oxygen control

The control of oxygen contamination is being dealt with in many ways. Some researchers are trying to obtain the purest powder available and use precautions in the handling to limit the exposure. Powders can be bought from many suppliers in various levels of metallic purity. However, this purity does not take into account the amount of oxygen present. Other researchers are attempting to use a getter (e.g. hydrofluoric acid wash) to reduce the oxygen contamination on the powders prior to processing. This seems to have "qualitatively" reduced the amount of oxygen in the specimens. These have only been analyzed using the microstructure of the final products and not an actual oxygen content analysis (58). However, the most promising method of contamination control seems to be the use of SHS to produce powders that are pure and using precautions in the production of a HIP specimen.

The HIPing process is done under argon and, therefore, there should be no potential for oxygen contamination during the cycle. However, care must be taken when "canning" the compacts prior to the run so that the specimen is not exposed to oxygen.

Self-Heating High Temperature Synthesis

Self-Heating High Temperature Synthesis can be done with any system that creates a large enough exotherm during the reaction of the elemental powders to propagate the reaction.

$$H_f^\circ = -31.4 \text{ kcal}$$

Since the reaction of molybdenum and silicon is quite exothermic, a self-sustaining reaction can be created. In the MoSi_2 system, it has been found that the reaction is due to liquid silicon diffusing into the solid molybdenum and reacting. This reaction is usually started by heating a compact of at least 59% theoretical density to 1460°C with a coil, once ignited, heating rates in the range of 10^4 to 10^6 $^\circ\text{C}$ per minute are found along the specimen. A schematic of the SHS reaction is shown in Figure 5.

Figure 5. Schematic of the Self-Heating High Temperature Synthesis of MoSi_2

If the powders are mixed in the appropriate ratio this reaction creates no intermediate reactions, such as Mo_5Si_3 or Mo_3Si . The large exotherm is also able to drive any volatiles out of the system, thereby, cleaning the product in the process (59-64).

OBJECTIVES OF RESEARCH

Prior to employing molybdenum disilicide as a next-generation material, its properties must be understood. The presence of silica in the monolithic material may have a deleterious effect on the properties of MoSi_2 . Therefore, the focus of this research is the analysis and control of oxygen contamination in the powder processing of molybdenum disilicide. The objectives of this research are listed below.

- a) Complete characterization of the MoSi_2 powders. This included normal powder characterization and a special emphasis to determine in what form the oxygen is present and its location.
- b) Analysis of other researchers' claim that purchased powders rapidly oxidize at room temperature.
- c) Develop an improved technique of powder processing that is simple and will minimize the oxygen contamination during the processing. This improved encapsulation method can be used to determine what, if any, gains a decrease of oxygen contamination allows.

d) Complete analysis of the microstructure created from powders of varying oxygen content. This is to determine what form oxygen is present in the compact and the location of this contamination. What effect this oxygen contamination has on the microstructure was also determined.

e) Attempt to develop a method to produce MoSi_2 of a relatively lower amount of oxygen present. This was attempted by oxide reduction of the powders and by producing powders from the elemental precursor powders.

The completion of this research should further the understanding of oxygen's role in the microstructure of molybdenum disilicide and the potential for controlling this contamination.

MATERIALS AND METHODS

The complete characterization of the powders was the first priority. Once characterization was complete, research was to be conducted to determine how the oxygen contamination is present on and in the powder. An improved process for HIPing was developed in order to produce fully-densified compacts of MoSi_2 . These compacts were then analyzed to determine any microstructural effects due to varying amounts of oxygen contamination in the powders. An overview of materials and methods used in the research of MoSi_2 is given below.

Powders Used

Powders were obtained that are representative of those commonly used in research. MoSi_2 powders were obtained from four different suppliers and one sample of each elemental powder (silicon and molybdenum) was obtained. These powders have been characterized by the suppliers and the characterizations received are displayed in Table 2.

Table 2. Powder characterization received from suppliers

Powder #	Supplier Data			
	purity (%)	mesh	Oxygen (ppm)	Nitrogen (ppm)
<u>Reacted Powders</u>				
Alfa	98.9	-325	7800	500
Cerac	99.5	-325	N/A	N/A
Noah	99.5	-325	N/A	N/A
Stark	98.5	1.11 μ^a	18000	400
<u>Elemental Powders</u>				
Alfa - Mo	99.9	-325	500	N/A
Noah - Si	99.5	-325	N/A	N/A
N/A - not available.				

a - average powder size.

Most of the suppliers would not divulge any information about how the MoSi_2 powders were made. However, HC Stark did say that a reactive sintering process was used to make their MoSi_2 powders. This was done by reacting a compacted billet of the elemental powders in a furnace. Any further details were not made available. It is quite possible that all of the powders were made in a similar fashion. The product of the reaction would be a solid billet of MoSi_2 that would need to be milled and classified.

Powder Characterization Techniques

Powder size analysis

All of the powders were analyzed to determine the average particle size and distribution using a Horiba Particle Size Distribution Analyzer, model CAPA-700. This technique is based on Stoke's law of sedimentation of small spherical particles. Stoke's law correlates a particle's diameter to a characteristic sedimentation rate in a fluid. By correlating light transmission through the dilute powder solution to a particle size's sedimentation rate, a particle size distribution can be determined. Centrifugal sedimentation was used for this experiment. The viscosity of the fluid and centrifugal rotation rate must be adjusted for each different powder size to ensure that the sedimentation rate is moderate enough to be measured accurately. Since the powders tested were not the ideal spherical shape some amount of error was incurred (65). The average particle size and distribution was compared against the data received from the supplier and was also used to estimate the surface area of the powders, assuming a spherical shaped powder.

Powder surface area analysis

A surface area analysis of the powder was completed to determine specific surface area. A B.E.T surface area

measurement, which uses nitrogen adsorption and dynamic flow principles, was completed on all of the purchased MoSi_2 powders at Pennsylvania State University. A clean powder surface is created and is exposed to nitrogen vapors. A measurement is made of how much gas has adsorbed on the powder surface versus the partial pressure (66). The surface area of the powders is used to determine the amount of shape irregularity by comparing the actual value to the estimated surface area using a spherical powder assumption. It can also be correlated to a known property to determine if the property is surface area dependant.

