IS-T 1889

Characterization of Electrical Resistivity as a Function of
Temperature in the Mo-Si-B System

by

Beckman, Sarah E.

MS Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: December 10, 1999

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

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Characterization of electrical resistivity as a function of temperature in the Mo-Si-B system

Sarah Elizabeth Beckman

Major Professor: M. Akinc
Iowa State University

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Measurements of electrical resistivity as a function of temperature from 25 to 1500°C were conducted on polycrystalline samples in the Mo-Si-B system. Single phase, or nearly single phase, samples were prepared for the following phases: Mo_3Si , Mo_5SiB_2 , $\text{Mo}_5\text{Si}_3\text{B}_x$, MoB , MoSi_2 , and Mo_5Si_3 . These materials all exhibit resistivity values within a narrow range ($4-22 \times 10^{-7} \Omega\text{-m}$), and the low magnitude suggests these materials are semi-metals or low density of states metals. With the exception of MoSi_2 , all single phase materials in this study were also found to have low temperature coefficient of resistivity (TCR) values. These values ranged from 2.10×10^{-10} to $4.74 \times 10^{-10} \frac{\Omega\text{-m}}{^\circ\text{C}}$, and MoSi_2 had a TCR of $13.77 \times 10^{-10} \frac{\Omega\text{-m}}{^\circ\text{C}}$. The results from the single phase sample measurements were employed in a natural log rule-of-mixtures model to relate the individual phase resistivity values to those of multiphase composites. Three Mo-Si-B phase regions were analyzed: the binary Mo_5Si_3 - MoSi_2 system, the ternary phase field $\text{Mo}_5\text{Si}_3\text{B}_x$ - MoB - MoSi_2 , and the Mo_3Si - Mo_5SiB_2 - $\text{Mo}_5\text{Si}_3\text{B}_x$ ternary region. The experimental data for samples in each of these regions agreed with the natural log model and illustrated that this model can predict the electrical resistivity as a function of temperature of multi-phase, sintered samples within an error of one standard deviation.

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1 INTRODUCTION

The high temperature oxidative stability of silicides has been studied since the turn of the twentieth century, initially for their potential use as heating elements in an electric furnace. More recently, since silicides have metallic behavior, the microelectronic industry has been interested in using these materials on devices as interconnections, contacts, and low resistivity gates [1]. The first patent was issued to Kanthal for their SuperkanthalTM molybdenum disilicide heating element in 1956. Since that time this material has been used extensively in high-temperature furnaces because of its favorable high oxidation resistance, which is due to the formation of a thin silica passivation layer.

The most significant engineering limitation of monolithic MoSi₂ is its poor mechanical properties. At room temperature it exhibits poor fracture toughness and at high temperatures it has poor creep resistance. Above 1200°C the MoSi₂ elements tend to creep under their own weight. Several attempts have been made to improve these properties by forming a composite consisting of reinforcing ceramic particles such as SiC, Si₃N₄, TiB₂, and ZrO₂ in a MoSi₂ matrix [2]. SiC and Si₃N₄, as reinforcements, have been shown to increase the creep resistance of the composite over monolithic MoSi₂ but require hot pressing which limits potential use due to the limited range of producible shapes [2, 3]. ZrO₂ additions appear to promote glassy phase formation during high temperature exposure that adversely affects the mechanical properties [2].

An alternative solution to prevent creep at high temperatures would be to replace MoSi₂ with a creep resistant material that has a high melting point and similar oxidation resistance. Mo₅Si₃ is a potential candidate due to its high melting temperature of 2180°C. Figure 1.1 [4] shows the relative creep rates for molybdenum silicides and composites. In this graph, points

on the lower right are more desirable for high temperature use. The creep rate for the Mo_5Si_3 based material is lower than for any of the MoSi_2 composites. Although pure Mo_5Si_3 has poor oxidation resistance [5], boron doping has been found to decrease the oxidation rate by 5 orders of magnitude at 1200°C [6]. Meyer [6] discovered that 2 weight % boron addition modified the behavior of Mo_5Si_3 such that, above 800°C , a coherent borosilicate glass scale formed after the volatilization of MoO_3 . In the case of undoped Mo_5Si_3 , a mixed MoO_3 and SiO_2 scale forms in which the MoO_3 volatilizes above 750°C leaving a porous silica layer. This discontinuous and highly viscous scale is a poor diffusion barrier for oxygen and allows for further deterioration of the material. By adding boron, the composition of the initial scale contains borosilicate glass and MoO_3 . Once the molybdenum oxide volatilizes, the borosilicate glass, due to its lower viscosity, flows and fills the voids left by the MoO_3 . The result is a continuous scale that limits oxygen diffusion.

Figure 1.1 Relative creep rates for molybdenum silicides and composites

Although the oxidation resistance of Mo-Si-B compounds was discovered around 1994, initial work on the Mo-Si-B system began in the 1950's by Nowotny et. al as an investigation of numerous ternary silicide systems [7]. As part of this research, an isothermal section of the phase diagram at 1600°C was published. In that study, samples were prepared by sintering elemental powders for 12 hours. Under these conditions, it is unknown whether equilibrium was attained and what effect impurities had on the samples. Nowotny reported that some boron was soluble in Mo_5Si_3 , yielding a ternary phase, T1, with a maximum solubility of 4.5 atomic % [7]. Recent work performed at Ames Laboratory suggests the solubility limit is much lower, closer to 1.8 atomic percent [8].

The phase diagram also suggests a second ternary composition, T2, corresponding to Mo_5SiB_2 , which has become a subject of several recent studies. Nunes et. al examined the binary Mo- Mo_5SiB_2 region in the Mo-Si-B system [9]. They found that reaction kinetics in the arc melted samples were slow, but after annealing at 1600 °C for long times, this binary region does exist. They also recognized that supersaturation of Mo in T2 was occurring during arc melting which resulted in small Mo_{ss} precipitates in the T2 after annealing. A second study was reported by Schneibel et al. as an investigation into the mechanical properties of arc cast materials in the Mo_{ss} - Mo_3Si - Mo_5SiB_2 region of the phase diagram [10]. Mechanical testing was performed on arc cast ingots of several compositions ranging from 20-50 volume% Mo_{ss} and various ratios of T2 and Mo_3Si . In ingots containing less than 25% Mo_{ss} , macroscopic cracks were apparent. Annealing was found to dramatically coarsen the microstructure at 1600°C. The differences in microstructure and composition gave room temperature strength values ranging from 300 to 600 MPa. This study also reports that oxidation of samples having around 50 volume% Mo_{ss} completely consumed the matrix material after 24 hours in air at 1473 K. The researchers noticed a dramatic increase in oxidation resistance with the addition of boron in compositions with approximately 25 volume% Mo_{ss} . They report that the oxidation resistance is far lower than the oxidation resistance of MoSi_2 at comparable temperatures, which is expected due to the low silicon content in the phase field which is needed to form a silica scale.

Although materials in the $\text{Mo}_{(ss)}\text{-Mo}_3\text{Si-Mo}_5\text{SiB}_2$ phase field do not have the oxidation resistance of MoSi_2 , phase triangles which have a higher percentage of silicon seem promising. The known excellent oxidation resistance of materials near the T1 phase as well as superior mechanical properties, suggests a material containing T1 as a major phase may be an excellent replacement for the current MoSi_2 heating element. In order to establish the feasibility of using this material as a heating element, several factors must be considered. One factor is whether the material may be fabricated reproducibly by an established process. Such a process has been demonstrated by Summers [11] using powder extrusion. Mechanical properties are also important factors to be considered for engineering applications. Researchers at Ames Laboratory have prepared two compositions containing T1 and have performed several mechanical tests to examine strength, fracture toughness, and creep resistance [12]. Another important factor in the development of a heating element material is the electrical properties of the material in the operating range of a resistance heating furnace. Knowledge of the electrical resistivity as a function of temperature is essential for consideration of this material as a heating element.

Resistivity is a material property that may be defined as the inverse of conductivity. It is related to the resistance of a material, R , by the relation:

$$R = \frac{L\rho}{A} \quad (1.1)$$

where L is the distance between the voltage leads, ρ is the characteristic resistivity of the material, and A is the cross-sectional area of the test specimen. If an electron is considered as a particle, resistivity may be described by collisions that a drifting electron has with certain lattice atoms. Resistance increases with increasing rate of electron collisions. This model may be used to explain why the resistivity increases as lattice imperfections increase [13]. It may also be used to relate the increase in resistance with increasing temperature. The increase in thermal energy increases the vibration of atoms in the lattice and this increases the probability of a passing electron colliding with an atom. If the electron is considered to have a wave nature, then an interaction with the lattice atoms would scatter the wave. As the wave is scattered, the energy may be absorbed by the atoms, which may become oscillators and re-emit the energy. If two or more atoms are involved, the scattered waves can interact. Defects such as

impurities, vacancies, grain boundaries, and thermal vibrations will produce waves that are out of phase creating destructive interference which will reduce the overall energy of the electron, and increase the overall resistance of the material [13].

