Oxidation Resistance and Compressive Creep Behavior of Boron Doped Mo_5Si_3

Mitchell K. Meyer and Mufit Akinc

Ames Laboratory* and Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA

Matthew J. Kramer

Ames Laboratory*, Iowa State University, Ames, IA 50011, USA

ABSTRACT

Use of Mo_5Si_3 in high temperature applications is limited by oxidation induced catastrophic failure above 800°C. Oxidation resistance of Mo_5Si_3 is substantially improved from 800°-1300°C by the addition of boron. The oxidation rate at 1200°C was decreased by five orders of magnitude with less than 2 weight percent boron addition. The improvement in oxidation resistance of B doped Mo_5Si_3 is due to formation of a protective scale layer due to viscous flow. The compressive creep rate of B doped Mo_5Si_3 was measured at various temperature/stress levels and found to be similar to that of the undoped material. The creep rate of B doped Mo_5Si_3 was measured as $1.8 \times 10^{-7} \text{ s}^{-1}$ at 1242°C and 138 MPa. Creep tests were conducted at 140-180 MPa and 1220°-1320°C. Average creep activation energy and stress exponent in this range were found to be $E_a \approx 400 \text{ kJ/mol}$ and $n=4.3$ respectively.

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INTRODUCTION

For structural applications in harsh environments, a material should have adequate strength, creep resistance, and oxidation resistance. Intermetallic materials have received considerable attention for use as high temperature structural materials. Silicides may be especially well suited for such applications due to the potential for good oxidation resistance at high temperatures. MoSi_2 has been investigated over the last several decades for such applications (1,2). Although MoSi_2 has excellent oxidation resistance at temperatures as high as 1700°C , it has a high creep rate (3,4) above 1200°C , making it unsuitable as a high temperature load bearing material. Mo_5Si_3 shows lower creep rates than MoSi_2 (5) however the oxidation resistance has been found to be unacceptable. Oxidation of Mo_5Si_3 is characterized by a porous scale formation and active oxidation of molybdenum below about 1650°C , with a transition to passive oxidation at higher temperatures (6,7,8).

The objective of this study was to improve the oxidation resistance of Mo_5Si_3 while retaining high creep resistance. It was found that boron additions to the base silicide of less than 2 weight percent lowered the oxidation rate five orders of magnitude at 1200°C . Boron had only a small effect on creep resistance.

EXPERIMENTAL

Sample Preparation

Mo_5Si_3 and boron doped Mo_5Si_3 ($\text{B-Mo}_5\text{Si}_3$) were synthesized by arc melting of the elements under argon atmosphere. Arc melt buttons were ground to submicron size powders. Powders were consolidated using sintering, HIPping, or a combination of the two techniques. Procedural details are given elsewhere (9,10). The region of interest near Mo_5Si_3 on the 1600°C isotherm of the Mo-Si-B phase diagram is shown in Figure 1. The compositions of samples used in this study are given in Table I.

Table I - Compositions of Mo-Si-B intermetallics.

Specimen	Composition*		
	Mo	Si	B
A	82	16.1	1.24
B2	85.7	13.0	1.3
C	81.2	18.2	0.61
D	81.5	18.3	0.14
E	82.2	16.9	0.91
F	86.3	12.6	1.1
G	88.2	10.8	1.0

*All compositions analyzed by ICP-AES.
All analysis $\pm 3\text{wt}\%$ relative to analyzed element.

High Temperature Oxidation

Thermogravimetric oxidation experiments were used to observe transient oxidation behavior and to determine isothermal oxidation rates. Coupons were suspended from a sapphire wire in a vertical tube thermogravimetric analyzer (TGA). Specimen mass change and temperature were continuously recorded. Interrupted oxidation experiments were also conducted to observe scale formation as a function of temperature. Samples were characterized prior to and following oxidation for scale composition and

microstructure using XRD, SEM/EDS, and electron spectroscopy for chemical analysis (ESCA) techniques.