Light microscopy

A light microscope was used for the initial characterization of the microstructure of densified samples. Polarized light is capable of distinguishing MoSi_2 grains and silica. These photographs were used for quantitative microscopy and for comparison with the SEM images.

Scanning Electron Microscope (SEM)

A Cambridge Stereoscan-200 scanning electron microscope was used in the characterization of the powders and for quantitative microscopy of the densified specimens. Secondary Electron Images (SEI) were taken to determine the powder's shape, which is useful when correlating the shape of the

powders with the process used to make the powder, the green strength of pressed compacts and the sintering properties.

The microstructure analysis was completed using SEI, Back-Scatter Electron (BSE) imaging, and Electron Dispersive Spectroscopy (EDS). SEI is most sensitive to topographical variations on the specimen. BSE imaging is most sensitive to orientation of the crystal planes. EDS, which uses X-ray emissions, was used to determine which elements are present in the specimen. Elemental mapping of the microstructure was done using a Jeol Model 840A SEM with a Kevex Delta-5 scanning EDS. By comparing this map with an SEI image and a light photograph any changes in the elemental constituents are correlated to visual and topographical effects.

Oxygen analysis

The ability to accurately measure the amount of oxygen present during all phases of the processing of MoSi_2 is crucial to this research. A LECO model TC-436 nitrogen and oxygen determinator, using the conventional inert gas fusion method, is capable of establishing the concentration of each element present in the sample. One can determine which nitrides and oxides are present and amounts of each by gradually increasing the temperature and observing at what temperature the gases are evolved. The range of contamination that this method is able to measure can be adjusted by in-

creasing or decreasing the mass of the sample tested. The accuracy for oxygen and nitrogen detection is $\pm 0.00005\%$ (0.5 ppm) or 1% of O_2 present (67).

Auger Electron Spectroscopy (AES) and Energy Dispersive Spectroscopy (EDS)

A Perkin-Elmer model 600 AES was used in this research. The AES allows determination of elemental constituents in the first few monolayers of a specimen, and to a less degree, the bonding of the elements by analyzing the Auger electrons. A six kilovolt electron beam was used because it gives good carbon $K\alpha$, oxygen $K\alpha$, silicon $K\alpha$, and molybdenum $L\alpha$ X-ray lines and also allows the EDS to work up to a depth of about 200 monolayers (1000Å).

Other researchers reported oxygen contamination on the powders as SiO_2 . This testing can determine the state of the oxygen (i.e. hydroxyl group, silicon oxide, molybdenum oxide, etc.) and relatively how much of each element is present. EDS, which was described in the last section, is done simultaneously with the AES. The combined data from these two techniques allows for comparison of surface and bulk oxygen concentrations.

Auger Electron Spectroscopy Depth Profiling

Auger Electron Spectroscopy and Energy Dispersive Spectroscopy, alternating with sputtering with an argon ion beam, can be used to determine the profile of the elemental constituents over a depth in the powders. This produces data that will determine whether the oxygen contamination is merely a surface phenomena, and to what depth, or also interstitial (68).

X-Ray Diffraction

To characterize the actual crystallographic phases present in the powders, X-Ray Diffraction (XRD) was used. A Scintag XDS-2000 was used for this research. XRD is capable of identifying crystalline phases in a material by diffracting X-rays off of the material's crystal planes. Since each material has a distinctive diffraction pattern, the phases can be identified. However, XRD is not capable of identifying amorphous phases, and a minimum amount of a phase ($\approx 2\%$) must be present to allow identification.

Density testing

Density measurements were carried out using a gas pycnometer and water buoyancy density testing. A pycnometer is capable of measuring a samples closed-pore density by using gas pressure-volume comparisons. This density measurement was

used to measure the initial density of the powders and the density of the fully-dense compacts. Water buoyancy density testing (ASTM B329-80) was attempted on the CIP compacts, but the sample was not able to maintain integrity during the testing. Water buoyancy density measurements are done by comparing the weight of the sample in air and the weight of the sample suspended in water. Since this method was not effective, an green density of the CIP compacts was estimated by correlating the weight of the compact to a rough volume measurement.

Processing Methods

Cold Isostatic Pressing

The green compacts were made using a ABB Autoclave Engineers cold isostatic press (CIP). The powders are placed in a sealed, flexible container. This container is usually made of rubber or polyurethane. This is then placed in a chamber of ethylene glycol, which is the pressure transmitting liquid. The liquid is then pressurized and the specimen is subjected to an isostatic pressure that densifies the powders.

It was found that a thin-walled bag was the best container. Thicker walled containers were found to pull the pressed sample apart after CIPing due to tensile effects caused by the container expanding to its original size while

the sample could not. It was found that a low pressure (≈ 12 ksi) was best for the brittle MoSi_2 powders. Brittle materials depend on mechanical interlocking to provide the green strength, and higher pressures will break the brittle particles and decrease the amount of interlocking. Higher pressures (≈ 30 ksi) were beneficial for the CIPing of elemental powders. Ductile materials, such as silicon powder, deform and allow for higher green strengths due to this deformation.

Hot Isostatic Pressing

To fully densify the powders, a International Pressure Service Eagle Hot Isostatic Press (HIP) was used. The sample is placed in a container that will be ductile at the sintering temperature. This container is then evacuated and sealed. The container is placed in a crucible for secondary containment, which is placed in the HIP chamber. The chamber is evacuated and purged with argon, which is used as the pressure transmitting gas during the HIP cycle. The chamber is pressurized and heated to the desired sintering pressure and temperature, respectively and held to allow the densification to occur. This combination of heat and pressure is capable of producing near-theoretical density specimens. Once the densification is complete the system is returned to ambient conditions and the sample is removed. The details of

the actual process used to produce MoSi_2 , which forms a major part of the objectives of this project, will be discussed more fully in a later section.