For temperature varying applications such as heating elements, it is important also to describe the temperature dependence of the material's resistivity. In a metal, the resistivity decreases linearly with decreasing temperature, until at low temperatures it has a finite value as seen in equation 1.2.

$$\rho = \rho_o + \alpha T \quad (1.2)$$

where ρ is the resistivity at any temperature T , ρ_o is the residual resistivity at $T = 0$ K, and α is the linear temperature coefficient of resistivity [14]. For an impure specimen, Matthiessen's rule states that the resistivity change due to impurities is independent of temperature, so that the overall resistivity at any temperature is simply additive as seen in equation 1.3.

$$\rho = \rho_{th} + \rho_{res}, \quad (1.3)$$

where ρ_{th} is the thermal contribution, and ρ_{res} is the residual resistivity due to impurities and defects [15]. The amount of impurities is usually constant in a given sample; however, the vacancy and grain boundary concentrations are dependent on the material's heat treatment. By annealing, vacancies can be annihilated, and grains can grow. Because of this, care must be taken to characterize the microstructure of each sample before comparing the results.

The van der Pauw theorem provides a technique for measuring the resistivity of a flat sample of arbitrary shape [16]. It states that the electrical resistivity of a material can be measured by attaching contacts to four points along the circumference of the sample, such that the following criteria are fulfilled:

- a. The contacts must be on the edge of the sample
- b. The contacts are small relative to the sample size
- c. The sample has a uniform thickness
- d. The sample does not have isolated holes

Figure 1.2 shows the position of the point contacts for an arbitrary specimen.

Van der Pauw defined the resistance $R_{AB,CD}$ as the resistance measured when current is input through contact A, leaves contact B and the potential is read as the potential at point D minus the potential at point C. $R_{BC,DA}$ is defined in a similar manner. From knowledge of these two quantities, the resistivity may be found from the following equation:

$$\rho = \frac{\pi d}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} f \left(\frac{R_{AB,CD}}{R_{BC,DA}} \right) \quad (1.4)$$

where d is the thickness of the sample and f is defined by the relationship:

$$\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} = f \operatorname{arccosh} \left(\frac{\exp \frac{\ln 2}{f}}{2} \right) \quad (1.5)$$

According to this equation, f is a factor which scales from zero to one. When $R_{AB,CD}$ and $R_{BC,DA}$ are equivalent, $f = 1$, and as the two values become more dissimilar, f becomes a fractional value. Once the properties have been measured by the van der Pauw technique,

Figure 1.2 Point contacts for an arbitrary sample

they must be related to the microstructure. In particular, the porosity of a sample must be correctly accounted for. Several studies have been performed on the effect of porosity on inherent material properties. In particular, R. W. Rice [17, 18], has presented significant analysis supporting the use of minimum solid area models for porosity-property modeling. He states that, for material properties governed by a rule of mixtures relation, an *average* area fraction model is appropriate. Properties such as heat capacity are modeled well with an averaging method because the average area fraction is equal to the average volume fraction. The use of area fraction is also reasonable in the case of properties based on stress or flux because they

are dependent on the amount of solid area. Although, in these cases, it is more appropriate to consider the minimum area for the transmission of stress or flux. Electrical conductivity is an example of a flux based property and subsequently is modeled by the minimum area fraction. Rice states that along with volume fraction, the minimum solid area parameter is needed to characterize the flux or stress properties of porous solids. The fraction of the property of the porous material with respect to a 100% dense sample may be approximated with a minimum solid area model of solid spherical particles. This model is described by a relation of the form e^{-bP} for a region with a low porosity fraction, P , where b is a parameter corresponding to different pore structures. Models has been calculated for various types of porosity. Rice gives an example of the curves for different particle stacking parameters [19]. Each curve shows this initial exponential relationship, but at a certain point the property starts to decrease drastically, going to zero at a certain critical porosity fraction, P_c . This is the percolation limit and is described as the point at which the bond area between particles goes to zero. Each model has 3 characteristics:

1. The initial linear slope on a semi-log plot, b
2. The porosity fraction, P , where the property can no longer be characterized with the linear slope
3. P_c , the critical porosity.

To use this model, the shape and volume fraction of the porosity must be characterized. If there is more than one shape, the final value range is calculated using a rule of mixtures equation. Since this is not a trivial task, the b parameter is usually calculated by producing samples with controlled porosity levels and fitting the data. Experiments have been conducted using sintered glass, lead zirconate titanate, epoxy, alumina, and other materials. Most tests measured the Young's modulus as a function of porosity, but thermal conductivity measurements were performed on alumina. For studying the effect of porosity on a property, this is an accurate model. For removing porosity from the equation, a less specialized method may be sufficient.

An equation which accounts for the effective conductivity of a material with up to 30 volume % porosity is presented by Skorokhod [20] as

$$\sigma_{ef} = \sigma_1(1 - \frac{3}{2}\theta_2) \quad (1.6)$$

where σ_{ef} is the effective conductivity, σ_1 is the actual conductivity of the material, and θ_2 is the volume fraction of the porosity. This equation is based on a two phase material equation and simplified assuming that the conductivity of the porosity is zero.

By applying this porosity correction to sintered materials, chapter 2 presents resistivity values as a function of temperature for single phase, or nearly single phase materials, that describe the properties of fully dense samples. The materials are characterized by x-ray diffraction, and lattice parameters are compared with values reported in the literature. These porosity corrected resistivity values are then used in chapter 3 to model the behavior of multiphase sintered samples.

In chapter 3, mixing rules are applied to samples in three areas of the phase diagram. First is the binary region between Mo_5Si_3 and MoSi_2 . Two samples were prepared in this region. Two other boron containing phase fields were analyzed by preparing several samples of varying compositions. Samples in the $\text{Mo}_5\text{Si}_3\text{B}_x$ – Mo_3Si – Mo_5SiB_2 phase triangle and $\text{Mo}_5\text{Si}_3\text{B}_x$ – MoSi_2 – MoB region were chosen to exploit the beneficial effect boron has on the oxidation resistance of materials in this system. Establishing a model that accurately characterizes the electrical properties of the materials in these phase fields would allow for the development of applications that require the optimization of electronic properties in addition to the currently characterized mechanical and oxidation properties.

Thesis Organization

This thesis is presented in an alternate format. Chapters 2 and 3 are presented as independent journal manuscripts. Chapter 4 presents general conclusions from the study of electrical properties of boron-doped molybdenum silicides and suggests future experiments to improve upon the present model.

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2 ELECTRICAL RESISTIVITY OF SINGLE PHASE MATERIALS IN THE Mo-Si-B SYSTEM

A paper to be submitted to the Journal of Materials Science

Sarah Beckman, Bruce Cook, and Mufit Akinc

Abstract

Electrical resistivity measurements as a function of temperature for single phase, or nearly single phase, multicrystalline materials in the Mo-Si-B system have been performed within the temperature range of 25 to 1500°C. These samples were also characterized with x-ray diffraction and the experimental lattice parameters are shown to agree with literature values. The Mo_5SiB_2 , MoB, Mo_3Si and Mo_5Si_3 samples have similar temperature coefficient of resistivity (TCR) values. The $\text{Mo}_5\text{Si}_3\text{B}_x$ sample has a higher resistivity value at all temperatures and a lower TCR than Mo_5Si_3 . Hall effect measurements were conducted on these two samples to determine differences in electronic structure which may influence resistivity and TCR. The electron concentration in $\text{Mo}_5\text{Si}_3\text{B}_x$ was an order of magnitude higher than Mo_5Si_3 possibly allowing for a difference in the TCR values between the two phases. The higher resistivity is suggested to be due to a difference in the degree of microcracking. MoSi_2 has a much higher TCR value compared with all other materials in this study, although the resistivity range of all phases studied is consistent with semi-metals or low density of states metals.

Introduction

The majority of the electrical studies on transition metal silicides have focused on thin film samples [1, 2, 3], although several silicides have been studied as single crystals [4, 5, 6].

Comparatively little literature is available on the electronic properties of single phase materials in the Mo-Si-B system. MoSi_2 is the only phase that has been the subject of significant study. The following is a brief introduction of the reported general studies of materials in this phase triangle, followed by a review of the electronic data available in the literature.

Material Preparation and Characterization

Initial work on the Mo-Si-B phase diagram was performed by Nowotny, resulting in a 1957 publication showing an isothermal section at 1600°C , which is reproduced in figure 2.1 [7]. Sample preparation may have skewed the overall result of the study, since it is unknown whether the samples were in equilibrium, and the impurities concentration was not reported. Specifically, the solubility of boron in the $\text{Mo}_5\text{Si}_3\text{B}_x$ or T1 phase has been challenged by recent work at Ames Laboratory. Nowotny claimed that T1 has a 4.5 atomic % solubility range, whereas Huebsch [8] suggests that the solubility is much lower, closer to 1.8 atomic %. The x-ray density and lattice parameters determined in the study at Ames Laboratory are presented in table 2.1.

The isothermal section also suggests a second single phase ternary composition, Mo_5SiB_2 , called T2, which has been a constituent of a three phase composition in creep studies [9], as well as the subject of a study evaluating the accuracy of the Nowotny isothermal section of the phase diagram and the existence of a $\text{T2} + \text{Mo}_{ss}$ binary phase field [10]. This study concluded that T2 has a small solubility range, 4.28 atomic % B and 2.97 atomic % Si [10], which is slightly larger than the solubility proposed by Nowotny. The lattice parameters suggested by Nunes et al. [10] for T2 are shown in table 2.1.

