

Mechanical behavior and interface design of MoSi₂-based alloys and composites

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Abstract

The mechanical behavior of hot pressed MoSi₂-based composites containing Mo₅Si₃, SiO₂, CaO and TiC as reinforcing second phases was investigated in the temperature regime 1000–1300 °C. The effects of strain rate on the flow stress for Mo₅Si₃-, SiO₂- and CaO-containing composites are presented. Effects of several processing routes and microstructural modifications on the mechanical behavior of MoSi₂-Mo₅Si₃ composites are given. Of these four composite additions, Mo₅Si₃ and CaO produce strengthening of MoSi₂ in the temperature range investigated. SiO₂ greatly reduces the strength, consistent with the formation of a glassy phase at interface and interphase boundaries. TiC reduces the flow stress of MoSi₂ in a manner that suggests dislocation pumping into the MoSi₂ matrix. The strain rate effects indicate that dislocation creep (glide and climb) processes operate over the temperature range investigated, with some contribution from diffusional processes at the higher temperatures and lower strain rates. Erbium is found to be very effective in refining the microstructures and in increasing the hardness and fracture properties of MoSi₂-Mo₅Si₃ eutectics prepared by arc melting. Initial results on microstructural modeling of the deformation and fracture of MoSi₂-based composites are also reported.

1. Introduction

There is increasing need for high-strength, oxidation-resistant materials for elevated temperature structural applications, particularly in aircraft gas turbines and spacecraft air frames. The silicides of refractory metals such as molybdenum, tungsten, niobium and tantalum have great potential as the matrix materials for new composites with service capabilities at temperatures above approximately 1200 °C. In particular, MoSi₂, which melts at 2030 °C, exhibits excellent high-temperature oxidation resistance because of the formation of a protective silica film and has already been used effectively as the major constituent in super kanthal (an MoSi₂-SiO₂ alloy) furnace windings for applications to temperatures as high as 1800 °C. The major problems in the use of MoSi₂ for load-bearing structural applications have been inadequate high temperature strength at significant applied stresses above 1200 °C and poor fracture toughness below the ductile-to-brittle transition temperature (DBTT) of approximately 1000 °C. Above 1000 °C, MoSi₂ yields plastically and deforms by dislocation motion similar to the behavior of metallic materials. The need for composite and alloy additions for strengthening at tem-

peratures above 1200 °C and for similar or alternative additions for toughening at lower temperatures has led to extensive investigation of MoSi₂ in the past few years [1].

The purpose of our research is to investigate promising composite approaches to obtain a more fundamental understanding of the mechanical behavior of MoSi₂ and MoSi₂-based composites at both ambient and elevated temperatures. In the present investigation, we report on the effects of several different single composite additions, including Mo₅Si₃, SiO₂, CaO and TiC, all in particulate form. Mo₅Si₃ was investigated as an elastically hard, strong, brittle second phase which can potentially strengthen MoSi₂ at high temperatures and impart low temperature toughness by crack deflection processes. SiO₂ was investigated in small part because of its use in the manufacture of super kanthal, but more importantly because of the role of silica as an interface and interphase contaminant during the processing of MoSi₂ and MoSi₂-based composites, which leads to extensive boundary sliding at elevated temperatures. Both of these additions have lower coefficients of thermal expansion (CTE) than MoSi₂ (see Table 1) and thus are capable of generating tensile residual stresses in the hoop direction in the matrix after fabrication and cooling to room temperature. Residual stresses in the radial direction are compressive in nature and are benign from the standpoint of crack generation. CaO

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TABLE 1. Coefficients of thermal expansion (CTE) and melting temperatures T_m for MoSi₂ and several potential particulate additions

Material	CTE (°C ⁻¹) @ 1000 °C	T_m (°C)
MoSi ₂	8.5×10^{-6}	2030
TiC	7.7×10^{-6}	3250
Mo ₅ Si ₃	6.7×10^{-6} (@ 500 °C)	2180
HfC	6.25×10^{-6}	3890
HfB ₂	5.5×10^{-6}	3250
SiO ₂ (vitreous)	0.55×10^{-6}	1710
CaO	13.1×10^{-6}	2570
MgO	15.7×10^{-6}	2800
Ce ₂ O	14×10^{-6}	2600

was examined as a more stable addition that might reduce boundary sliding. The CTE of CaO is large compared with that of MoSi₂, which allows analysis of effects of thermally induced residual stresses. TiC, with a melting temperature above 3000 °C, offers the unique prospect of having higher strength than MoSi₂ at low temperatures but comparable or somewhat lower strength and higher plasticity at temperatures near and above the DBTT. The CTE of TiC is approximately the same as that of MoSi₂. These results serve as experimental data with which we can compare parallel attempts to model the deformation and fracture behavior of composite microstructures and to develop methods by which the controlling microstructural parameters and physical properties can be optimized. An initial report of these modeling methods and their results is included.

2. Experimental details

2.1. Fabrication of materials

MoSi₂. For most experiments, the monolithic MoSi₂ was prepared from as-received powders screened to -325 mesh obtained from Cerac, Incorporated. The powders were hot pressed at 1700 °C under 25–30 MPa pressure for 1–2 h in grafoil-lined graphite dies and an argon atmosphere. The typical grain size (d) of MoSi₂ after such treatment was 30 μm. The processing schedule for MoSi₂ was always identical with that used for the MoSi₂-based composite being compared. In some selected experiments on MoSi₂-Mo₅Si₃ eutectics, the monolithic material and eutectics of various volume fractions of Mo₅Si₃ were prepared by arc melting under an argon atmosphere. The densities of the hot-pressed MoSi₂ specimens were in the range 94%–96%. Porosity in arc-melted MoSi₂ was larger and depended on the exact solidification conditions. Densities ranged from 70%–85%. In some experiments, post-solidifi-

cation hot isostatic pressing was used to reduce the range and total amount of porosity observed in arc-melted materials.