Creep Testing

Compressive creep experiments were carried out at constant stress under flowing argon using a feedback controlled electromechanical system to apply load. Experiments were conducted at temperatures of 1220°-1320°C and the stresses of 140 -180 MPa (20.3 -26.1 ksi). Creep specimens were held at constant stress and temperature until approximately 1% strain was measured, at which time temperature was increased 20°C, and another data point taken. Microstructures were characterized before and after creep testing by scanning electron microscopy (SEM) energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). Total strain on each sample was 5-7%. Creep behavior was found to be consistent with a simplified power law creep equation,

$$\dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q_a}{RT}\right) \quad (1)$$

Figure 1. Molybdenum rich area of Mo-Si-B phase diagram at 1600°C (11).

RESULTS AND DISCUSSION

Oxidation

Plots of oxidation induced mass change versus time for Mo_5Si_3 and B- Mo_5Si_3 (composition A) at 800°-1300°C are shown in Figure 2. These plots include the initial ramping up to temperature at 20°C/minute. On all compositions, there is an initial mass gain due to formation of MoO_3 and SiO_2 on the

silicide surface. As the oxidation temperature is ramped past 750°C, a rapid mass loss is observed due to volatilization of MoO₃. The volatilization of MoO₃ leaves a porous silica (or borosilicate) layer behind. This scale provides little in the way of a diffusion barrier for oxygen unless flow can occur to seal the pores and provide a passivating layer. Rate constants for oxidation of Mo₅Si₃ and B-Mo₅Si₃ are given in Table II.

Table II - Rate constants for the oxidation of Mo₅Si₃ based materials.

Temperature, °C	Kinetic model	Steady state* rate constant	Run time, hr.
Mo₅Si₃			
800	none	pest	35
1000	linear	-7.2x10 ⁻²	80
1100	linear	-2.9x10 ⁻¹	10
1200	linear	-1.3x10 ⁻³	3
B-Mo₅Si₃ (A)			
800	linear	-6.0x10 ⁻⁴	15-150
1000	linear	-4.4x10 ⁻⁵	410
1100	parabolic	+5.9x10 ⁻⁵	300
1300	parabolic	+2.8x10 ⁻⁴	115

*Rate constants given in units of mg cm⁻² hr⁻¹ for linear rates and mg² cm⁻⁴ hr⁻¹ for parabolic rates. Negative rate indicates mass loss.

Figure 2. Oxidation data for Mo₅Si₃ and composition A from 800°-1300°C.

Oxidation of Mo_5Si_3

Mo_5Si_3 oxidized isothermally at 800°C (Figure 2) shows oxidation behavior similar to the pest (12) commonly observed in low temperature oxidation of MoSi_2 . After 35 hours at 800°C a mass of loosely held yellow-green oxide powder remains, as shown in Figure 3(a). The oxidation rate at 1000°C is slow relative to that at 800°C, but much too fast for consideration as a useful high temperature oxidation resistant material. An SEM micrograph of a cross section of an oxidation coupon after 80 hours of oxidation at 1000°C is shown in Figure 3(b). The fracture cross section shows large transverse voids in the scale, with needle-like molybdenum oxide crystals growing into the voids. Oxidation at temperatures above 1000°C becomes very rapid, with the rate at 1100°C being 400 times faster than at 1000°C. An SEM image of a fracture cross section of the substrate after oxidation for 10 hours at 1100°C is shown in Figure 3(c). The oxidation coupon shows little silicide (bright phase) remaining. Oxidation coupons remain intact at 1100°-1200°C, in contrast to the pest oxidation observed at 800°C. X-ray diffraction shows strong peaks due to cristobalite, with no other phases present.