There are also several binary compositions of interest in the Mo-Si-B system. The relevant phases for this study include: MoB, Mo_3Si , Mo_5Si_3 , and MoSi_2 . The first, MoB, consists of α -MoB, the low temperature phase which is stable to 2180°C , and the high temperature β -MoB which exists from 1800°C to its melting temperature at 2600°C . Both phases have a small solubility range [11] of ± 1 atomic % from the stoichiometric 50-50 Mo to B ratio. The study performed by Nunes et al. suggests that the solubility of Si in MoB is less than suggested

Figure 2.1 Isothermal section of the Mo-Si-B phase diagram at 1600°C

by Nowotny, only 0.02 atomic %. Lattice parameters from Cutler [12] are given in table 2.1.

Mo_3Si single crystals were prepared and characterized by Christensen in 1983 [13]. The crystals were made using a modified float zone technique with a molten zone that had a nominal composition of Mo_4Si . The initial feed rod and final crystals were Mo_3Si , and the crystal size was 1 cm^3 . A result of the crystal growth was the formation of both single crystal Mo_3Si and Mo_5Si_3 . Both were ground, combined with a silicon standard and analyzed by x-ray diffraction with a Guinier detector with $\text{CuK}\alpha$ radiation. The unit cell parameters for Mo_3Si and Mo_5Si_3 recorded by Christensen are reported in table 2.1. Neutron diffraction was also performed on the Mo_3Si single crystals using a four-circle neutron diffractometer and the ω - 2θ technique. The results of this analysis suggest that the composition does not deviate largely from the stoichiometry of A_3B . Nunes et al. suggest that there is negligible solubility of boron in Mo_3Si [10], which agrees with Nowotny's proposed diagram.

While preparing single crystal Mo_3Si , Christensen also prepared Mo_5Si_3 . The lattice parameters he reported are tabulated in table 2.1. Recently, single crystals were produced by

Table 2.1 Reported crystallographic data for single phases in the Mo-Si-B system

Phase	Type	Space Group	Lattice Parameters (Å)			Reference
			a	b	c	
Mo ₅ Si ₃ B _x	Tetragonal	I4/mcm	9.622-9.649		4.880-4.902	[8]
Mo ₅ SiB ₂	Tetragonal	I4/mcm	6.0060-6.0413		11.0525-11.0948	[10]
α -MoB(L.T.)	Tetragonal	I4 _r /amd	3.105		16.97	[12]
β -MoB(H.T.)	Orthorhombic	Cmcm	3.16	8.61	3.08	[12]
Mo ₃ Si	Cubic	Pm3-n	4.897			[13]
Mo ₅ Si ₃	Tetragonal	I4/mcm	9.650		4.911	[13]
MoSi ₂	Tetragonal	I4/mmm	3.206		7.846	[14]

Chu et. al [15] and were used to determine the thermal expansion anisotropy of this material, however, no lattice parameters were reported.

Since MoSi_2 has been a subject of study since the early 1900's, many reports have been published on the lattice parameters and crystal structure of this material. A more recent report provided by Thomas et al. in 1985 [14], investigates the lattice parameters of single crystals as part of a study on the thermal expansion and resistivity of MoSi_2 . The crystals were grown using the Czochralski technique and were 9mm in diameter and 30 mm long. The lattice parameters were measured using a powder diffraction technique on powder from the single crystal rod and are reported in table 2.1.

Electrical Resistivity

There are few studies on the electrical resistivity of phases within the Mo-Si-B system. Amorphous $\alpha\text{-Mo}_3\text{Si}$ is a superconductor with $T_c=7.5\text{K}$, and was therefore the subject of a study of the Hall resistivity at low temperatures. This study reports a sign reversal on the Hall resistivity at low temperatures. No data is available on the change in resistivity as a function of temperature for crystalline Mo_3Si [16]. A general overview of borides states that the electrical resistivity of $\alpha\text{-MoB}$ (low temperature) and $\beta\text{-MoB}$ (high temperature) at room temperature is 0.045 and 0.025 $\text{m}\Omega\text{-cm}$, respectively [12]. There have been no reports of resistivity data as a function of temperature for these phases. Other borides in the Mo-Si-B system have been characterized but are not the subject of this investigation and will not be reported here.

The electrical resistivity as a function of temperature has been well studied for MoSi_2 . This is due to its extensive use as a high temperature heating element, the potential use as a temperature sensor, or for use in very large scale integration (VLSI) structures. In 1987, Nava et al. [2] prepared an amorphous thin film of molybdenum disilicide and crystallized it by heating to 950°C for 30 minutes in flowing helium. The MoSi_2 film was then electrically characterized using a van der Pauw technique from 2-1100K. The results of this study may be found in figure 2.2. Due to the presence of impurities, grain boundaries, and residual stress, the measured resistivity of these thin films may not have been intrinsic to MoSi_2 . This led Nava's

research group to prepare single crystal molybdenum disilicide for electrical characterization [6]. These results are also shown in figure 2.2. When comparing the results of the thin film and single crystal, there is a noticeable upward shift in the resistivity of the polycrystalline thin film. There is also an obvious positive deviation from linearity in the single crystal MoSi_2 . The suggested cause for this deviation is that the electronic structure of MoSi_2 is different from other silicides [4].

Figure 2.2 Resistivity as a function of temperature for Single crystal and polycrystalline thin film MoSi_2 reported by Nava et al. [2, 6]

A study by Ho et. al [1] involved the preparation of molybdenum disilicide films for temperature sensors in high temperature, oxidative environments because it forms a protective SiO_2 scale. They found that an increase in the amount of time at high temperature results in a drift in the electrical resistance. The composition of the film was found to change due to a loss of silicon to the silica scale which is compensated by some MoSi_2 changing into Mo_5Si_3 . Also, the consumption of the material to produce a non-conductive oxide changes the thickness of the film as well as microstructure. The overall result is an increase in electrical resistance with time. With the proper drift corrections, the authors suggest the material may be used as a temperature sensor.

Due to the absence of prior research on the single phases present in the Mo-Si-B system and interest in resistivity at high temperatures, single phase, polycrystalline samples have been prepared of the following compounds: $\text{Mo}_5\text{Si}_3\text{B}_x$, Mo_5SiB_2 , Mo_3Si , $\alpha\text{-MoB}$, MoSi_2 , and Mo_5Si_3 . In this text, the preparation method for each compound is described as well as the resistivity values measured using the van der Pauw method.

Experimental Procedure

$\text{Mo}_5\text{Si}_3\text{B}_x$, Mo_5SiB_2 , Mo_3Si , and MoSi_2 were prepared by arc melting elemental materials, Mo(99.97%), Si(99.9999%), and B(99.95%), under argon on a water cooled copper hearth. Each sample was melted several times to increase homogeneity. Before melting the sample, a zirconium button was melted 3 times to getter any residual oxygen. Each of the arc melted samples was weighed and subsequently ground for four intervals of 10 minutes each in a tungsten carbide SpexTM vial in an argon glovebox with less than 0.6 ppm oxygen. Stearic Acid (0.1 weight %) was added to the powder to act as a binder during pressing. Pellets of 1.27 cm in diameter were either uniaxially cold pressed or isostatically pressed at 137 MPa. The samples were then placed in a tube furnace under flowing, high purity argon along with Ti sponge to getter oxygen. The samples were heated at 1.5 degrees/minute to 550°C and held for 2 hours to remove the stearic acid. These pellets were subsequently sintered in a high temperature furnace under flowing argon. The furnace was ramped at 20 degrees/minute to the sintering temperature, held 30 minutes and then cooled slowly (3 degrees/min.) to room temperature. The sintering temperature used for each material is listed in table 2.2.

These samples were then cut using a high speed diamond saw into sections of 0.9mm in thickness. One section was ground with a mortar and pestle and sieved through a 635 mesh sieve and used for x-ray diffraction. Another section was instrumented for electrical resistivity measurement. The remainder was saved for future analysis.

Arc melting elemental Mo and B proved to be unsuccessful for the production of MoB, however commercial powder was available and was pressed and sintered using the same technique described previously. Furnace limitations allowed for a maximum sintering temperature

Table 2.2 Sintering temperatures for single phase compositions

Material	Sintering Temperature (C)
$\text{Mo}_5\text{Si}_3\text{B}_x$	1850
Mo_5SiB_2	1900
Mo_3Si	1800
MoSi_2	1800

of 1900°C, which did not prove adequate for densification. The sintered sample also showed signs of chemical reaction, possibly with the tantalum crucible used to contain it during sintering. These problems lead to an alternate method of acquiring MoB. A sputtering target was purchased from Cerac, Inc.(Milwaukee, WI) which had a density of only 50 % of theoretical. This target was then hot pressed at Sienna Technology, Inc.(Woodenville, WA) at a temperature of 1800°C and achieved 80 % of theoretical density. A section near the center of this target was removed and sliced into pieces of 0.8–0.9 mm thickness. One slice was ground and sieved for x-ray diffraction, while another was instrumented for resistivity measurement.

The Mo_5Si_3 sample was prepared by cold pressing commercial powders (Cerac, Inc., Milwaukee, WI) in an argon glovebox. This powder was reported to be 99.5% pure. The pellet was sintered in argon at 1800°C and a section was cut for XRD as well as electrical characterization.