MoSi₂-Mo₅Si₃ composites. Most of the MoSi₂-based composites containing Mo₅Si₃ in the range 15–30 vol.% were made by slurry milling mixtures of the MoSi₂ matrix and molybdenum reinforcement powders (-325 mesh) for periods of at least 24 h. The mixtures were hot pressed at 1700 °C at 25 MPa for 2 h. This treatment was sufficient to form the MoSi₂-Mo₅Si₃ eutectic mixture in the equilibrium proportions of 15%–30% expected from the phase diagram. In some experiments, the eutectic mixtures were prepared by arc melting MoSi₂ and molybdenum powders followed either by hot pressing or hot isostatic pressing. These were done at 1700 °C at 25–28 MPa for 1.5–2 h. Some arc-melted eutectics were also crushed to produce powder and subsequently hot pressed to produce materials with potentially less silica at interface or interphase boundaries. Erbium was added to some arc-melted eutectics as a potential microstructural refiner and as an additional means of removing oxygen from the melt in experiments based on solidification methods.

MoSi₂-SiO₂ composites. These composites which contained approximately 15 vol.% silica were obtained as a commercial super kanthal. The composites were typically 94% dense.

MoSi₂-CaO composites. The MoSi₂-CaO composites were made by ball milling CaO and MoSi₂ powders of -325 mesh for 24 h and then hot pressing the mixtures at 1700 °C at 25 MPa pressure for 2 h. The CaO powder was obtained from Johnson Matthey, Incorporated. The hot-pressed composites of 20 vol.% CaO were 95% dense.

MoSi₂-TiC composites. MoSi₂-10vol.%TiC composites were prepared by dry blending in a ball mill for 20 h prior to hot pressing at 1700 °C at 30 MPa for 1 h. The TiC was obtained from Johnson Matthey, Incorporated as 2.5–4 μm size powder with the stoichiometry of TiC_{0.95}. The hot-pressed composite was approximately 95% dense. The TiC particles were well distributed through the matrix, but because of agglomeration the final particle sizes varied from 5 to 60 μm, with a mean value of 10 μm.

2.2. Microstructural characterization

Monolithic and composite microstructures were examined by light optical, scanning and transmission electron microscopies (SEM and TEM). Optical and SEM methods were used to assess grain and second-

phase structure, shape and distribution before and after deformation. TEM was used to characterize the composite substructures in more detail, including analysis of dislocation substructures and phase boundary structures by high-resolution TEM (HRTEM). Conventional TEM studies were done on a JEOL 2000FX microscope, while HRTEM observations were done on a JEOL 4000EX microscope.

2.3. Mechanical properties

Microhardness indentation techniques were used to evaluate the temperature dependence of the strength of monolithic MoSi₂ and the several composites investigated, as well as the behavior of some of the composite additions. Hot hardness testing was done at temperatures of 25–1300 °C with a Nikon QM-2 hot hardness tester. Diamond Vickers indentations at a load of 1 kgf (9.8 N) were used in most experiments.

Most mechanical testing was done in compression at a constant crosshead speed corresponding to an initial strain rate of 10^{-4} s^{-1} on specimens of dimensions $6 \times 3 \times 3 \text{ mm}^3$. All tests were done in air at temperatures up to 1300 °C. Yttria was used as a platen lubricant to minimize friction. Step-strain rate experiments at 10^{-6} – 10^{-3} s^{-1} were also performed on most composites at several temperatures in the range 1000–1300 °C to determine stress exponents and activation energies for deformation. Most specimens were cut from the hot-pressed compacts or arc-melted and/or hot isostatically pressed ingots using a diamond saw. Compression samples of MoSi₂-SiO₂ alloys were cut from 3 mm diameter super kanthal heating elements.

3. Results and discussion

3.1. MoSi₂

The monolithic MoSi₂ prepared by hot pressing exhibited microstructures and mechanical properties similar to those reported previously by other investigators [1, 2]. The typical microstructure of the as-processed material is given in Fig. 1. Regular equiaxed grain sizes of 25–35 μm and densities of $95 \pm 1\%$ with mainly fine dispersed porosity in the range of a few to several micrometers in diameter were observed. Deformation had little or no effect on the microstructure given in Fig. 1 except at the higher temperatures and lowest strain rates examined, where dynamic grain growth occurred during mechanical testing. Dislocation substructures and dislocation types were much the same as those reported by Umakoshi *et al.* [3] and Unal *et al.* [4]. Specifically, dislocations with Burgers vectors $\langle 100 \rangle$, $\langle 110 \rangle$ and $\frac{1}{2}\langle 111 \rangle$ were observed in specimens deformed at 1300 °C. At 900 °C $\frac{1}{2}\langle 331 \rangle$ dislocations were found [5].

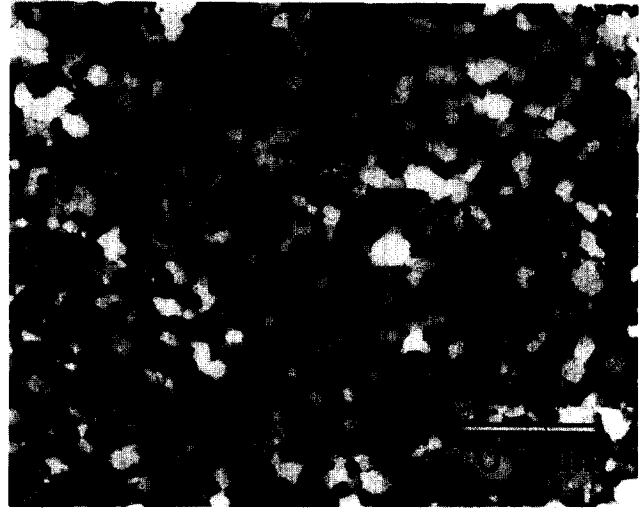


Fig. 1. Grain structure in polarized light of as-hot-pressed MoSi₂, hot pressed at 1700 °C for 1 h under 29.4 MPa. The average grain size is 30 μm .