RESULTS AND DISCUSSION

The focus of this research will be the development of an improved powder processing method using a glass can, the understanding of the role of oxygen contamination in the system and the procedures required to make compacts with minimal contamination. The mechanical property effects of this contamination will be left for future research.

Initial Powder Characterization

Initially it was necessary to fully characterize the powders. This information would be compared to the supplied information to ensure that the powders were appropriate and what was expected. When powders were manufactured in-house, these same techniques were used to control the process. The results of the initial powder characterization are below.

Oxygen analysis

To establish their original contamination, the oxygen content of the powders was tested with the LECO nitrogen and oxygen determinator upon arrival. Most researchers are unable to determine the oxygen content and, therefore, are obligated to believe the analysis done by the supplier. The ability to freely use this oxygen testing technique is exceptional and

produces information that is indispensable to MoSi₂ researcher. Four samples of each powder were tested to accurately determine the oxygen contamination of the powders. The results are displayed in Table 3.

Table 3. Data from initial oxygen analysis of powders compared to the powder analysis data provided by the suppliers

Powder #	LECO analysis		Supplier Data	
	Oxygen (ppm)	Standard Deviation	Purity (%)	Oxygen (ppm)
<u>Reacted Powders</u>				
Alfa	12803	192.2	98.9	7800
Cerac	4903	112.9	99.5	N/A
Noah	6884	161.1	99.5	N/A
Stark	24100	430	98.5	18000
<u>Elemental Powders</u>				
Alfa - Mo	6405	15.0	99.9	500
Noah - Si	12750	50.0	99.5	N/A

N/A - not available.

By comparing the LECO analysis data and the supplier's data, it is apparent that the declared purity only accounts for the metallic purity of the powders and does not account for the oxygen contained in the powder. For example, Stark's powder was sold as 98.5% pure, but contains almost 2.5%

oxygen. Also, the proclaimed amount of oxygen present in the powders, when provided by the supplier, does not necessarily represent what the powder will have in the as-received condition. Stark emphasized the need for exceptional care in the handling of the powders, but then supplied the powder with the worst contamination. The Stark Grade-C MoSi_2 powder is a commonly used powder in MoSi_2 research and it contained nearly 2.5% oxygen in the as-supplied condition. This large amount of inherent silica content has the potential of seriously affecting other researcher's conclusions.

The elemental powders also had a significant amount of oxygen present. However, this can be improved when the powders are reacted using self-heating high temperature synthesis or reactive sintering. As stated previously, these reactions are known to volatilize oxygen from the sample, due to their exothermic nature. This will be discussed more thoroughly in a later section.

X-Ray Diffraction

X-ray diffraction was used on all bought samples to ensure that the powder was pure. An example of a typical MoSi_2 spectrum and the standard diffraction patterns for MoSi_2 , Mo_5Si_3 , and crystalline SiO_2 is shown in Figure 6. However, the silica present is probably amorphous, which would be recognized by a curving of the background signal. However,

none of the powders, reacted MoSi_2 or elemental molybdenum and silicon, displayed anything other than the appropriate peaks.

Figure 6. Typical X-ray Diffraction pattern for MoSi_2 and the standard diffraction patterns for possible materials present in the powders

Powder size analysis

The powders were analyzed to ensure that the powder's size was accurately reported by the suppliers and to approximate the specific surface area of the powders. The data is listed in Table 4.

Table 4. Powder Size in microns (μm)

Powder Supplier	Percentiles			Standard Deviation	Surf Area ^b (m^2/g)
	90% ^a	50%	10% ^a		
Alfa	4.86	2.56	0.496	1.88	0.745
Cerac	19.25	6.96	1.26	11.70	0.319
Noah	35.10	11.75	1.47	11.75	0.186
Stark	2.51	1.23	0.28	0.74	1.294

a - by interpolation.

b - assumes spherical powders.

The first three powders were sold as -325 mesh ($\sim 45 \mu\text{m}$) powders which is generally in agreement with the actual values. Stark powder was sold to us as having an average particle size of $1.11 \mu\text{m}$ which is nearly identical to our calculation. It is also apparent that these four lots of powder vary greatly in size, and therefore, also in specific surface area.

Powder surface area analysis

To get an accurate measurement of the powder specific surface area, 5-point BET measurements were made of the four reacted powders. The specific surface areas of the MoSi_2 powders are given in Table 5.

Table 5. MoSi₂ powder surface areas

Powder Supplier	BET Surface Area (m ² /g)	Powder Size Analysis Surface Area (m ² /g)	Shape Factor
Alfa	1.568	0.745	2.10
Cerac	0.4006	0.319	1.26
Noah	0.4776	0.186	2.57
Stark	2.873	1.294	2.22

The powder size analysis surface area is an ideal area calculated by using the average particle size and assuming spherical powders. The shape factor is determined by dividing the actual BET surface area by the ideal surface area. The shape factor was found to be about two. The shape factor is due to the irregular shapes of the powders and surface roughness. It can be seen in the photos of the next section that the powders are irregular and would therefore have more surface area than a sphere of equivalent volume.

Imaging of the powders

A Scanning Electron Microscope was used to produce photographs of each bought powder, four reacted powders and two elemental powders. All of the photographs were taken at 600x using secondary electron imaging. These are shown in Figure 7 through 9.

Figure 7. (a) Alfa MoSi_2 powder SEI taken at 599x
(b) Cerac MoSi_2 powder SEI taken at 599x

(a)

(b)

Figure 8. (a) Noah MoSi_2 powder SEI taken at 599x
(b) Stark MoSi_2 powder SEI taken at 599x

(a)

(b)

Figure 9. (a) Alfa Mo powder SEI taken at 599x
(b) Noah Si powder SEI taken at 599x

(a)

(b)

All of the MoSi_2 powders (photos 12a through 13b) look similar, only their relative size is different. It is presumed that all of the powders were made by reaction sintering followed by mechanical milling. This would seem to match the rough shape of the powders in the photos. Their relative sizes are the same as predicted by the particle size analysis.