The x-ray diffraction sample was prepared by grinding the pellet in air in a mortar and pestle and sieving through a 635 mesh screen. These powders were x-rayed using a Scintag diffractometer with a copper target and a 2θ range of 10 to 120 degrees. The XRD patterns were analyzed by the Rietveld method using GSAS refinement software(General Structure Analysis System, Los Alamos National Laboratory, Los Alamos, NM).

The van der Pauw method was used to measure the resistivity in these studies with the following design setup. The sintered 1.27 cm diameter pellet was cut using a high speed diamond saw into a 0.5–1 mm thick sample. Four holes of 0.5 mm diameter were drilled in the slice at 90 degree intervals along the edge of the sample. These holes were threaded with a 0.079 mm diameter tantalum wire numerous times to ensure good electrical contact. The sample was then loaded into a vacuum furnace where the wire leads from the sample were sequentially spot-welded to tantalum feed through wires corresponding to designated

connections with a Keithley Hall effect card. The furnace was ramped to 1500°C at 10°C per min., and measurements were taken every 25 degrees while regulating the input current and monitoring the corresponding potential difference.

Results and Discussion

Sample Characterization

Each sample was characterized by Archimedes density measurements and x-ray diffraction. The resulting density measurements for each of the single phase materials are presented in Table 2.3. The bulk densities were generally between 90 and 94 % of their theoretical density with the exception of MoB. These values were used with porosity correction equations (as previously described) to scale the electrical resistivity.

The lattice parameters for the materials found by refinement of the x-ray diffraction patterns using GSAS are listed in table 2.4. The x-ray diffraction pattern for Mo_5SiB_2 , $\text{Mo}_5\text{Si}_3\text{B}_x$, and Mo_5Si_3 showed signs of small amounts of second phase. The Mo_5SiB_2 sample contained 2.5 volume % Mo_3Si , suggesting that the lattice parameters represent the boundary of the T2 phase field with the lowest boron content. The $\text{Mo}_5\text{Si}_3\text{B}_x$ diffraction pattern shows 2 volume% MoB, suggesting the lattice parameters refer to the upper boundary of the T1 phase field. The sintered Mo_5Si_3 sample also contained Mo_3Si as a second phase, with 6 volume % identified in the x-ray diffraction scan. All other materials reported in this study were identified as being single phase.

Table 2.3 Experimental density measurements

Sample	Bulk Density ρ_b , g/cc	X-ray Density ρ_{XRD} , g/cc	% of X-ray Density $100 \cdot \rho_b / \rho_{XRD}$
$\text{Mo}_5\text{Si}_3\text{B}_x$	7.41	8.22	90.1
Mo_5SiB_2	7.86	8.74	89.9
MoB	6.93	8.61	80.5
Mo_3Si	8.41	8.95	94.0
Mo_5Si_3	7.59	8.24	92.1
MoSi_2	5.66	6.27	90.3

Table 2.4 Experimental crystallographic data for single phases in the Mo-Si-B system

Phase	Lattice Parameters (Å)	
	a	c
Mo ₅ Si ₃ B _x	9.65132±0.00012	4.89406±0.00010
Mo ₅ SiB ₂	6.02791±0.00006	11.07150±0.00013
α-MoB	3.11745±0.00003	16.95209±0.00020
Mo ₃ Si	4.89383±0.00003	
Mo ₅ Si ₃	9.64718±0.00014	4.91096±0.00009
MoSi ₂	3.20500±0.00004	7.84484±0.00015

The lattice parameters for Mo₅Si₃B_x are in good agreement with those reported by Huebsch [8]. The Mo₅SiB₂ lattice parameters are within the range of values reported by Nunes et. al [10]. The a lattice parameter agrees with the value reported for T2 from samples within the Mo_{ss}-Mo₅SiB₂-Mo₃Si phase triangle, however the c lattice parameter is smaller than the literature value. This suggests that the Mo₅SiB₂ prepared for this report may not contain the maximum Mo content.

The α-MoB lattice parameters appear to be slightly larger in the a direction and slightly smaller in the c direction than the data presented by Cutler [12]. This is not unexpected due to the solubility of Mo and B in the compound. It is very possible that the composition prepared for this report has a different Mo to B ratio than the sample reported in the literature.

The lattice parameter for Mo₃Si is slightly smaller(0.004 Å) than that reported by Christensen [13]. The error in Christensen's data was not presented but is likely to be significant since his analysis required the use of a Guinier film. In this case, the lattice parameter reported here is most likely within Christensen's error for single phase Mo₃Si.

The lattice parameter for Mo₅Si₃ is quite similar to the one reported by Christensen [13]. This is expected since the Mo₅Si₃ that Christensen prepared was part of the Mo₃Si single crystal melt and therefore was probably on the Mo rich side of the Mo₅Si₃ solubility region. This is the same region that the sample prepared for this study resides in.

The lattice parameters for MoSi₂ are very close to those reported by Thomas et. al [14]. This is expected since many researchers have produced high quality MoSi₂. Modern analysis

techniques have been used to calculate the lattice parameters with very low error.

Electrical Resistivity

In order to validate the accuracy of the measurement technique, a sample of NIST graphite was instrumented and measured for resistivity. The data was then compared with the data reported from a “round-robin” survey [17] as seen in figure 2.3. The data presented here shows that the technique used in this study is accurate, within the limitations of the NIST study.

Figure 2.3 Experimental NIST graphite data compared with published data

Significant data has been published on the resistivity of MoSi_2 , in the form of thin films as well as single crystals. The resistivity data corresponding to the sintered sample prepared for this study was compared with the results of Nava et. al [18]. Figure 2.4 shows the comparison of the published data to the data obtained in this study from room temperature to 800°C, after porosity correction. The resistivity data for the porosity-corrected, sintered sample shows a resistivity range similar to that of the polycrystalline thin film. Both the film and the sintered sample are higher in resistivity than the single crystals. This is expected due to the effect

of impurities on resistivity, following Matthiessen's rule (equation 1.3) which states that the resistivity change because of impurities is independent of temperature, so that the overall resistivity at any temperature is additive. This also suggests that the thermal component seen in the slope of the resistivity curve as function of temperature should be similar regardless of preparation method for the same composition, and impurities should be seen as a vertical displacement of the curve. This is in fact what is observed in figure 2.4 when comparing the sintered sample prepared for this study and the single crystal literature data, suggesting that the measurement presented here is of a single phase sample with grain boundaries and defects increasing the resistivity over that of the single crystal.

Figure 2.4 Experimental data compared to published data for MoSi₂

A comparison of the resistivity as a function of temperature for Mo₅Si₃B_x(T1) and Mo₅Si₃ in figure 2.5 shows a higher resistivity and lower temperature coefficient of resistivity (TCR) for T1 after porosity correction. In order to determine if the addition of boron may have altered the electronic structure, the Hall effect technique was used to calculate the concentration of mobile charge carriers in each sample. The results of this test gave a carrier concentration of 4.69×10^{22} electrons/cm³ for T1 and 2.59×10^{21} electrons/cm³ for Mo₅Si₃. These values indicate

that both compositions are either semi-metals or low density of states metals. Depending on the type of bonding, the presence of additional atoms, such as boron, can vary the relative concentrations of electrons and holes. The addition of impurity states may change the band structure of the material, which dictates the electrical properties such as the temperature coefficient of resistivity. The lower TCR in the T1 sample may be due to the higher density of impurity states. However, even with the increased carrier concentration, T1 still shows a higher overall resistivity.

According to the relation

$$\sigma = ne\mu \quad (2.1)$$

where σ is the conductivity, n is the number of carriers, e is the charge of an electron, and μ is the mobility, T1 must have a much lower mobility than Mo_5Si_3 to account for the increase in resistivity. There are two significant contributors to the electron mobility; electron-electron scattering rate and microcracking in the sample. The higher carrier concentration in T1 will increase the electron-electron scattering rate over Mo_5Si_3 , increasing the overall resistivity. To quantify the effect of this type of scattering on the resistivity, a crack free, large (or single) grained sample would need to be prepared. The second factor resulting in a decrease in electron mobility is the presence of cracks. Figure 2.6 shows the difference in crack density between the two measured samples. The calculated crack density for T1 is $0.015 \text{ cracks}/\mu\text{m}^2$, which is 20% higher than the corresponding crack density for Mo_5Si_3 ($0.012 \text{ cracks}/\mu\text{m}^2$). This implies that the crack density may be related to the effective mobility of the material. With additional cracking there is a significant reduction in carrier mobility due to the introduction of these conduction barriers. It appears that in these samples, the presence of cracks has a more significant effect than the presence of small amounts of secondary phases. This is reasonable since the electronic behavior of the secondary phases (Mo_3Si for Mo_5Si_3 and MoB for T1) are very similar to the properties of the matrix phases. Whereas these secondary phases create a small difference in the resistivity, cracks act as barriers to conduction, greatly increasing the scattering of electrons and phonons, and therefore increasing the effective resistivity. It follows that the more significant the cracking in the sample, the greater the deviation between

Figure 2.5 Comparison of porosity corrected experimental data for Mo_5Si_3 and $\text{Mo}_5\text{Si}_3\text{B}_x$

the measured resistivity and the actual material property. For this reason, the resistivity measurement on Mo_5Si_3 is considered more reliable and will be used in chapter 3 to model the properties of multiphase compositions.