The mechanical properties of the monolithic MoSi₂ and the various MoSi₂-based composites are given in Figs. 2–7. The results are presented in the form of compressive flow stress–strain rate data obtained from step-strain rate experiments (Figs. 2–4), selected elevated temperature compressive stress–strain curves (Fig. 5), and hot hardness data for the MoSi₂ and selected reinforcements and composites (Figs. 6 and 7). At 1200 °C, the compressive flow stress of MoSi₂ ranges from about 300–340 MPa at a strain rate $\dot{\epsilon}$ of 10^{-4} s^{-1} to about 75 MPa at $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$. The corresponding stress exponent n varies from 5 to 2–2.5 over the same range of strain rates. At 1100 °C, the compressive flow stress is about 420 MPa at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and falls to 160 MPa at $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$. The stress exponent changes from about 8 to 3 over this same range of strain rates [6]. The implication is that dislocation creep, with both glide and climb contributions, dominates at these temperatures and strain rates. Glide processes dominate at the lower temperatures and higher strain rates, and diffusional creep may contribute in addition to climb at the higher temperatures and lower strain rates.

In the stress–strain curves of Fig. 5, MoSi₂ exhibits significant apparent work hardening, but we have not yet unambiguously sorted out the relative contributions of plastic flow and cracking in these materials as a function of strain. The temperature dependence of the hardness of MoSi₂ up to 1300 °C given in Fig. 6 is much more gradual than that typically reported for the yield strength, probably because microhardness does not sample a sufficient volume of material to be affected as much by the rapidly decreasing viscosity of the glassy silica grain boundary phase with increasing

temperature to the same extent as uniaxial compression or bend tests of bulk materials. The typical indentation width along the major axis at 1 kgf is 50–80 μm over the temperature range 25–1300 °C compared with the typical grain size of 30 μm.

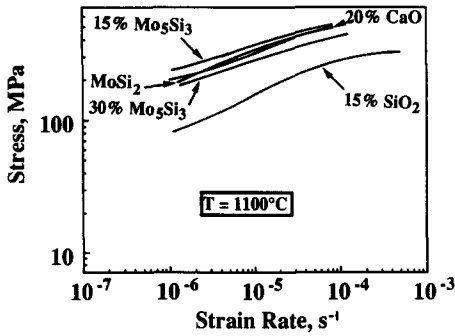


Fig. 2. Flow stress as a function of strain rate as determined from decremental step-strain rate test in compression conducted on MoSi₂-based composites at 1100 °C.

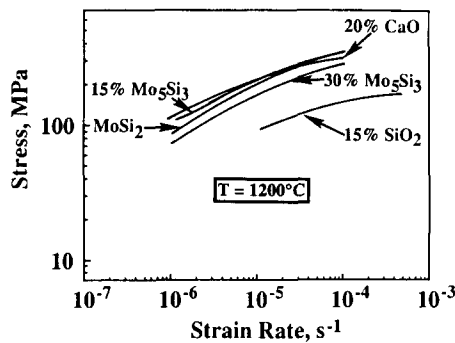


Fig. 3. Flow stress as a function of strain rate as determined from decremental step-strain rate test in compression conducted on MoSi₂-based composites at 1200 °C.

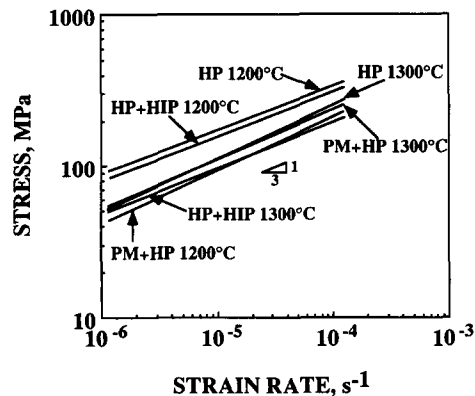


Fig. 4. Compressive stress vs. strain rate test results for MoSi₂-45vol.%Mo₅Si₃ samples processed by hot pressing arc-melted buttons (HP), hot-pressed and hot isostatically pressed arc-melted buttons (HP + HIP) and arc-melted buttons which were crushed to produce powder and subsequently hot pressed (PM + HP). Note that the stress exponent is approximately 3 for all processing paths at 1200 °C and 1300 °C.

3.2. MoSi₂-Mo₅Si₃ composites

The microstructure of the hot-pressed MoSi₂-Mo₅Si₃ particulate composites is typified by the micrographs for the 30 vol.% composite given in Fig. 8. The MoSi₂ matrix in the as-processed state maintains the

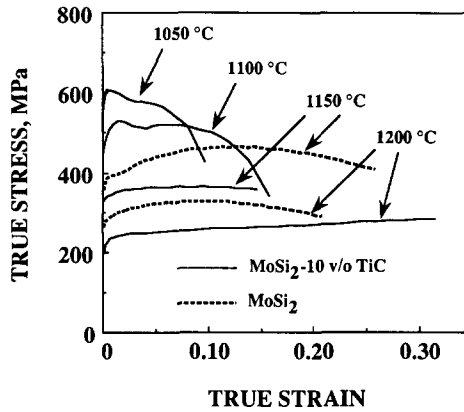


Fig. 5. True stress vs. true strain in compression for MoSi₂ and MoSi₂-10vol.%TiC. The initial strain rate in the constant cross-head speed tests is 10⁻⁴ s⁻¹.

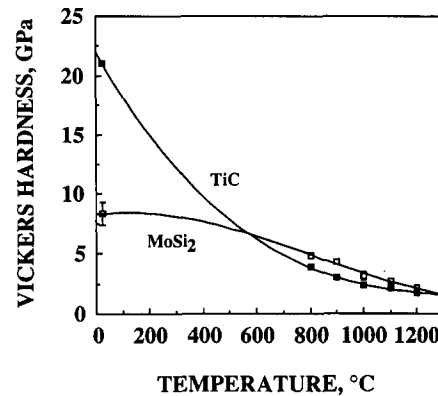


Fig. 6. Vickers hardness vs. temperature for MoSi₂ and TiC tested as separate specimens.