Auger Electron Spectroscopy and Energy Dispersive Spectroscopy analysis of powders

AES and EDS were used to determine the location and state of the oxygen in the MoSi_2 powders. The AES is able to probe the top few monolayers while the EDS's probe depth is a function of the potential of the electron beam. A 6 kV beam was used, which should lead to an AES probe depth of about 5 to 30Å and an EDS probe depth of about 0 to 1000Å. All of the purchased MoSi_2 powders were tested using this method. After testing many points on each powder, it was not possible to distinguish any differences between the powders by their surface oxygen contents.

However, on all of the powders the surface oxygen was not found to be a continuous layer. About five percent of the points that were analyzed on the surfaces were found to have a significantly lower amount of oxygen than the surrounding area.

This points to a localized oxidation of the powders surface rather than a continuous scale forming that passivates the surface. A couple of explanations for this behavior have been theorized. First, the rate of oxidation can be a function of the crystallographic orientation at the surface of the powder. This can lead to widely varied oxidation rates that would lead to oxidation that was localized. This localized oxidation could also occur if hot spots were produced on the surface of the powders that would activate the oxidation, much like would occur during milling. It has been found by other researchers using NdFeB powders that the oxygen content rose as a function of milling time, and was inversely proportional to the powder's size. This seems to be much like our findings. This is shown in Figure 10.

Figure 10. Effect of milling time on the oxygen pick-up (left scale) and particle size (right scale) during ball milling in freon of NdFeB [69]

It is possible to determine what the oxygen is bonded to by observing which Auger peak changes when oxygen is present. By comparison of the silicon Auger peaks (at about 70 eV) and the oxygen Auger peaks (at about 500 eV) in Figures 11 and 12 it can be seen that when there is an increased amount of oxygen the silicon peaks are distorted. Therefore, it can be deduced that the oxygen is bonded to the silicon in the form of SiO_2 .

Since all of the powder's surface oxygen content was similar, only Stark MoSi_2 powder was analyzed using depth profiling. An argon ion beam was used to sputter the powder's surface for eight minutes. This would be equivalent to about

500 to 1500Å of SiO_2 removal. Due to the lack of any standards for comparison it is impossible to determine exactly how much of the MoSi_2 's powder surface was eroded. However, it can be roughly approximated that 2000Å or less of the surface was sputtered.

Examples of the Auger spectrum before and after the ion beam sputtering are shown in Figures 11 and 12.

Figure 11. Auger spectrum of Stark MoSi_2 powder prior to ion beam sputtering

Figure 12. Auger spectrum of Stark MoSi_2 powder after argon ion beam sputtering for eight minutes

By comparing the oxygen Auger peaks (at about 500 eV) before and after the sputtering, it can readily be seen that there is a significant reduction in the amount of oxygen present. This implies that most of the oxygen is confined to the top 2000 Å of the MoSi_2 powders. This would concur with the previous statement that the powders could not be distinguished by the amount of oxygen per unit surface area even though their total oxygen contents may be different.

Significance

Many other researchers emphasized the need for extraordinary precautions when handling the received MoSi_2

powder, so that it does not collect more oxygen. We have attempted to resolve this issue of whether this care is needed using controlled experiments. The amount of oxygen was correlated to the approximate surface area of each powder, which was determined using the powder size analysis data. It was found that oxygen content seemed to be wholly a function of surface area. This is shown in Figure 13.

Figure 13. Plot of Oxygen Contamination vs. Approximate Surface Area of each MoSi_2 powder. The regression R-factor was 0.953

Since the surface area data used in Figure 13 was approximated by assuming spherical powders, which does not

account for the powder's morphology, a new graph was made using the powder's actual surface area. This new graph is shown in Figure 14.

Figure 14. Plot of Oxygen Contamination vs Actual Surface Area of each MoSi_2 powder. The regression R-factor was 0.989

Therefore, the oxygen contamination is entirely a function of surface area. This means that the purchased powders do not become more contaminated over time, but that their surfaces are passive at room temperature. All of the

powders received from suppliers were passivated in the as received condition.

Another experiment was completed to verify that the MoSi_2 powders did not collect oxygen when placed in contact with air. Twelve samples of Stark powder were used for this experiment. Four samples of the control group were tested at the beginning of the experiment and the remaining four control samples were sealed in an argon atmosphere within an argon glove box. Four powder samples were placed in a desiccator that was partially exposed to the air. The powders were then exposed to dry air for thirty days. After the exposure time was complete, these four powders and a control group of four samples were tested for oxygen content. This data is shown in Table 6.

Table 6. Thirty day MoSi_2 powder exposure test results

Powder	Oxygen (ppm)	Standard Deviation
<u>Prior to experiment</u>		
Control Group	24100	669
<u>After 30 day exposure</u>		
Exposed Powders	23540	459
Control Group	24100	458

The amount of oxygen in the control group powders did not change. The exposed powders remained relatively unchanged also. Therefore, the powders did not increase in oxygen content during the exposure to dry air for thirty days as was predicted by other researchers. These experiments only indicate that the as-received MoSi_2 powders are already saturated with oxygen and do not require extensive precautions during handling. A powder that does not have a passivated surface may oxidize rapidly until a thin protective layer is created. Nevertheless, it remains prudent to use precautions when handling the powders to ensure that they remain as pure as possible. Also, these precautions would keep the powders

free of moisture that may convert to oxygen species during the high temperature processing required in powder processing.

Processing of Fully-Dense Compacts

A technique to produce near-theoretical density compacts was needed so that research on the microstructure could be completed. This technique had to insure the powders had no exposure to the atmosphere so that the variation of oxygen contamination could be maintained throughout the duration of processing. This precaution was taken even though earlier discussions indicated that oxygen pick up may not be a problem at room temperature. However, since this passivation could fail at increased temperatures during the processing, a way to control the amount of oxygen in the sample was needed. A new technique of "canning" has been developed, referred to as "glass encapsulation".