A comparison of the resistivity as a function of temperature of each of these samples is presented in figure 2.7. Notice that with the exception of MoSi_2 , all of the measured samples seem to have similar resistivity values that vary similarly as a function of temperature. Due to the variation in density of each of these samples, such a graph may not be appropriate for direct comparison. To eliminate the effect of porosity, the resistivity at each temperature was modified using the porosity equation described previously. The modified resistivity curves for each of these samples is presented in figure 2.8. The maximum difference between resistivity in these samples, except for MoSi_2 , is only $5 \times 10^{-7} \Omega\text{-m}$. Notice in all samples, other than MoSi_2 , there is a slight negative deviation from linearity as well as a low slope. This slope trend is one seen in many other silicide compositions. It is quite pronounced in V_5Si_3 , V_3Si , and many others [4]. The explanation for this deviation from Matthiessen's rule, suggested by Nava et. al [4], is saturation of the resistivity. This saturation is thought to occur when the

Figure 2.6 Microstructure of sintered (a) Mo_5Si_3 and (b) $\text{Mo}_5\text{Si}_3\text{B}_x$ showing microcracking

conduction-electron mean free path becomes on the same order as interatomic spacings, and the electron-phonon interaction is the dominant scattering mechanism. The resistivity no longer follows a proportional relationship with the mean-square amplitude of the lattice vibration ($k_b T$) but rather rises less than linearly and tends toward saturation [4]. After studying many silicide single crystals, Nava et. al [4] suggest that the resistivity saturation seems to be most pronounced for materials that have a room temperature resistivity of $5\text{--}10 \times 10^{-7} \Omega\text{-m}$, which is the range of resistivity values that materials in the Mo-Si-B system exhibit. The saturation is noticeable in measurements that start at zero Kelvin as seen in figure 2.9 for vanadium silicides. The materials in the Mo-Si-B system, with the exception of MoSi_2 , show behavior very similar to the vanadium example, suggesting the saturation effect explanation is equally valid in this system.

MoSi_2 has a very different and distinct curve which shows a positive deviation from linearity and does not exhibit this saturation behavior. This is due to differences in electronic structure between MoSi_2 and the other materials in this study. MoSi_2 is dominated by s-p bands, where the other materials are dominated primarily by d bands. The s-p bands have a higher temperature dependence than the d bands which leads to a higher TCR for MoSi_2 .

Figure 2.7 Resistivity vs. Temperature for all single phase compositions between room temperature and 1500°C

Figure 2.8 Resistivity vs. Temperature for all single phase samples after porosity correction

Figure 2.9 Resistivity vs. Temperature for V_5Si_3 and V_3Si

Conclusion

With the exception of $MoSi_2$, the silicide and boride compositions examined in this study exhibit a resistivity saturation within the temperature range examined in this study. This suggests that the materials are most likely similar in electronic structure, since they exhibit such similar electronic characteristics. The resistivity values for these materials are similar to other silicides [4]. $MoSi_2$ has a very different electronic structure which allows for scattering between bands, and this is exhibited in a continuing positive increase in resistivity even to temperatures of $1500^\circ C$. Individually, these compositions do not meet all of the requirements for useful high temperature materials, such as oxidation resistance and mechanical behavior. Together, however, they may combine their best properties to produce a material which does meet engineering criteria. It is therefore the subject of chapter 3 to compare these single phase resistivity values with the resistivity values of multiphase samples.

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3 ELECTRICAL RESISTIVITY OF MULTI-PHASE Mo-Si-B MATERIALS AS A FUNCTION OF TEMPERATURE

A paper to be submitted to the Journal of Materials Science

Sarah Beckman, Bruce Cook, and Mufit Akinc

Abstract

The electrical resistivity values as a function of temperature are presented for several multiphase compositions in the Mo-Si-B system in the temperature range of 25 to 1500°C. A logarithmic rule-of-mixtures relationship is used to correlate these curves to the resistivity curves of the single phase constituents. Error values for the model are calculated based on the experimental error in the volume fraction calculation, porosity estimations for each single phase, and error in the line estimation of the single phase resistivity values as a function of temperature. Experimental resistivity values for multiphase samples in the Mo_5Si_3 - MoSi_2 , $\text{Mo}_5\text{Si}_3\text{B}_x(\text{T1})$ - MoB - MoSi_2 , and $\text{Mo}_5\text{Si}_3\text{B}_x$ - $\text{Mo}_5\text{SiB}_2(\text{T2})$ - Mo_3Si phase fields are shown to be in agreement with the model within one standard deviation.

Introduction

For many properties such as Young's modulus, heat capacity, and electrical conductivity, it is useful to have a method of resolving the properties of a composite based on the individual component properties. Ideally a model that is not geometry dependent would yield the most applicable results. The following is a description of models which have been proposed to describe composite behavior. Some are geometry independent while others apply simple

geometric constraints. All of these models are proposed for electrical conductivity, however they may also be used for various other materials properties including Young's modulus and heat capacity.

The most general model available does not give a discrete value, but a range of values as seen in equation 3.1:

$$\sigma_{ef}^n = \sum_{i=1}^m \theta_i \sigma_i^n \quad (3.1)$$

In this model, when $n = 1$, the Voight average (upper limit) is obtained, and when $n = -1$, the Reuss average (lower limit) is obtained. This model is useful for multiphase materials. In equation 3.1, m identifies the number of phases. The upper boundary represents a situation in which the phases are aligned in sheets parallel to the direction of current. The lower boundary describes these sheets aligned perpendicular to the direction of the current. Values within these boundaries correspond to intermediate cases, such as $n = 1/3$ for materials with similar conductivities [1]. When $n = 0$, a logarithmic function describes the relationship (as n approaches zero, $\sigma^n = 1 - n \ln \sigma$):

$$\ln \sigma_{ef} = \sum_{i=1}^m \theta_i \ln \sigma_i \quad (3.2)$$

This equation represents the case where the phases are randomly distributed in the material and is the median value between the two boundaries.

Since electrical conductivity may vary from $10^{-16} \Omega^{-1}m^{-1}$ for a good insulator to $10^8 \Omega^{-1}m^{-1}$ for a highly conductive material, mixing materials with significantly different conductivities may produce inaccurate results using the generalized rule of mixtures model. In these cases the effective resistivity is highly structure dependent. This leads to conductivity models that account for microstructure.

If a material has a small amount of the second phase present as spherical inclusions, a linear relationship is produced:

$$\sigma_{ef} = \sigma_0 + \frac{3(\sigma_1 - \sigma_0)\sigma_0}{\sigma_1 + 2\sigma_0} \theta_1, \quad (3.3)$$

where σ_0 is the conductivity of the primary phase, σ_1 is the conductivity of the inclusions, and θ_1 is the volume fraction of inclusions [1]. Similar, yet more complex equations have been

derived for ellipsoidal, randomly oriented infinite cylinders, and thin flat plates of the second phase [1]. Once the phase concentrations become large, such that the second phase has some degree of connectivity, these equations do not apply and a different type of equation needs to be specified.

With large fractions of second phase, the structure of the system needs to be defined. There are two major types of systems available for the characterization of the microstructure. The first is the matrical system. In this case, the second phase material exists as inclusions set at 'nodes' in a matrix [1]. It is important to distinguish that only the matrix is connected in this system. The second system is a framework structure. In this system, both the matrix and the second phase are connected in three dimensions forming an interconnected framework. Using the knowledge of these two types of systems, several relationships have been derived. In statistical systems (the microstructure being a random framework) the connectivity of each phase allows the model to consider the phase as an average quasi-homogeneous field, whose value may be found using the following relation:

$$\sum_{i=1}^m \frac{\sigma_i - \sigma_{ef}}{\sigma_i + 2\sigma_{ef}} \theta_i = 0. \quad (3.4)$$

Equations have been derived for different shaped matrical inclusions in which the increase in shape complexity increases the complexity of the equation [1]. These equations currently predict the behavior of materials composed of two distinct phases, however this study is concerned with three (four, including porosity) phase mixtures. Even equations that have been simplified by several assumptions are difficult to use as a predictive model if they require knowledge of the microstructure. Due to the need for a predictive model, the natural log equation (equation 3.2) derived from the general rule of mixtures model has been chosen to represent the behavior of the materials in this study.

In order to adequately compare different samples to each other and to any model, it is imperative that the samples are well characterized. The first step in characterization is to identify phase fractions which is done primarily by x-ray diffraction. In this study, the x-ray diffraction was used in conjunction with computer software that models the experimental diffraction pattern. The volume fractions calculated from this software as well as the error in

the calculated values are used in the natural log model to predict the electrical behavior.

Another characterization method is microstructural analysis. When comparing samples to each other, many factors such as grain size, phase distribution, and degree of cracking may contribute to the overall understanding of collected resistivity data. For this reason, scanning electron microscopy is utilized to identify microstructural character. Specifically, backscattered electron imaging is used to identify the various phases based on contrast difference. If two phases are similar in contrast, chemical etching is used to distinguish between the two phases.

Microstructural analysis and x-ray diffraction have been used in this study to develop a relationship between the resistivity curves and the sample character of multiphase materials in the Mo-Si-B system. Chapter 2 describes the processing and resistivity results of the single phase constituents and shows that all of these phases have very similar resistivity values and TCRs. A linear regression of the resistivity curve for each phase from chapter 2 is used to generate the single phase resistivity values which are entered into the natural log model.