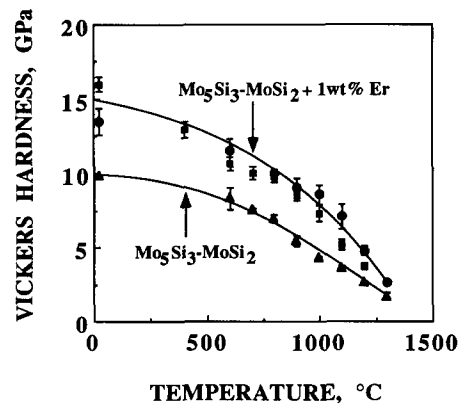


Fig. 7. Hot hardness tests of the erbium-modified and untreated eutectic alloys. Results show an increased hardness for erbium-modified alloys.

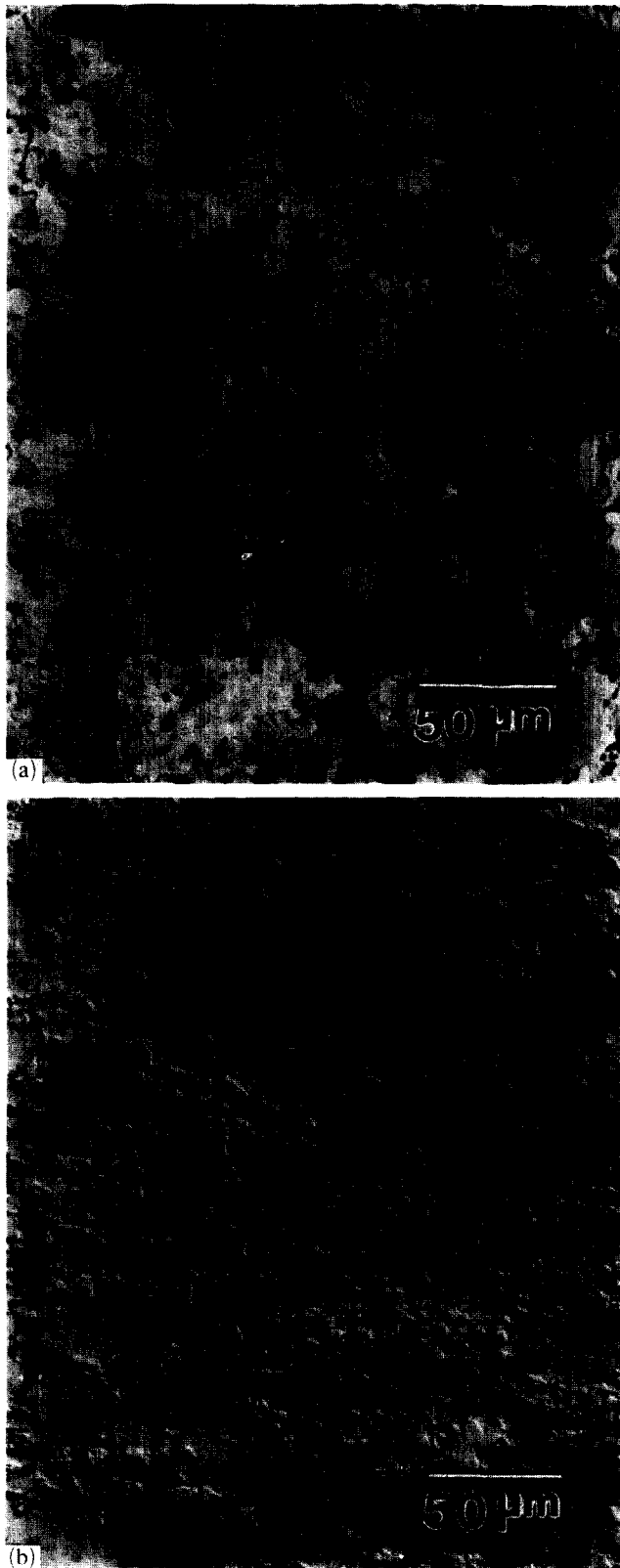


Fig. 8. Microstructures of the MoSi₂-30vol.%Mo₅Si₃ composite (a) before and (b) after deformation at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and $T = 1200^\circ\text{C}$. Dynamic grain refinement of the matrix in the vicinity of Mo₅Si₃ is observed in (b) (phase identification, A MoSi₂, B Mo₅Si₃): (a) $\epsilon = 0$, $d = 29 \mu\text{m}$; (b) $\epsilon = 0.81$, $d = 25 \mu\text{m}$ and $d = 7.5 \mu\text{m}$.

same $30 \mu\text{m}$ grain size and equiaxed shape given for the monolithic material in Fig. 1. The Mo₅Si₃ exists in relatively large regions and is irregularly distributed in the matrix. Upon deformation at 1200°C and $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$, the Mo₅Si₃ breaks up into much smaller particles, and the MoSi₂ matrix nearest these particles has developed into a grain structure of about $8 \mu\text{m}$ in average grain size. This microstructure constitutes about two thirds of the total area fraction. The remainder of the matrix microstructure consists of larger, slightly elongated grains of MoSi₂ with an average intercept of $25 \mu\text{m}$.

The mechanical behavior of the hot-pressed MoSi₂-Mo₅Si₃ particulate composites at 1100°C and 1200°C is given in Figs. 2 and 3 respectively, along with data for other hot-pressed particulate composites. The compressive yield stress decreases with a decrease in strain rate and an increase in temperature for all composites. The addition of 15 vol.% Mo₅Si₃ increases the strength of MoSi₂ at all strain rates, but increasing the volume fraction of Mo₅Si₃ to 30% decreases the strength to values below that observed for the monolithic material over all strain rates and temperatures investigated. The strengthening of MoSi₂ by 15 vol.% is less at 1200°C than at 1100°C , but it is still significant at the lower strain rates.