Oxidation of B- Mo_5Si_3

The addition of boron gives a significant increase in oxidation resistance. At 800°C no pesting behavior is observed, in contrast to the behavior of undoped Mo_5Si_3 . An SEM micrograph of the polished scale cross section after oxidation at 800°C is shown in Figure 3(d). The scale is glassy in appearance, nonporous, and about 7 μm thick. At 800°-1000°C slow mass loss occurs in the isothermal oxidation regime. A scale cross section after oxidation at 1000°C is shown in Figure 3(e). In contrast to undoped Mo_5Si_3 , no molybdenum oxide crystals form in the scale. Scale thickness is on the order of 8 μm . The scale shows no cracking or porosity. In the range 1050°-1300°C specimens show a slow mass gain at long times. The mass gain on oxidation at 1100°C is approximately 0.05 mg/cm^2 over fifty hours. XRD indicates that a molybdenum layer forms between the oxide scale and substrate, indicating that active oxidation of molybdenum is slow or not occurring. An SEM image of a polished scale cross section after oxidation at 1300°C is shown in Figure 3(f). An activation energy for oxidation of 134 kJ/mol was calculated for composition A in the range 1050°-1300°C. This value agrees well with previously measured activation energies for oxygen diffusion in borosilicate glass (13), and is also in the range of values measured for diffusion in vitreous silica (14).

Oxidation rate data at 1000°C for other Mo-Si-B compositions in Table I are given in Table III. An improvement in oxidation resistance is attained over a wide range of sample composition and microstructure. ESCA analysis indicates that the scale surface resembles borosilicate glass in chemical bonding, and that the B/Si ratio in the scale is proportional to the B/Si ratio in the substrate.

Table III - Steady state oxidation rates at 1000°C
for other compositions shown in Figure 1.

Composition	Steady state [*] rate, $\text{mg}/\text{cm}^2 \text{ hr}$
C	-3.34×10^{-3}
D	-3.63×10^{-3}
E	-1.9×10^{-3}
F ⁺	-5.0×10^{-3}
G	$+7.3 \times 10^{-4}$

^{*}linear rate: 20-100 hrs. ⁺30-100 hrs.

Figure 3. Oxide scale formation after time shown in Table II for Mo_5Si_3 at (a) 800°C, (b) 1000°C, (c) 1100°C, and 'A' at (d) 800°C, (e) 1000°C, (f) 1300°C.

Mass gain on oxidation, the formation of a molybdenum interlayer, and scale morphology indicate that oxygen diffusion through a coherent scale is the rate limiting step in the oxidation of boron modified Mo_5Si_3 at 1050°-1300°C. The growth of a coherent scale due to boron additions is attributed to formation of a low viscosity borosilicate glass which can flow to close pores that initially form in the scale. Similar behavior has been described by Fitzer (6) for germanium additions to MoSi_2 that prevent low temperature pest.

Creep

An SEM back scattered electron image (BSE) of a typical sintered creep sample (B2) is shown in Figure 4(a). Creep samples were synthesized with a three phase microstructure composed of tetragonal

Mo_3Si_3 (T1, dark phase), cubic Mo_3Si (bright phase), and tetragonal $\text{Mo}_3(\text{Si},\text{B})_3$ (T2, etched phase). The presence of these three phases was confirmed by x-ray and electron diffraction. Image analysis of the microstructure shows that the T1 matrix makes up 54% by area, while Mo_3Si and T2 are approximately equally represented in the remainder. Image analysis showed that sintered samples contained 2.2 percent porosity prior to creep.

Figure 4. Microstructure of creep sample (composition B2) (a) prior to creep, showing distribution of phases and porosity, and (b) after creep showing crack stopping due to Mo_3Si and T2 phases.

Creep rates for temperatures from 1220°-1320°C and loads of 138-180 MPa are plotted as a function of reciprocal temperature in Figure 5. Apparent activation energies obtained from a least squares fit to the data are also shown in Figure 5. These activation energies fall in the range 386-412 MPa. This indicates the same or similarly activated creep processes dominate the creep behavior throughout this regime. Also included in Figure 5 is the temperature dependence of the creep of undoped Mo_3Si_3 at 140 MPa. The creep rate of Mo_3Si_3 is slightly lower than that of B2 under the same deformation conditions. Activation energies are similar. Figure 6 shows calculated creep stress exponents for B2, along with errors associated with the calculation of the stress exponent. The average stress exponent for all conditions tested is 4.3. Stress exponents in this range often indicate creep by dislocation climb. Figure 4(b) shows the microstructure after 13.3% strain. At this strain, the sample shows extensive cracking of the T1 matrix, while the occurrence of cracks in the Mo_3Si and T2 phases is much lower. Cracks that extend through T1 grains stop at the boundaries with the other phases.