The model has been applied to three distinct regions of the Mo-Si-B phase triangle. The first is a binary system between Mo_5Si_3 and MoSi_2 . The second is a ternary system involving $\text{Mo}_5\text{Si}_3\text{B}_x$ (T1), MoB , and MoSi_2 . Finally, the ternary system consisting of $\text{Mo}_5\text{Si}_3\text{B}_x$, Mo_5SiB_2 (T2), and Mo_3Si has been prepared and compared with the predictive model. Each of these regions is highlighted in figure 3.1. In this chapter, the single phase resistivity vs. temperature curves from chapter 2 as well as the results of sample characterization will be used in a general model and compared to the resistivity values of multiphase materials in the Mo-Si-B system.

Experimental Procedure

Multiphase compositions were chosen in each of the regions in this study and arc melted from elemental materials, Mo(99.97%), Si(99.9999%), and B(99.95%), in a cooled copper hearth under argon. Before melting the sample, a pure zirconium button was melted 3 times to getter residual oxygen.

With samples containing large amounts of elemental boron, a method was developed to

Figure 3.1 Regions of the Mo-Si-B phase diagram selected for study

limit the fragmentation of the boron when struck by the arc. The technique was designed to cover the boron, either with Mo or Si so that it is not directly exposed to the arc and heats relatively slowly. Initial attempts to arc melt the boron by direct contact with the arc resulted in unrecoverable explosive fracture of the boron pieces. For successful melting, pieces of boron were placed in the copper hearth surrounded on three sides by silicon. On the remaining side, two thin discs of Mo (3–4 mm) rested on the copper hearth and leaned against the other materials to cover the boron fully. The Mo was heated slowly with the arc, and at the point it started to glow, the current of the arc was increased and the Mo readily absorbed the Si and B, without any of the materials fracturing. For samples with less boron, one Mo disc was used in a similar manner to cover the boron and silicon. After the initial melting of all of the compositions, the button was flipped and melted again. This procedure was repeated a total of 6 times to ensure homogeneity.

These arc melted samples were processed and sintered in an argon filled glovebox as outlined in chapter 2. The bulk density of the sintered pellets was measured using the liquid immersion method. Next the samples were cut into multiple sections for scanning electron microscopy, electrical resistivity measurement and x-ray diffraction. Scanning electron microscopy (SEM) was performed on each of the multiphase samples in order to determine the porosity level, degree of microcracking, grain size and phase distribution in each material. In the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field, the polished samples were etched using Murakami's etchant. This etchant consists of potassium ferrocyanide, potassium hydroxide and water in equal proportions. This etchant is useful for etching $\text{T2}(\text{Mo}_5\text{SiB}_2)$. Several micrographs were used to calculate volume fractions of each phase using Image 1.58, an analysis program, and compared with the results from x-ray diffraction. Resistivity values were measured on samples prepared using the same procedure as described in chapter 2.

X-ray diffraction powders were prepared by grinding one section of the pellet to less than 20 microns with a mortar and pestle in air. A ScintagTM diffractometer was used for scans with a 0.03 step size and a 2 second count time. The diffraction patterns were analyzed using GSAS (General Structure Analysis System, Los Alamos National Laboratory, Los Alamos, NM) software which conducts whole pattern refinements of x-ray data. Values for volume fractions and standard deviations were taken from the output of this program.

Results and Discussion

The general rule-of-mixtures equations were initially considered for use in modeling the behavior of the multiphase materials. Since the resistivity curves for the single phase samples are so similar, the difference between upper and lower boundaries of the model ($n=-1$, $n=1$) is small. The maximum difference between the boundaries and the natural log model ($n=0$) is $0.1 \times 10^{-7} \Omega\text{-m}$ for a hypothetical composition as seen in figure 3.2, which is less than the error due to the resistivity measurement technique and eliminates the ability to determine the best fitting model. This also excludes the use of any model which attempts to use microstructure to further model the electronic properties.

Figure 3.2 Various Rule of Mixtures models for a hypothetical multiphase sample with 33 volume% MoB, 33 volume% MoSi₂, and 34 volume% Mo₅Si₃B_x

Since the models yield virtually indistinguishable results, the natural log model was chosen for the analysis of these samples. This model represents a randomly mixed microstructure, essentially an averaging of the two rule of mixtures boundaries. Since micrographs of the experimental samples seem to indicate a random mixture of phases, the use of the natural log model is appropriate and has been used for all of the samples in this study in the form:

$$\ln(\rho_{ef}(T)) = \sum_{i=1}^m v_i \ln(\rho_i(1 - \frac{3}{2}\theta_i)) \quad (3.5)$$

which may be written as:

$$\rho_{ef}(T) = \prod_{i=1}^m (\rho_i(1 - \frac{3}{2}\theta_i))^{v_i} \quad (3.6)$$

In these equations, ρ_{ef} is the predicted resistivity at temperature T, ρ_i is the value of the resistivity at T for phase i based on a linear fit of single phase data, $(1 - \frac{3}{2}\theta_i)$ is a porosity correction for the single phase data in which θ_i is the volume fraction of the porosity in each single phase calculated from bulk density and x-ray density values using the relation:

$$\theta_i = 1 - \frac{\rho_i^{bulk}}{\rho_i^{x-ray}}. \quad (3.7)$$

Also, v_i is the volume fraction of phase i from x-ray diffraction of the multiphase sample. Table 3.1 presents the slope and intercept output from the linear regression of the single phase resistivity curves reported in chapter 2.

The overall error in this model consists of three main parts: error in the volume fraction values, error associated with the porosity correction of the single phases, and error from the linear regression of the single phase data. The volume fraction is calculated from the x-ray diffraction pattern by GSAS, which also calculates the standard deviation for this value (Δv_i). This value is used in the volume fraction error calculation. The error due to the porosity correction ($\Delta \theta_i$) is due to limits in the bulk density measurement and is equivalent for all phases at a value of 0.01. The error from the linear regression of the single phase data may be calculated using statistics as seen in equation 3.8.

$$\Delta \rho_i = \sqrt{MSE \left(\frac{1}{n} + \frac{(T_h - \bar{T})^2}{\sum (T_i - \bar{T})^2} \right)} \quad (3.8)$$

where, n is the total number of data points used in the linear regression, T_h is the input temperature for the model, T_i is the experimental temperature, $\bar{T}$ is the average value of T_i . The MSE is the mean square error and is given by the equation:

$$MSE = \frac{\sum (\rho_i - \hat{\rho}_i)^2}{n - 2} \quad (3.9)$$

where $\hat{\rho}_i$ is the calculated estimate value for the resistivity at a given T_i . The MSE values for each phase are given in table 3.1.

Table 3.1 Results from linear regression analysis of single phase samples analyzed in chapter 2

Phase	Slope($\frac{\Omega-m}{^\circ C}$) ($\times 10^{-10}$)	Intercept($\Omega - m$) ($\times 10^{-7}$)	MSE ($\times 10^{-8}$)
Mo ₅ Si ₃ B _x	2.10	12.29	1.5
Mo ₅ SiB ₂	3.11	5.89	1.9
MoB	4.74	6.70	2.8
Mo ₃ Si	3.11	6.85	0.7
Mo ₅ Si ₃	3.70	8.56	1.8
MoSi ₂	13.77	3.44	3.8

These three major sources of error are additive resulting in the following overall error equation derived from partial derivatives:

$$\frac{\Delta\rho_{ef}}{\rho_{ef}} = \sum_{i=1}^m (\ln \rho_i \Delta v_i + \frac{3v_i \Delta \theta_i}{2 - 3\theta_i} + v_i \frac{\Delta \rho_i}{\rho_i}) \quad (3.10)$$

This equation multiplied by the ρ_{ef} for each temperature gives a value that is $\pm$ one standard deviation from the model. This value represents a confidence interval of 65.8%.

Mo₅Si₃-MoSi₂ region

These equations were applied to each sample within the three regions of the phase diagram selected for this study. The first region is the binary system of Mo₅Si₃ and MoSi₂. Two samples were successfully prepared and the volume fractions, as calculated by GSAS, are presented in table 3.2. Figure 3.3 shows the microstructure for these two samples. Neither of these samples

Table 3.2 Volume fractions for samples in Mo₅Si₃-MoSi₂ phase field

Sample	volume fraction	
	Mo ₅ Si ₃	MoSi ₂
α	.537	.463
β	.25	.75

show cracking, even though Mo₅Si₃ has a highly anisotropic thermal expansion [2]. This is most likely due to the brittle to ductile transition which MoSi₂ experiences at 1000°C [3]. The ductility of MoSi₂ at high temperatures may compensate for the expansion anisotropy upon cooling of the Mo₅Si₃ by dislocation plasticity [4] which would have an unknown effect on the electrical properties. Figure 3.4 shows the experimental resistivity curves for both of the phases. Figure 3.5 shows the experimental data for α compared to the model calculated from equation 3.6. This figure shows that the experimental data is within one standard deviation for most of the temperature range. Figure 3.6 shows the experimental data for β compared to the model predicted for the corresponding volume fractions. This sample seems to have a slope that is higher than predicted. The discrepancy is most likely due to the resistivity data input into the model. In order to simplify error calculations, MoSi₂ was considered linear. However, MoSi₂ has a well documented positive deviation from linearity [5] that has not been accounted

Figure 3.3 The BSE image of samples α and β , the lighter phase is Mo_5Si_3 , the darker grey phase is MoSi_2 , and the black areas are pores

for. Using a parabolic regression for MoSi_2 , the predicted model has a higher value for high temperatures. With a parabolic relationship, the model more closely agrees with experimental data, but also increases the complexity of the error analysis. For α and other three phase materials with lower amounts of MoSi_2 , deviation from the model at higher temperatures is not seen suggesting that for most cases, the assumption of linearity for MoSi_2 is acceptable. When the volume fraction of MoSi_2 is small, it does not have much influence in the model and values entered for the MoSi_2 linear or otherwise are not expected to change the overall shape of the model.