The most commonly used method for canning of these types of powders is to use tantalum as a canning material. A Cold Isostatically Pressed (CIPed) sample is placed in the tantalum can. The can is then placed under a vacuum and heated to volatilize any contaminants and vacuum sealed. It was beneficial to develop glass encapsulation so that this process could be completed under a controlled atmosphere. Also, due to the amount of tantalum and specialized welding required in

the manufacture of tantalum cans the cost could be reduced by using a glass encapsulation method. The glass encapsulation methods have been found to be very simple and only require the aid of a glass-working shop.

Glass encapsulation uses a glass as the container. There are two possible methods of glass encapsulation. The first is to use a water-soluble glass as the container. The advantage of using a water-soluble glass is that it is easy to remove from the sample after the process is complete. The sample is CIPed to a green density of $\approx 50\%$ and then coated with boron nitride, which acts as a barrier between the MoSi_2 and the glass. The coated sample is then placed in a graphite crucible and covered with glass frit while in an argon atmosphere (70). A molybdenum disk is placed above the sample to ensure that the sample does not breach the surface of the glass during the HIP cycle. A thin layer of tantalum is then placed over the mouth of the crucible to ensure that the sample is sealed during transport to the HIP and to "getter" any oxygen in the chamber during the cycle. The setup for the water-soluble glass encapsulation is shown in Figure 15.

Figure 15. Crucible Configuration Used for Water-Soluble Glass Encapsulation

Once in the HIP, the chamber is purged with argon. The temperature is then increased to 1000°C to melt the glass frit and allow the encapsulation to occur. After the encapsulation of the sample, the temperature and pressure are increased to the desired value (about 1600°C and 45 ksi). After the desired dwell time, the pressure was released rapidly so that the glass would "foam". This foaming of the glass is due the rapid release of gas that is present in the glass and causes the glass to be porous after the process is complete which aids in the removal of the glass. After the pressure venting, the temperature is slowly decreased to avoid cracking the specimen. This method was used in the first attempt at

producing fully-dense MoSi_2 specimens. The profile of the HIP run is shown in Figure 16.

Figure 16. HIP profile for glass frit encapsulation

Unfortunately, the aggressive action of the rapid pressure vent fractured the specimen into many pieces. Also, the sample was exposed to the atmosphere for a short while during transfer from the glovebox to the HIP chamber, and there is no way to bake-out the sample prior to HIPing to ensure all volatiles are eliminated. Therefore, another

method of encapsulation was developed that could solve all of these problems.

The second glass encapsulation method uses glass tubing as the container (71,72). This process keeps the material under a controlled atmosphere from the opening of the powder manufacture's bottle to the densified state. This process is shown in Figure 17.

Figure 17. Glass encapsulation technique. I) Exploded view of the sample. The felt and tantalum liner are used to prevent the infiltration of the powder sample by the glass II) The sample is placed in the glass apparatus while under a controlled atmosphere III) The large end of the apparatus is sealed off. The apparatus is then placed under a vacuum and heated to degas the sample IV) The sample is then vacuum sealed in the glass and is ready to be HIPed

First, an appropriate glass must be chosen. When choosing a glass for the encapsulation material it is

important to ensure that the glass will be ductile, at the temperature that the HIPing will be done at. This allows the pressure to be fully transmitted to the HIP sample without the glass cracking. It is also important that the glass remains viscous enough to maintain the encapsulation at temperature. Data for some of the possible glasses to be used in encapsulation is shown in Table 7.

Table 7. Characteristic of different glasses used in choosing an appropriate glass to be used as an encapsulation material

Glass	Minimum Use Temp (°C)	Maximum Use Temp (°C)
Pyrex	650	1300
Vycor	1300	>1700
Quartz	1400	>1800

Since the MoSi_2 is to be HIPed at 1600°C , vycor was chosen as the glass encapsulation material. Vycor is also very thermally shock resistive, which makes it a good choice for the heating and cooling it will experience during the HIP cycle.

Once the encapsulation apparatus is made from the glass suited for the desired temperature range, the sample can be placed in the glass encapsulation. This is done in a glove

box filled with argon so that the sample is not exposed to air. As shown in Figure 17, a tantalum liner and zirconium felt is placed between the sample and the glass container to ensure that the glass does not infiltrate the sample during the HIP cycle. Either powder or a CIPed compact can be placed in the encapsulation apparatus. Once the apparatus is loaded, the large end is sealed off. The apparatus is placed under a vacuum and heated to $\approx 600^{\circ}\text{C}$ to degas any volatile species that may be present in the encapsulation. The vacuum level attained in the encapsulation was found to be $\approx 10^{-6}$ torr. The valve is then sealed off and the small end of the apparatus is sealed. At this time the sample is ready to be HIPed, and it has never been exposed to the atmosphere.

The vycor encapsulation technique met all of the requirements for the MoSi_2 system. The powder could be completely protected from any exposure to the atmosphere. It is also easy to degas the sample and vacuum seal the container.

A new HIP profile was needed for this new system. It is necessary to heat the vycor to a temperature where it is ductile prior to applying any pressure. Once at this temperature ($\approx 1350^{\circ}\text{C}$) a small amount of pressure (≈ 10 ksi) is added to press the glass around the sample. Once this is complete, the temperature is increased to the desired sintering temperature ($\approx 1600^{\circ}\text{C}$) and then the pressure is

raised to the final value (≈ 45 ksi). These values for the sintering temperature and pressure were determined by reviewing previously completed MoSi_2 HIP consolidation experiments. Various examples of processing conditions used by other researchers can be found in Table 1.

Many different profiles were tested to find the best method to return the sample to ambient conditions without fracturing. The vent method used in the first glass-frit encapsulation was obviously no good, due to the pressure shock that was created. A simultaneous slow cooling and pressure release was used to allow the mechanical energy to be released at a slow rate. The pressure and temperature profile for this method is shown in Figure 18.

Figure 18. HIP profile for the vycor encapsulation method, using a simultaneous pressure and temperature reduction to ambient conditions

This method produced full-density compacts, however, since much of the mechanical energy of the system was released below the ductile transition of the vycor and MoSi_2 , fracturing of the specimen occurred. The best method found was to reduce as much of the pressure as possible at a moderate rate while maintaining the temperature above the ductile transition and then followed with a slow cool to room temperature. This is shown in Figure 19.