TEM images before and after 5.0% strain indicate that pore coalescence is occurring. Prior to deformation, nearly spherical pores 0.1-0.3 μm in size are distributed along grain boundaries. The post deformation pore size is 0.3-3 μm , with pores more often found at three grain junctions and as elongated voids between grains. The appearance of larger voids in the microstructure indicates that pullout of small grains has occurred during sample preparation.

No dislocations were observed in the Mo_3Si_3 matrix phase. TEM evidence for dislocation activity was found in the T2 phase. Based on stereographic analysis of line directions, extinction conditions, and unit cell geometry it is likely that $\{001\}\langle 010 \rangle$ and $\{001\}\langle 110 \rangle$ slip systems are operating. Mo_3Si exhibited a high density of dislocations after creep relative to the other phases present. TEM shows that the dislocation structure consisted of free dislocations and well defined subgrain boundaries. This

Figure 5. Arrhenius plot of the steady state rate constants for the creep of Mo_5Si_3 with and without boron additions. Filled symbols are B2, open symbols are Mo_5Si_3 .

Figure 6. Stress dependence of the creep rate for B2 from 1242°-1302°C.

indicates that polygonization is actively occurring in Mo_3Si at 5% strain, and is evidence for dislocation climb. Dislocation analysis indicates that $\{001\}\langle 100 \rangle$ slip is operative. The observed $\{001\}\langle 100 \rangle$ slip system for Mo_3Si is consistent with previous work on V_3Si (15).

At small strains ($\approx 5\%$), the rate determining deformation mechanism for the three phase B2 material appears to be plastic deformation due to dislocation motion within the Mo_3Si and/or T2 phases. The creep rate may be decreased below that of monolithic Mo_3Si or T2 by partitioning of stress onto the creep resistant Mo_5Si_3 phase. At larger strains ($\approx 13\%$) the T1 phase exhibits cracking, indicating that motion of T1 grains is not fully accommodated by plastic strain in Mo_3Si and T2. The fact that cracks nucleating in T1 did not propagate through T2 and Mo_3Si suggests that these phases exhibit resistance to crack growth at high temperatures.

SUMMARY

The oxidation behavior of Mo-Si-B compositions was studied using x-ray diffraction, thermogravimetric analysis, and microscopic observation of the scale layer. Initially, a mixed molybdenum and silicon oxide scale forms. At 750°C , molybdenum oxide volatilizes, leaving a porous scale. In the case of Mo_5Si_3 , the porous scale allows pest to occur on isothermal oxidation at 800°C . The scale provides provides marginal oxidation resistance at 1000°C , and virtually no protection at 1100°C and above. The addition of boron gave an improvement in oxidation resistance over a wide range of compositions. The improvement in oxidation resistance occurs due to the formation of a glassy scale of lower viscosity that sinters rapidly to close pores.

Creep tests indicate that the effect of boron on creep resistance is small. Specimens were deformed in compression at 1220°C - 1320°C and stresses of 140-180 MPa. The average activation energy for creep of B- Mo_5Si_3 in the temperature range 1240°C - 1320°C was ≈ 400 kJ/mol. No dislocations were observed in the T1 phase. Basal plane dislocations were observed in the T2 phase, and $\{001\}\langle 100 \rangle$ dislocations were observed in Mo_3Si . At small strains, the rate limiting deformation mechanism for the three phase (B2) material appears to be plastic deformation due to dislocation motion within the Mo_3Si and/or T2 phases. The creep rate may be decreased below that of Mo_3Si or T2 by partitioning of stress onto the creep resistant Mo_5Si_3 phase. After 13.3% deformation, microstructural cracking was observed in T1. These cracks did not propagate through Mo_3Si or T2, indicating that these phases stopped crack growth at high temperature.

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