$\text{Mo}_5\text{Si}_3\text{B}_x$ - MoSi_2 - MoB region

The second region of interest contains $\text{Mo}_5\text{Si}_3\text{B}_x$, MoSi_2 , and MoB . In this study, 7 samples were prepared. The x-ray diffraction calculated volume fraction values are listed in table 3.3 and these compositions are marked on the phase diagram displayed in figure 3.7. Although this region and the $\text{Mo}_5\text{Si}_3\text{B}_x$ - Mo_3Si - Mo_5SiB_2 region are comprised of $\text{T1}(\text{Mo}_5\text{Si}_3\text{B}_x)$ a boron containing phase, the data used in the model is for Mo_5Si_3 without boron. As discussed in chapter 2, the T1 sample has a higher resistivity than the Mo_5Si_3 which is partially due to the extensive microcracking in T1. Since the values for T1 are unreliable, the data from Mo_5Si_3 has been chosen to represent the T1 phase in the model.

Figure 3.4 Experimental resistivity data for α (54%Mo₅Si₃, 46%MoSi₂) and β (25%Mo₅Si₃, 75%MoSi₂) in the Mo₅Si₃-MoSi₂ phase field

Figure 3.5 Experimental resistivity data versus natural log model for sample α

Figure 3.6 Experimental resistivity data versus natural log model for sample β

Table 3.3 Volume fractions for samples in the $\text{Mo}_5\text{Si}_3\text{B}_x$ - MoSi_2 - MoB phase field

Sample	volume fraction	volume fraction	volume fraction
	$\text{Mo}_5\text{Si}_3\text{B}_x$	MoSi_2	MoB
A	.180	.133	.687
B-1	.402	.207	.391
B-2	.325	.263	.412
C	.421	.333	.246
D	.732	.194	.074
E	.420	.510	.070
F	.091	.863	.046

Figure 3.8 shows the BSE micrographs for each of these samples. The micrograph for sample A shows some cracking in the MoB grains, however the cracking is not nearly as extensive as the cracking in B-1 and B-2, and C. Whereas sample A has a high fraction of MoB, and only 20 volume % T1 ($\text{Mo}_5\text{Si}_3\text{B}_x$), samples B-1 and B-2 are high in both MoB and T1. Borides are known for very high hardness values [6] and as previously discussed, Mo_5Si_3 has a highly anisotropic thermal expansion. It appears that if the concentration of T1 is fairly high (> 30%),

Figure 3.7 Location of samples in the $\text{Mo}_5\text{Si}_3\text{B}_x$ -MoB-MoSi₂ phase field of the Mo-Si-B phase diagram

as well as a high concentration of MoB ($> 25\%$), the thermal expansion anisotropy on cooling of the T1 is relieved by extensive cracking in the T1 and MoB phases, rather than dislocation movement in the MoSi₂ as seen in the binary Mo_5Si_3 -MoSi₂ region. Both A and D show some cracking, yet not at the level of B-1, B-2, C, which suggests that a major phase of either MoB or T1 alone is not enough to cause extensive cracking, that is most likely the presence of both phases is necessary for such dramatic defects. Since E and F are very similar to samples α and β in the Mo_5Si_3 -MoSi₂ regime, they are not expected to show cracking due to the dislocation plasticity of MoSi₂ at higher temperatures. This prediction is verified by the micrographs of these samples.

The resistivity as a function of temperature data for all of these samples are shown in figure 3.9. The majority of these samples have a similar slope, the exceptions being E and F. These compositions have large fractions of MoSi_2 the only composition of the single phase materials presented in chapter 2 to have a significantly different slope. As the amount of MoSi_2 increases, the slope of the resistivity curve is expected to increase, which is verified by experimental results. Figure 3.10 shows the modeling prediction and experimental data for sample A. The data for this composition fits very well to the predictive model and is well within the one standard deviation error limits. Figure 3.11 shows the model and experimental data for B-1. This experimental data also fits very well with the predicted outcome. Figure 3.12 shows the data and model for B-2. This experimental data is just outside of one standard deviation. It is curious that two samples, B-1 and B-2, can have such similar microstructures and volume fractions and yet not fit the modeled behavior to the same degree. It is possible that the micrographs are not representative of the two materials and therefore, B-1 has less cracking or porosity than B-2. Although they show a slightly different relationship with their corresponding models, it is still within the limits of the error and therefore not statistically significant. The results of experiment and model for sample C are presented in figure 3.13. This data fits the model within one standard deviation with a slightly different slope than predicted. Figure 3.14 shows the resistivity curves for experimental data and model of sample D. This phase appears to be slightly higher than one standard deviation from the model, however a porosity correction on this phase reduces the deviation from the model. With a density of 94% of theoretical, the porosity correction results in a significant reduction in the overall experimental resistivity curve. Another possibility is the degree of cracking in this sample. Sample D is primarily composed of T1 and as seen in chapter 2, the degree of cracking may have a significant effect on the resistivity. If this sample has a high crack density, its resistivity may be artificially high. In fact, if the linear regression for T1 is used in place of Mo_5Si_3 , the model accurately predicts the behavior of sample D. This suggests that the same mechanisms that caused the higher resistivity in the T1 sample discussed in chapter 2 are operative in this sample. Figure 3.15 shows sample E to also have values within one standard

deviation of the model's prediction. Finally, figure 3.16 shows the model to be an accurate prediction for experimental data for sample F.

Overall, these samples agree with the natural log model within the error of the prediction and do not show any specific trends relating to the microstructure. This is most likely due to the extreme similarity of the resistivity of the constituent phases. Without large differences in the resistivity or temperature coefficient of resistivity between phases, it is very likely that there is interaction between them. The model fits this data independent of microstructure partially due to the similarity between phases as well as the high standard deviation of the model.

$\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_3\text{Si-Mo}_5\text{SiB}_2$ region

The final region of study is the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_3\text{Si-Mo}_5\text{SiB}_2$ phase field. Six samples were prepared in this region of the phase diagram and their volume fraction values according to GSAS calculations are listed in table 3.4. These values are plotted on the phase diagram in figure 3.17.

Table 3.4 Volume fractions for samples in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_3\text{Si-Mo}_5\text{SiB}_2$ phase field

Sample	volume fraction $\text{Mo}_5\text{Si}_3\text{B}_x$	volume fraction Mo_3Si	volume fraction Mo_5SiB_2
1	.147	.152	.701
2-A	.304	.553	.143
2-B	.357	.379	.264
3	.181	.721	.098
4	.499	.433	.068
5	.731	.176	.093

Figure 3.8 BSE images of samples A-F, the lightest phase is MoB, the light grey is $\text{Mo}_5\text{Si}_3\text{B}_x$, the darker grey phase is MoSi_2 , and the darkest is porosity(all within the MoB-T1- MoSi_2 phase field -See table 3.3 and figure 3.7)

Figure 3.9 Experimental resistivity data for the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ region

Figure 3.10 Experimental resistivity data versus natural log model for sample A in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ phase field

Figure 3.11 Experimental resistivity data versus natural log model for sample B-1 in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ phase field

Figure 3.12 Experimental resistivity data versus natural log model for sample B-2 in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ phase field

Figure 3.13 Experimental resistivity data versus natural log model for sample C in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ phase field

Figure 3.14 Experimental resistivity data versus natural log model for sample D in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-MoSi}_2\text{-MoB}$ phase field

Figure 3.15 Experimental resistivity data versus natural log model for sample E in the $\text{Mo}_5\text{Si}_3\text{B}_x$ - MoSi_2 - MoB phase field

Figure 3.16 Experimental resistivity data versus natural log model for sample F in the $\text{Mo}_5\text{Si}_3\text{B}_x$ - MoSi_2 - MoB phase field

Figure 3.17 Location of samples in the $\text{Mo}_5\text{Si}_3\text{B}_x$ - Mo_3Si - Mo_5SiB_2 phase field of the Mo-Si-B phase diagram

The micrographs for these samples are presented in figure 3.18. For sample 1, the secondary electron image shows some noticeable cracking in the major phase, Mo_5SiB_2 (T2). The pits seen in the large T2 grains are most likely the result of chemical etching. The BSE image of sample 2-A shows minor cracking in the $\text{Mo}_5\text{Si}_3\text{B}_x$ (T1) phase, but no noticeable defects in the Mo_3Si or T2 phases. In this micrograph, the lightest phase is the Mo_3Si , the darker grey is T1, and the small pits are mostly T2, however there is also some porosity which is difficult to distinguish. The micrograph of sample 2-B shows cracking in the T1 phase(dark grey) and some minor cracking in the T2(medium grey). The black spots in this micrograph are porosity. The micrograph for sample 3 reveals cracking in both T1, and the major phase Mo_3Si . Around the T2(outlined in black) as well as around the T1, small particles(white spots) of $\text{Mo}_{(ss)}$ were identified. This suggests that the sample most likely failed to reach equilibrium,

or that the silicon is being removed in the form of glass and leaving molybdenum rich regions. Since the micrograph does not show obvious glassy areas, the presence of $\text{Mo}_{(ss)}$ is most likely due to the short sintering temperature employed for this sample. Such a small amount of this additional phase (undetectable by x-ray diffraction) should not influence resistivity outcomes. The micrograph for sample 4 also shows these small particles primarily around the T1 phase suggesting it is not in thermal equilibrium. In this sample, cracking seems to occur in the T1 and continues into the Mo_3Si . The major difference between samples 3 and 4 is that 4 has a much higher volume fraction of T1. This would suggest a higher stress level due to thermal expansion anisotropy in T1 during cooling. It appears that although Mo_3Si is cubic, it relieves the stress from T1 by cracking as well. In the case of sample 5, T1 is such a large constituent that it appears to be the only phase to exhibit cracking.