Figure 19. HIP profile for the vycor encapsulation method using a moderate reduction in pressure followed by a slow cool to ambient conditions.

This method allowed most of the mechanical energy to be removed while the encapsulation and MoSi_2 sample were ductile enough to compensate. After this reduction in pressure, a slow cool to ambient conditions prevented any fracturing of the sample. This method will allow the production of mechanical testing specimens to be used in further research.

Analysis of Specimens with Varying Amounts of Oxygen Contamination

To allow for investigation of oxygen's role in the processing of MoSi_2 it is necessary to be able to produce specimens containing varying amounts of oxygen. The easiest solution is to use powders that contain varying amounts of oxygen. Since it has been determined that oxygen contamination is purely a function of surface area, it is only necessary to use powders that have a variation in the amount of surface area present. Considering the powders used in this research, a variation of oxygen contamination from 4900 ppm to 24,100 ppm can be studied. A near fully-dense specimen of each of these powders was produced so that the microstructure could be studied, to determine the effects of oxygen contamination. All of these were produced using the same variables, so that the only difference should be the surface area of each powder and, therefore, a different amount of oxygen content. However, the size of the powders is an additional variable which controls the microstructure as well. A compilation of the four microstructure's characteristics is given in Table 8.

Table 8. Characteristics of the microstructure of the fully-dense compacts

Supplier	Powder Oxygen ppm	Compact Oxygen ppm	Compact Density (g/cm ³)	Percent SiO ₂	Grain Size (microns)
Alfa	12803	11700	N/A	7.14	50.1
Cerac	4903	4347	6.20 (99.4%)	2.47	16.8
Noah	6884	5772	6.19 (99.2%)	2.05	14.1
Stark	24100	22400	N/A	13.13	14.8

N/A - not available.

The oxygen content decreased slightly compared to that of the precursor MoSi₂ powders during the HIP processing. This removal of oxygen probably occurred during the degassing of the specimen prior to HIPing. All of the specimens were not of adequate size for gas pycnometer density testing, but the two that were tested were near full-density as seen above. All of the compacts were found to be near fully-dense when analyzed with the SEM. The percent SiO₂ and grain size measurements were taken from photos similar to those in Figure 20 through Figure 23. SEM photos of these four microstructures of HIPed compacts can be seen in Figure 20 through Figure 23. All photographs were taken at about 400x. The top photograph of each set was taken using polarized light while the bottom photograph was taken using back-scattered electron imaging.

Figure 20. Cerac MoSi_2 HIPed compact with 4347 ppm oxygen
(a) Polarized light photograph taken at 400x
(b) BSE image taken at 398x

(q)

(a)

Figure 21. Noah MoSi_2 HIPed compact with 5772 ppm oxygen
(a) Polarized light photograph taken at 400x
(b) BSE image taken at 398x

(a)

(b)

Figure 22. Alfa MoSi_2 HIPed compact with 11,700 ppm oxygen
(a) Polarized light photograph taken at 400x
(b) BSE image taken at 398x

(a)

(b)

Figure 23. HC Stark MoSi_2 HIPed compact with 22,400 ppm oxygen
(a) Polarized light photograph taken at 400x
(b) BSE image taken at 398x

(a)

(b)

It is easy to see the MoSi_2 grain structure in the polarized light photographs. The grains are different shades of gray due to the orientation brought out by using polarized light. The grain sizes of the Cerac, Noah, and Stark microstructures are comparable ($\approx 15 \mu\text{m}$). However, the Alfa powder has shown a significantly larger grain size ($\approx 50 \mu\text{m}$). The microstructures which have a smaller grain size have silica that has coarsened on the grain boundaries. Inclusions that are found at the grain boundaries are known to inhibit grain growth by grain boundary drag, which would account for the small grain size in the Cerac, Noah, and Stark microstructures (73). In the Stark powder, it can be seen that there are intragranular silica inclusions, however, they are less abundant and much smaller than the grain boundary inclusions.

The diffusion of silica required for inclusion growth seems to be the rate limiting step, and once the diffusion distance between inclusions is large the MoSi_2 grain growth is slowed. The smaller powders have very short diffusion paths between silica particles and the silica is able to coalesce rapidly at first, allowing for MoSi_2 grain growth. The areas that contain large powders do not grow much since they already have large distances between silica particles, and therefore the rate of silica coalescence is slow. Therefore, it would seem that the grain growth is controlled by the rate at which

the silica inclusions are able to coalesce, which leads to a similar grain size in the three samples.

The Alfa powder, however, seems to have predominantly intragranular silica inclusions. The Alfa microstructure also had a double case morphology. A thin case of large grains was found on the surface of the compact with another thin case of small grains located just below this. The bulk of the Alfa sample, however, exhibited very large grains as shown in Figure 22. Therefore, due to some anomaly in the Alfa sample, most of the grains were able to overcome the grain growth restraint due to the inclusions and produced abnormal grain growth in the bulk of the microstructure. The predominantly intragranular silica is due to the fact that the diffusion for inclusion growth is much more difficult through the lattice compared to along the grain boundaries.

The black and white dots in the polarized light pictures correlate to the black dots in the BSE images. This can be seen by comparing one image of each type of the same area shown in Figure 24.

Figure 24. Images taken of the same area of microstructure
(a) Polarized light photograph taken at 200x
(b) BSE image taken at 210x

(a)

(b)

All of the dark areas in the MoSi_2 seem to be amorphous SiO_2 inclusions (56). This was determined by doing EDS of the different points on the microstructures' surface. Also, EDS mapping was done of the surface and is shown in Figure 25.

Figure 25. EDS map of MoSi_2 surface
(upper left) concentration of Molybdenum
(upper right) concentration of Oxygen
(bottom left) concentration of Silicon
(bottom right) SEI of area taken at 300x

HIP Run 4 1000

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By comparing the molybdenum, oxygen and silicon maps with the SEI image in the bottom right corner, the relative amounts of each element in each area can be determined. The silicon has about the same concentration in all areas. However, it can be seen that all of the dark areas in the SEI images have a lack of molybdenum and an abundance of oxygen. Therefore, it can be presumed that all dark areas in an SEI image are that of a silicon-dioxide, SiO_2 .