Although the strength of Mo₅Si₃ is greater than that of MoSi₂, the expected strengthening in these composites due to Mo₅Si₃ is not observed. The most probable explanation lies in the dynamic grain refinement, illustrated in part in Fig. 8, which increases with increasing strain and is especially large for the 30% Mo₅Si₃ composite. The presence of smaller grains enhances the rate of dislocation climb and other diffusional creep processes and can produce both the small strengthening effect observed for the 15% Mo₅Si₃ composite and the reduced strength of the 30% Mo₅Si₃ composite. The values of the stress exponent n obtained from Figs. 2 and 3 are consistent with this explanation. The stress exponent for the 15% Mo₅Si₃ composite at 1200°C falls from about 11 at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ to 2.5 at $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$. At 1100°C , n falls from about 8 to 5-6 over the same range of strain rates. At 1000°C , n was in the range 18-11 over these same strain rates. However, n was much smaller for the 30% Mo₅Si₃ composites: 5-2.5 for $\dot{\epsilon} = 10^{-4}$ to 10^{-6} s^{-1} at 1200°C and 6-5 for $\dot{\epsilon} = 10^{-4}$ to 10^{-6} s^{-1} at 1100°C [6]. Thus, the overall small values of n , the low flow stresses, and the very substantial dynamic grain refinement of the 30% Mo₅Si₃ composite suggest that the strength of the MoSi₂-Mo₅Si₃ composites is controlled by grain size effects over a wide range of temperatures and strain rates and is not influenced significantly by other softening processes. The significant strengthening at the lower strain rates for the 15% Mo₅Si₃ composite is

probably associated with the breakdown of the larger particles during deformation. The smaller particles then act to hinder dislocation motion in the manner expected for small particle dispersion strengthening at elevated temperatures.

Similar investigations on MoSi_2 - Mo_5Si_3 composites were carried out on arc-melted materials with microstructures of the type illustrated in Fig. 9. These materials are near the eutectic composition and contain Mo_5Si_3 as a script microstructure, which can be substantially refined by the addition of small amounts (1 wt.%) of erbium. Microalloying with erbium was also investigated as a means of reducing the oxygen concentration in the eutectic material by acting as a gettering agent and removing oxygen from the melt. The presence of rare-earth oxides may also contribute to the creep strength of the eutectic microstructure. The microstructure of Fig. 9 illustrates two effects of erbium additions: the scale of the script microstructure is reduced and the occurrence of pro-eutectic MoSi_2 is greatly diminished. Erbium-rich particles are present in the observed microstructures as inclusions associated with the Mo_5Si_3 phase (B in Fig. 9). Microprobe analysis reveals that these particles are rich in oxygen compared with either silicide phase. The volume fraction of Mo_5Si_3 is larger than that obtained in hot-pressed MoSi_2 - Mo_5Si_3 composites of Figs. 2, 3 and 8, of order 45% for the materials illustrated in Fig. 9.

Mechanical behavior data for the arc-melted MoSi_2 - Mo_5Si_3 composites are given in Figs. 4 and 7. Figure 4 gives compressive flow stress-strain rate results similar to those presented for the hot-pressed particulate composites in Figs. 2 and 3. Data at 1200 °C and 1300 °C are presented for arc-melted alloys which were processed by hot pressing (HP), by hot pressing and hot isostatic pressing (HP + HIP), and by crushing to produce powder and subsequent hot pressing (PM + HP). There is no systematic difference in the strength effected by these three processing routes in the results obtained at 1300 °C. At 1200 °C, the HP and HP + HIP materials are consistently stronger than the PM + HP composites. All three sets of materials appear to be characterized by a stress exponent of approximately 3 at both temperatures, consistent with many of those obtained for the hot-pressed particulate materials of Figs. 2 and 3. The strengths appear to be somewhat lower than the hot-pressed particulate materials in Figs. 2 and 3, but consistent with possible effects of the larger volume fraction of Mo_5Si_3 . We have not yet compared detailed MoSi_2 matrix microstructures and properties between the hot-pressed and arc-melted materials as a source of these strength differences.

The effects of erbium modification on the mechanical properties of the arc-melted eutectic composite