The experimental resistivity data for the samples in this phase field are presented in figure 3.19. All of these samples have very similar resistivity values, varying $3 \times 10^{-7} \Omega \cdot m$ between the lowest and the highest of the curves. They also show similar temperature coefficient of resistivity (TCR) values which is expected because the single phase materials that contribute to these samples also have similar TCR values. Figure 3.20 shows the experimental data for sample 1 compared to the natural log rule of mixtures model and its associated error. This graph shows that the experimental data falls just outside of one standard deviation. A porosity correction for this data based on bulk density measurements lowers the curve to fit well with the model. Experimental data and the appropriate model for 2-A are shown in figure 3.21. The data for this sample is largely within the error limits of the model. Sample 2-B (figure 3.22) shows similar behavior to 2-A, which is expected since the compositions are very similar. Another sample which shows similar behavior is composition 3 (figure 3.23). It is slightly lower than the model, as are 2-A and 2-B although all are within one standard deviation of the model. Sample 4 shows very good agreement with the model as seen in figure 3.24. Composition 5 is similar to composition 1 in that without porosity correction, the data is within one standard deviation, but after correction for porosity, the data agrees very well. This is illustrated in figure 3.25.

Since the overall range of resistivity values in this phase field is small and the resistivity values of the single phase constituents are also very similar, the results of experiment and model are expected to be similar for all compositions. It is interesting to note that while there is no statistically significant difference, 2-A, 2-B, and 3 all seem to be lower than the model while the other samples are higher. All three of these phases have very little cracking. In this case, the fact that the values input for Mo_5Si_3 are from a cracked sample suggests that the model may be artificially high. Besides for these three samples, all other ternary samples seem to show cracking. Perhaps this is why they agree well with the model, while 2-A, 2-B and 3 are lower than the model. To verify this hypothesis, a single crystal sample of each of the single phase compositions would need to be characterized electrically and used for the model. Even this new data would not be a definitive solution because the error in the model itself would need to be reduced in order to establish a statistically significant difference.

Conclusion

From each of these regions in the Mo-Si-B phase diagram it has been established that the natural log expression of the rule of mixtures model is effective in describing the resistivity behavior within the limits of the error involved in the model. In order to get a better understanding of the effect of microstructure, it is necessary to reduce the error limits of model. One possible alteration in the technique used in this chapter would be nonlinear modeling, however the error associated with the equation is not likely to change significantly. To drastically increase the confidence in the model, more accurate values for the volume fraction must be determined. Another way to increase the overall confidence in the model would be to do several runs on each of the single phases in order to create a more statistically accurate linear regression model of the data. Ideally, single crystal or at least fully dense, crack-free single phase materials would be produced and characterized in order to increase the accuracy of the model. All of these alterations would improve the model possibly revealing the effect of microstructure on the properties of the multiphase samples.

Figure 3.18 Secondary image of sample 1, BSE images of samples 2-A-5, the lightest phase is Mo_3Si , the light grey is Mo_5SiB_2 , the darker grey phase is $\text{Mo}_5\text{Si}_3\text{B}_x$, and the darkest is porosity

Figure 3.19 Experimental resistivity for the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_3\text{Si-Mo}_5\text{SiB}_2$ region

Figure 3.20 Experimental resistivity data versus natural log model for sample 1 in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field

Figure 3.21 Experimental resistivity data versus natural log model for sample 2-A in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field

Figure 3.22 Experimental resistivity data versus natural log model for sample 2-B in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field

Figure 3.23 Experimental resistivity data versus natural log model for sample 3 in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field

Figure 3.24 Experimental resistivity data versus natural log model for sample 4 in the $\text{Mo}_5\text{Si}_3\text{B}_x\text{-Mo}_5\text{SiB}_2\text{-Mo}_3\text{Si}$ phase field

Figure 3.25 Experimental resistivity data versus natural log model for sample 5 in the $\text{Mo}_5\text{Si}_3\text{B}_x$ - Mo_5SiB_2 - Mo_3Si phase field

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4 GENERAL CONCLUSIONS

The electrical resistivity measurements of several samples in the Mo-Si-B system have shown these materials to be semi-metals or low density of states metals. The single phase samples Mo_3Si , Mo_5SiB_2 , and Mo_5Si_3 have such similar resistivity ranges and temperature coefficient of resistivity (TCR) values that any sample containing a mixture of these phases also shows a similar TCR value and resistivity range. This similarity suggests that any composition selected from this phase field for meeting other engineering criteria in use as a high temperature heating element would have a predictable resistivity curve as function of temperature.

MoSi_2 on the other hand, has a much higher TCR values than the other phases in the $\text{Mo}_5\text{Si}_3\text{B}_x$ -MoB- MoSi_2 phase triangle. This causes an increase in the slope of a multiphase material in this region as the amount of MoSi_2 increases. Below 50 volume percent MoSi_2 , the TCR value of the multiphase material is quite similar to that of the other phases in the field. Above 50%, the TCR tends to increase drastically as the MoSi_2 content increases. This is seen in figure 4.1 which compares the predicted with the experimental TCR values as function of MoSi_2 content.

This figure also shows the agreement of the TCR values for the natural log rule-of-mixtures model and experimental data. If a composition were chosen from the $\text{Mo}_5\text{Si}_3\text{B}_x$ -MoB- MoSi_2 phase triangle for use as a heating element, the model presented in chapter 3 could predict the resistivity as a function of temperature given the volume of each phase present in the sample.

It should be noted, however, that many of the sintered compositions prepared in this study from the $\text{Mo}_5\text{Si}_3\text{B}_x$ -MoB- MoSi_2 phase triangle are not likely to be considered for engineering application as a heating element. Samples with high MoB content are not expected to have the superior oxidation resistance of $\text{Mo}_5\text{Si}_3\text{B}_x$ based materials and also would be expensive to

Figure 4.1 Calculated and experimental TCR values as a function of MoSi₂ content

produce due to the high boron content. Sintered samples which have volume fractions greater than 25% of both Mo₅Si₃B_x and MoB have shown extensive cracking which would greatly limit the mechanical properties necessary for engineering application. As MoSi₂ becomes the major phase, it is anticipated that the mechanical properties will be dominated by this phase, similar to the change in electrical resistivity with increasing MoSi₂ content. Since high creep rates in MoSi₂ are the primary reason for considering alternative heating element materials, a material with a similar creep rate (or only a small improvement) would not be worth the additional cost to replace the current material and processing routes. It is possible that a sample that is mostly Mo₅Si₃B_x with high enough MoB to provide boron for oxidation resistance and low enough MoSi₂ content to maintain the creep resistance of Mo₅Si₃ would be an acceptable composition for engineering considerations. However, there seems to be no particular advantage to this material over one that is mostly Mo₅Si₃B_x with small amounts of Mo₅SiB₂ and Mo₃Si when considering oxidation resistance, creep behavior, and electrical resistivity. The outcome of mechanical testing may be the deciding factor between compositions with equal amounts of boron content and volume fraction of Mo₅Si₃B_x residing in the two ternary phase fields.

In general, this study shows that the resistivity as a function of temperature changes very little with changing composition, which suggests that the best selection for a heating element material will be based on other engineering criteria.

ACKNOWLEDGEMENTS

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States Government has assigned the DOE Report number IS-T 1889 to this thesis.

I would like to thank Dr. Mufit Akinc for his support and suggestions which were a major part of the resulting research project. Bruce Cook has been a significant influence on this research project, lending time, insight and equipment to my experimental endeavors. I would also like to thank Jason Williams for listening and contributing ideas for this research project with infinite patience as well as teaching me many things about research and equipment.

I would also like to thank my family and friends for their patience and support throughout my graduate education. I am deeply indebted to my husband, Scott Beckman for his long hours listening to my frustrations and his expertise in $\text{\LaTeX}$. I would like to thank my dear friend Iman for her ability to focus my thoughts when everything around us was moving at tremendous speeds. I would not be here without the support and encouragement of my parents and other family members. I also would like to thank Tiffany, Neha, and Suruchi for their never ending cheers of encouragement.