It is possible to determine whether the silica found in the microstructure is merely the inherent silica from the powders. Knowing the amount of oxygen present on the powders, the volume percent of silica expected to be found in the microstructure can be calculated and compared to the actual amount present. A graph correlating the actual and calculated volume percent of silica in the fully-dense compacts to the amount of oxygen on the starting powders is shown in Figure 26.

Figure 26. Plot correlating the actual and calculated volume percent silica in the microstructure to the amount of oxygen present on the starting powders

Therefore, since the actual volume percent silica in the microstructure fits the calculated values reasonably well, the silica found in the microstructure is the inherent silica found on the surface of the purchased powders. Therefore, if the amount of silica on the initial powders can be reduced, the amount of silica in the microstructure should also be reduced. The manner in which these silica inclusions affect the mechanical properties of the MoSi_2 will be studied in a future paper.

Production of Powders with a Lower Relative Amount of Oxygen

Most of the other research of MoSi_2 has been completed using powders similar to the powders that were purchased for this research. These have all been found to have oxygen saturation of the surface. However, by using Self-heating High temperature Synthesis (SHS) and Reaction Sintering (RS) as described before, a few researchers have been able to produce powders of a lower relative amount of oxygen (56). These researchers have described changes in the properties of the monolithic material caused by this reduction in oxygen present. Thus, it was determined to be beneficial to produce powders containing a similarly low amount of oxygen.

Reduction of the powders

Initially, a method of reducing the purchased powders was attempted by passing heated hydrogen gas over the powders. The Ellingham diagram for this reduction is shown in Figure 27.

Figure 27. Ellingham Plot of Reduction Reactions Using 5.09% Hydrogen

As can be seen, at 1200°C this would require hydrogen gas with a dewpoint of $\approx -80^\circ\text{C}$. Since it is difficult to obtain hydrogen gas that is this dry, it will have to be dried. To dry the gas, it was passed through yttrium filings at 1200°C. If the gas flow is low enough through the yttrium, the yttrium will remove most of the oxygen, through the oxidation reaction shown below.

AIM

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2 of 2

Once it has passed through the yttrium, the gas will be drier than the equilibrium point for the silica reaction shown below. Therefore, reduction of the MoSi_2 powder should occur.

Of course, all of these predictions were determined using thermodynamics, and whether the kinetics of the reaction would be fast enough to allow the necessary reduction to occur would be determined in an experiment.

An experiment was set up to test the theory that the reduction of silica on the powders was possible. A tube furnace was used with an alumina muffle tube. Alumina was used because it is more stable than silica (quartz) and therefore the silica on the powders would reduce before the alumina could. The tube furnace was heated to 1200°C . The hydrogen gas was flowed through yttrium filings first, to dry the gas. Then the dried gas was passed over a thin layer of MoSi_2 powder in an alumina boat. This setup is shown in Figure 28.

Figure 28. Apparatus used for the reduction experiment

The experiment was run for 8 hours to determine whether the reduction was possible. Following the reduction experiment the powders were handled using every precaution so that the amount of oxygen in the powders could be determined accurately. The "potentially" reduced powders were tested using the LECO determinator and the results are in Table 9.

Table 9. Powder reduction test results

Powder	Oxygen (ppm)	Standard Deviation	Nitrogen (ppm)	Standard Deviation
Reduced Powders	26800	316	1170	108
Control Group	25533	329	848	14

As can be seen by the data, the powders were not reduced, and may have become contaminated even worse. There are two possible reasons for this failure. Either the H_2 gas was not

in equilibrium with the yttrium filings or the time was not sufficient for the reduction to succeed. If it was a case of insufficient time, the powders should have reduced, if only slightly. However, the powders actually oxidized somewhat, and therefore the explanation of this lack of reduction can most likely be found in the inability to dry the gas the required amount. Therefore, it was determined that another avenue must be taken to produce powders with a lower relative amount of oxygen contamination.

Self-Heating High Temperature Synthesis

A technique to produce powders that have a low amount of oxygen contamination was needed. Other researchers have had success with Self-Heating High Temperature Synthesis (SHS) and Reaction Sintering (RS) because the exothermic reaction of molybdenum and silicon purifies the specimen by evolving any volatiles. This reaction is shown below.

Both methods were tested in our research. A CIPed sample of the elemental powders mixed in the ratio of MoSi₂ is the starting point for both techniques.

SHS is done by igniting the reaction at one point on the CIPed sample and the ensuing exotherm allows the reaction to propagate through the entire specimen. A CIPed sample was placed in a arc-melting box on a water-cooled copper plate. A schematic of this is shown in Figure 29.

Figure 29. Schematic of SHS experiment

Ultra-high purity argon at about atmospheric pressure was used in the arc-melting box to eliminate any contamination. An arc was struck about four inches from the specimen and then moved toward the specimen. When the arc was about one inch from the specimen the reaction ignited, and the arc was removed. The reaction was self-sustained through the entire length of the specimen. A photo of the specimen after SHS is shown in Figure 30.

Figure 30. Sample of MoSi_2 produced using Self-Heating High Temperature Synthesis

RS of the elemental powders was also done. This uses the same type of exothermic synthesis as the SHS, but an induction furnace is used to initiate the reaction. When doing SHS there is not enough activation energy available to produce any other compounds other than MoSi_2 . However, in RS a preheat is used, which provides the extra activation energy that may allow other compounds of molybdenum and silicon to be produced in areas where an off-stoichiometric mixture of molybdenum and silicon powder is present. However, if the appropriate ratio of molybdenum and silicon and a minimal amount of preheating is used, only MoSi_2 should be found in the final specimen. For the RS reaction a CIPed sample of molybdenum and silicon powder is placed in a quartz crucible. This quartz crucible is surrounded by a tantalum susceptor, and this entire assembly is placed in a graphite crucible for containment. This setup is shown in Figure 31.