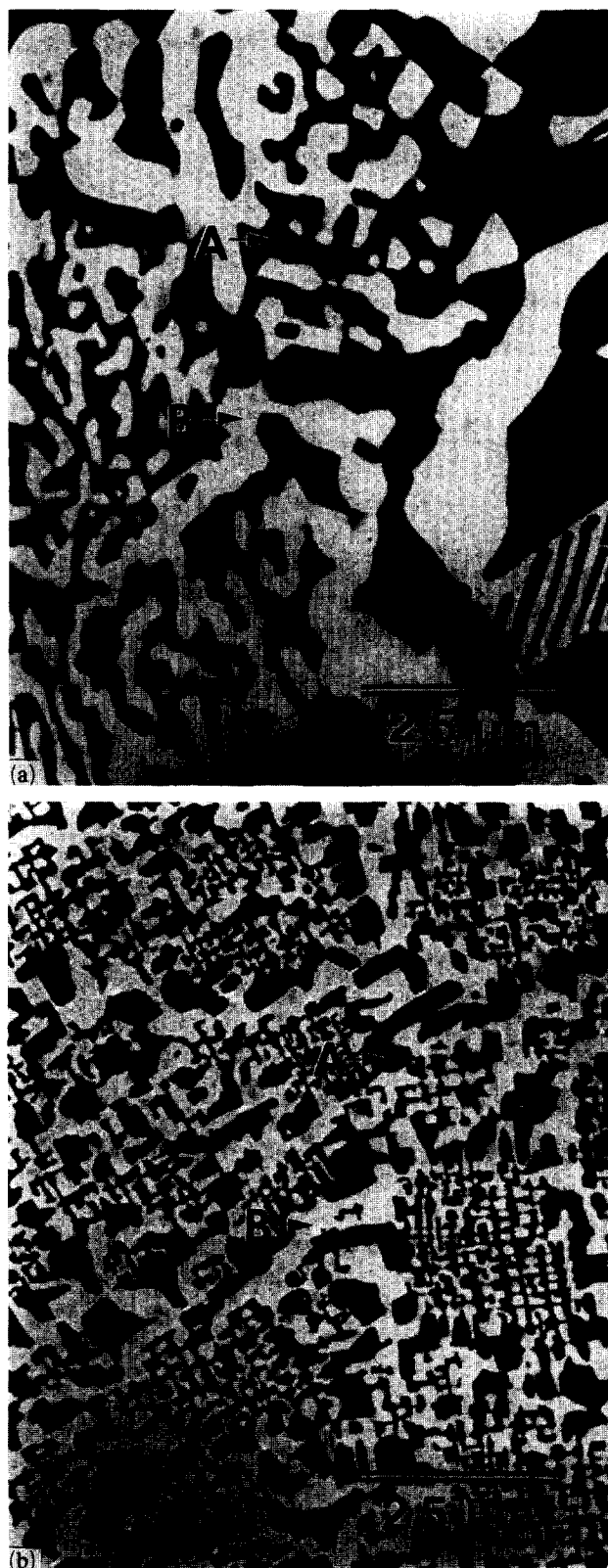


Fig. 9. Backscattering electron micrographs of the MoSi_2 - Mo_5Si_3 eutectic: (a) a typical arc-cast eutectic alloy; (b) a 1 wt.% Er modified eutectic alloy. Note the microstructural refinement with the addition of erbium. An erbium-rich phase appears as bright particles within the Mo_5Si_3 phase (phase identification, A MoSi_2 , B Mo_5Si_3).

were examined by hot hardness testing methods, as illustrated in Fig. 7. The erbium-treated material was found to have a substantially higher hardness at all temperatures from 25 °C to 1300 °C. This increase in hardness is probably due to the increased constraint placed on the MoSi₂ matrix by the Mo₅Si₃ as the microstructure becomes more refined. At high temperatures, the increased constraint has its origin in the reduced mean free path of dislocations in the MoSi₂ phase effected by the finer two-phase microstructure. At low temperatures, crack deflection processes are more effective in the finer microstructure. There may also be a residual solid solution strengthening effect and additional strengthening associated with the erbium-based oxide particles present in the Mo₅Si₃ phase. These effects will be sorted out in future experiments.

The microstructural refinement resulting from the addition of erbium most likely occurs from a decrease in the interfacial surface energy and a subsequent change in the solidification mechanism. Similar results have been observed in rare-earth-modified Al-Si eutectics [7]. We speculate at this point that the microstructural refinement results from oxygen gettering by erbium and that removal of these interstitials may improve the fracture characteristics of such MoSi₂-Mo₅Si₃ composite microstructures. Our initial studies to investigate the fracture characteristics have been limited to use of room temperature hardness indentations to observe the extent of cracking and the resulting crack paths in erbium-modified and untreated eutectic alloys. We have found that the crack path is deflected around the finer Mo₅Si₃ particles of the erbium-modified alloys and that these alloys are not as extensively cracked as the untreated alloys. Thus, it may be possible to improve the fracture toughness by microstructural refinement, but we have not yet shown that such improvement is a direct result of microalloying.

3.3. MoSi₂-SiO₂ composites

The microstructure of the super kanthal used in this study is shown in Fig. 10. It consists of 1–20 μm discrete particles of SiO₂ located at the grain boundaries of the MoSi₂ matrix which has an average grain size of about 30 μm. During deformation at 1100–1200 °C, the soft SiO₂ is squeezed along and between the grain boundaries of the matrix, as illustrated by arrows in Fig. 10(b). The effect on the mechanical properties is very large. In Figs. 2 and 3, the strength of the MoSi₂-SiO₂ composite at 1100 °C and 1200 °C respectively, is well below that of any other composite and the monolithic material. The stress exponent is in the range 2.5–5 at all strain rates investigated at both temperatures and does not change much as a function of strain rate.