Figure 31. Reaction sintering apparatus

This apparatus was placed in an induction furnace chamber with a slight over-pressure of ultra-high purity argon. The sample was slowly heated in increments until the reaction started. The specimen's temperature was determined by using an infra-red spectrometer focused on the surface of the sample. The reaction started at 1285-1300°C and quickly heated to $\approx 1690^{\circ}\text{C}$. Once the reaction was initiated the induction furnace was turned off and the sample was allowed to cool in the chamber. A photo of the specimen after reaction sintering is shown in Figure 32.

Figure 32. Sample of MoSi_2 produced using Reaction Sintering

Comparing the specimens produced in each method, significant differences can be seen. The SHS specimen has circumferential lines produced as the reaction moved from one end to the other. It has a dull grey color and a consistency similar to that of the elemental powders it was produced from. Whereas, the RS specimen has a shiny luster and is quite porous. The RS reaction off-gassed many volatiles that are presumed to be oxides such as SiO_2 and MoO_3 . These volatiles were coated on the quartz crucible. The volatiles deposited on the quartz crucible were analyzed using X-ray diffraction. The testing was not conclusive since only MoSi_2 peaks were found. No significant volatilization was noted during the SHS reaction.

Both of these samples were tested for oxygen contamination. By using the elemental powder's oxygen content, it can be estimated that the initial amount of oxygen present in the CIPed sample was $\approx 11,000$ ppm. Four samples of each method, SHS and RS, were tested. The results are in Table 10.

Table 10. Self-Heating High Temperature Synthesis and Reaction Sintering test results

Production Method	Oxygen (ppm)	Standard Deviation
HC Stark Powder	24100	430
SHS	9925	484
RS	4140	1889

The amount of oxygen in the SHS specimen was left nearly unchanged during the reaction. However, the amount of oxygen in the RS sample decreased by $\approx 70\%$ relative to the initial powders. There was great variability of oxygen content in the RS specimen. One of the oxygen test samples contained 1950 ppm oxygen and another had 6970 ppm oxygen. This was probably caused by some of the oxygen-containing volatiles being trapped in the sample in pores and then plating back on the sample.

Therefore, the use of RS is capable of producing specimens of MoSi_2 that have a lower relative amount of oxygen. By using cleaner starting powders and having a slight vacuum in the chamber during the reaction, it should be possible to produce a specimen containing less than 1000 ppm. This will be of use in the future for producing mechanical test specimens of a lower relative amount of oxygen content than the MoSi_2 powders that can be purchased. This technique

for production of mechanical test specimens of low oxygen content will be pursued by another researcher in continuing research.

SUMMARY AND CONCLUSIONS

A solution to all of molybdenum disilicide problems must be found before it can be used as the next generation high-temperature structural material. These problems include low temperature fracture toughness, high temperature creep resistance, and the "pest" phenomena. The oxygen content introduced by powder processing of MoSi_2 may be the cause of some of the problems in the MoSi_2 system. Previous researchers have either been unable measure the oxygen contamination due to lack of equipment or have simply assumed that the powder oxidation is inherent to the processing. Regardless, they have pursued development of MoSi_2 applications without fully understanding the detriment of oxygen contamination.

The main conclusions of this research are listed below.

a) The supplied powders have significant amounts of oxygen present even prior to processing (up to 2.5%). This oxygen contamination was found to be in the form of silica on the surface of the purchased powders. This silica is then introduced into the microstructure upon densification of the specimens.

b) The oxygen contamination was not found to increase by exposure to air at room temperature and was purely a function of the surface area of each powder. This may only mean that the powder's surface was passivated in the as received condition.

c) An improved technique of powder processing was developed that allows for complete atmospheric control throughout the entire process. This is done by using a glass as the canning material. The powders are only exposed to a controlled atmosphere from the time the manufacturer's bottle is opened until the fully-dense specimen is complete. Also, it is possible to degas the powders and evacuate the powder-filled container prior to HIPing to ensure that all of the volatiles are removed.

d) Analysis of microstructures created from powders that contained from 4900 ppm to 24,100 ppm oxygen was completed. The inherent silica on the powders was transferred to the microstructure of the fully-dense MoSi_2 as SiO_2 inclusions. These inclusions are predominantly found on the MoSi_2 grain boundaries, but in the microstructures with a large amount of inclusions, some were found to be intragranular. The volume percent silica in the microstructure could be directly correlated to the amount of oxygen present in the starting

powders. MoSi_2 grain growth seems to be controlled by the rate at which the silica inclusions are able to coalesce, which leads to a similar grain size for microstructures with varying amounts of silica present..

e) A method of creating MoSi_2 that had a relatively lower amount of oxygen was attempted. An initial attempt to reduce the powders by passing dried hydrogen gas over the powders at 1100°C was found to be unachievable. However, by reacting molybdenum and silicon powders it was possible to create a sample of MoSi_2 with a lower amount of oxygen content than the starting powders. This is believed to be due to the exotherm created during the reaction, which volatilizes any oxides and other unwanted compounds. This process requires more research to fully utilize its potential in producing fully-dense compacts that have low oxygen contents.

This research has been focused on the thorough analysis of the role of oxygen in the powder processing of MoSi_2 and developing an improved powder processing technique. By using Auger analysis of the MoSi_2 powders, the oxygen was found to be in the form of silica on the surface of the powders. This silica was then transferred to the microstructure as silica inclusions. A glass encapsulation technique was developed that was simple, yet allowed for complete atmosphere control

throughout the process. Also, a technique to produce MoSi_2 that had a lower amount of oxygen content was attempted. This was found to reduce the amount of oxygen in the MoSi_2 . This research should improve the understanding of oxygen contamination in the MoSi_2 system, and provide improved techniques for the production of fully-dense MoSi_2 compacts with reduced amounts of oxygen.

Future Research Possibilities

Parallel research by a another researcher will determine the effects that this oxygen contamination has on the mechanical properties of MoSi_2 (74).

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