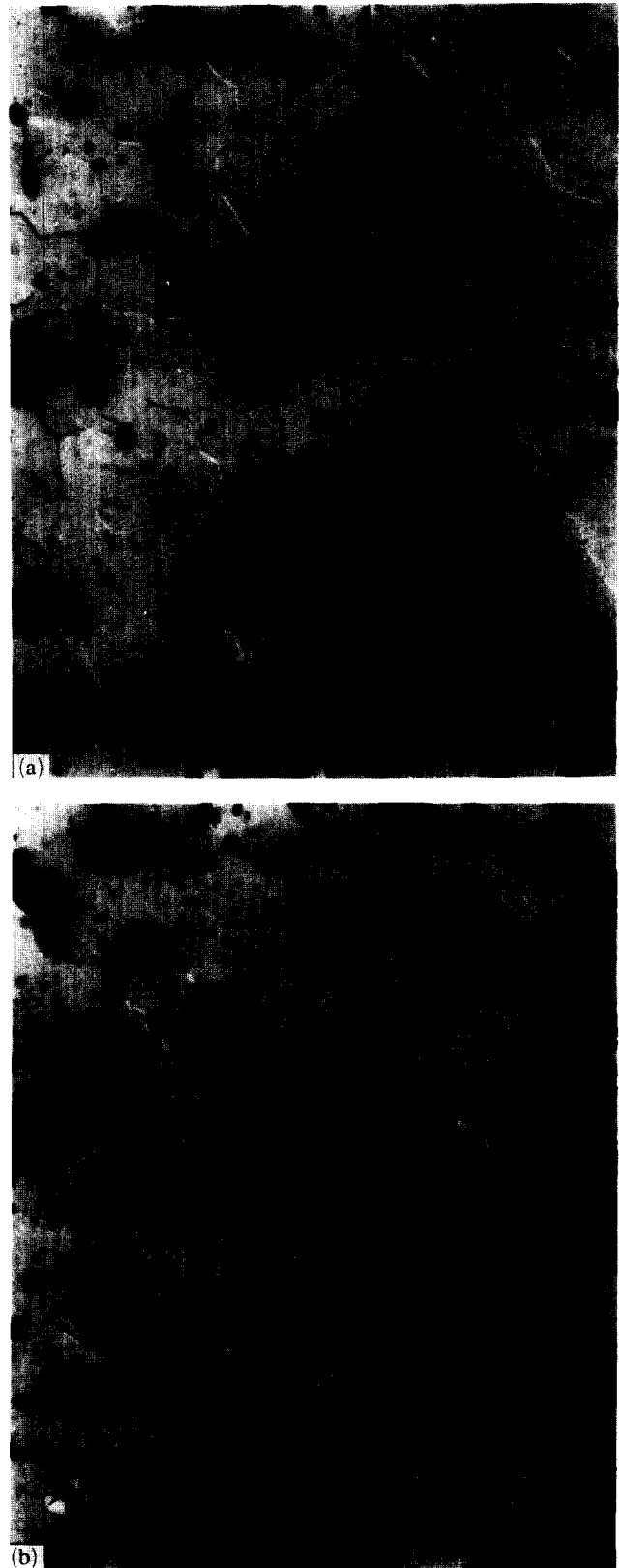


Fig. 10. Microstructures of the MoSi₂-15vol.%SiO₂ composite (a) before and (b) after deformation at $\dot{\epsilon} = 10^{-4} \text{ s}^{-1}$ and $T = 1200 \text{ °C}$. The SiO₂ is the dark phase. Intrusion of the SiO₂ phase into the MoSi₂ grain boundaries is observed in (b), e.g. at the arrows. (a) $\epsilon = 0$, $d = 20 \text{ }\mu\text{m}$; (b) $\epsilon = 0.69$, $d = 18.5 \text{ }\mu\text{m}$.

The significant weakening caused by intentionally added SiO₂ to MoSi₂ is associated with its penetration of the matrix grain boundaries illustrated in Fig. 10. SiO₂ at the grain boundaries acts as a shearable film at the higher temperatures, which eases the sliding of matrix grains. This probably accounts for the MoSi₂ grains remaining equiaxed, even after substantial straining at 1200 °C. The present results on silica-containing MoSi₂ illustrate dramatically the importance of minimizing silica as a grain boundary and phase boundary contaminant during the processing of advanced MoSi₂-based composites for applications at temperatures above 1100–1200 °C [8].

3.4. MoSi₂-CaO composites

The microstructure of hot-pressed MoSi₂ reinforced with 20 vol.% CaO consists of equiaxed grains of MoSi₂ about 23–35 μm in size with smaller 1–15 μm CaO particles distributed regularly throughout the matrix, but primarily along the MoSi₂ grain boundaries. On deformation, severe deterioration of the particulate microstructure is observed. The matrix grains deform substantially and become slightly smaller and elongated with an aspect ratio of 1.5–2. These observations are illustrated in Fig. 11.

The results of mechanical tests for the MoSi₂-CaO composites in Figs. 2 and 3 do not disclose negative effects on the strength of MoSi₂ as does SiO₂. In fact, over much of the temperature and strain rate ranges investigated, there is a slight improvement in strength. The high CTE value of CaO compared with MoSi₂ is expected to lead to separation of the CaO particles from the matrix and grain boundary separation of the matrix, since the calcia is present primarily as a grain boundary phase. The general effect of CaO in both Figs. 2 and 3 appears to be modest strengthening associated with retardation of grain boundary sliding. The values of the stress exponent for the MoSi₂-CaO composite were obtained from Figs. 2 and 3 in the range 2–5 at both temperatures (except for the largest strain rates examined at 1100 °C, where *n* increases with increasing strain rate) [6] and are consistent with such analysis.

3.5. MoSi₂-TiC composites

TiC has potential as a toughening phase for MoSi₂ in the temperature regime near and above the DBTT of about 1000–1300 °C. As a monolithic material, TiC flows plastically to significant strains at these temperatures and has a relatively low DBTT of about 600 °C [9]. The plasticity can be further enhanced by decreasing the carbon content below the stoichiometry TiC_{0.97}. The density of TiC is relatively low (4.93 g cm⁻³), and the CTE is nearly the same as that for MoSi₂. Moreover, observations to date on MoSi₂-TiC composites

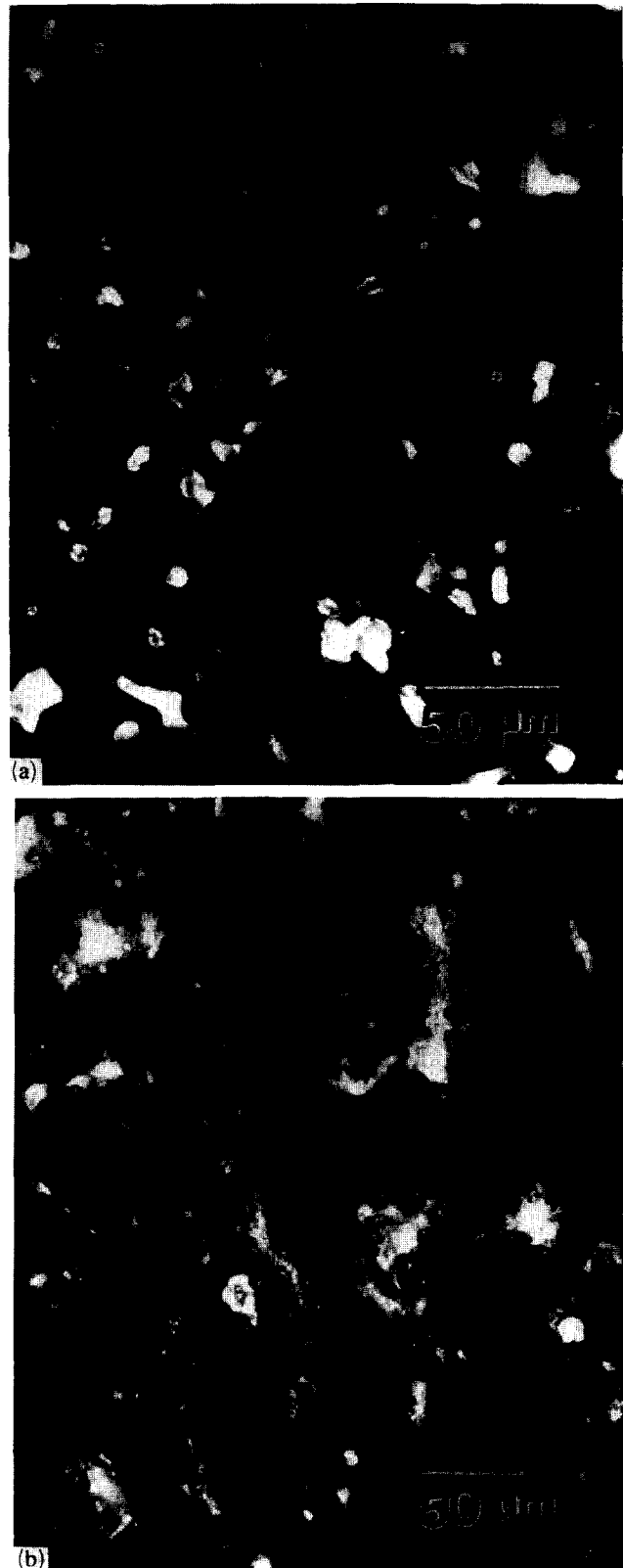


Fig. 11. Microstructures of the MoSi₂-20vol.%CaO composite (a) before and (b) after deformation at $\epsilon = 10^{-4} \text{ s}^{-1}$ and $T = 1200 \text{ °C}$. The CaO particles are the smaller, usually white phase in (a). Extensive plastic deformation of the MoSi₂ grains and fracture of CaO particles are observed in (b). (a) $\epsilon = 0$, $d = 29 \text{ μm}$; (b) $\epsilon = 0.69$, $d = 18 \text{ μm}$.

hot pressed at up to 1700 °C or heat treated extensively at 1600 °C (e.g. 100 h [10]) have not revealed any reaction layers or other forms of interphase instability. Our current studies have confirmed such findings for the as-processed composite, as well as after subsequent deformation at temperatures in the range 1100–1200 °C.

Figure 12 gives a representative microstructure of the as-processed composite microstructure. TiC appears as the darker phase. The interface remains intact during deformation at 1100–1200 °C, perhaps in part because a Kurdjumov–Sachs-like orientation relationship can exist between the MoSi₂ C11_b structure and the TiC NaCl type (f.c.c.) structure. This is similar to strong interfaces observed in simpler systems such as b.c.c.–f.c.c. metallic interfaces or B₂– γ or B₂– γ' interfaces in intermetallic systems [11].

The data given in Fig. 6 illustrate the relative changes in hardness of MoSi₂ and TiC as a function of temperature. TiC is much harder than MoSi₂ at room temperature, but softens much more rapidly with increasing temperature. In the temperature range 800–1300 °C, TiC is softer and exhibits more plasticity than MoSi₂. Because of the higher melting temperature of TiC and perhaps because of the effects of silica-induced boundary sliding of most monolithic MoSi₂ materials made to date, TiC becomes harder than MoSi₂ at temperatures above 1300 °C.

Compression test results on the MoSi₂–TiC composites over the temperature range 1050–1200 °C are given in Fig. 5 and are compared with similar results for the monolithic MoSi₂ at two temperatures, 1150 °C and 1200 °C. The composite exhibits lower flow stresses than the monolithic material at both temperatures. At 1200 °C, the composite also exhibits greater

apparent plasticity in compression. No visible cracking was noted during deformation of both materials tested at 1200 °C. At lower temperatures, all specimens exhibited cracking during deformation, and the cracking became more severe as the temperature was decreased toward 1000 °C.

These results suggest that TiC might toughen MoSi₂ at these temperatures near the DBTT of MoSi₂. A possible mechanism of toughening could involve dislocation generation into the matrix phase afforded by second-phase plasticity and a favorable orientation relationship for effective slip transfer or other dislocation generation processes into the matrix. Such a mechanism has been shown to be operative in Ni–Fe–Al two-phase β –($\gamma + \gamma'$) alloys [11]. The lower relative hardness of TiC might also produce toughening by second-phase crack bridging, but at this time we have no clear evidence for the operation of any specific mechanism. Greater softening and/or toughening of the matrix may be possible through variation of the carbide volume fraction and the particle size, distribution and morphology. Additionally, improvement in processing methods to produce cleaner matrix microstructures should also allow optimization of the TiC-induced softening of MoSi₂ presented here in preliminary form.

3.6. Microstructural modeling

We are currently attempting to model the microstructural effects observed experimentally in Figs. 1–12 so that the important microstructural factors and physical properties that affect deformation and fracture in composites can be determined. The modeling effort also allows development of analytical methods by which the interplay of these factors can be optimized. A simple spring model description of the matrix, fiber or particle, and interface mechanics is used. Such a model allows incorporation of a wide range of microstructural features and properties into a fracture simulation experiment. The basic first-order model consists of a two-dimensional array of linear elastic springs. These springs behave linearly until they are stretched beyond a critical extension and then they break irreversibly. Microstructure can be incorporated by ascribing a different modulus (spring constant), internal stress (equilibrium spring length), and fracture energy (critical extension) to each element of microstructure. The computational approach involves applying a strain to the model microstructure, relaxing the total energy of the system, determining the maximum bond energies, finding which bonds break, and then repeating the procedure as the crack propagates.

The first-order model applies well to systems that are linear elastic and perfectly brittle, such as all four of the composite systems examined experimentally in this

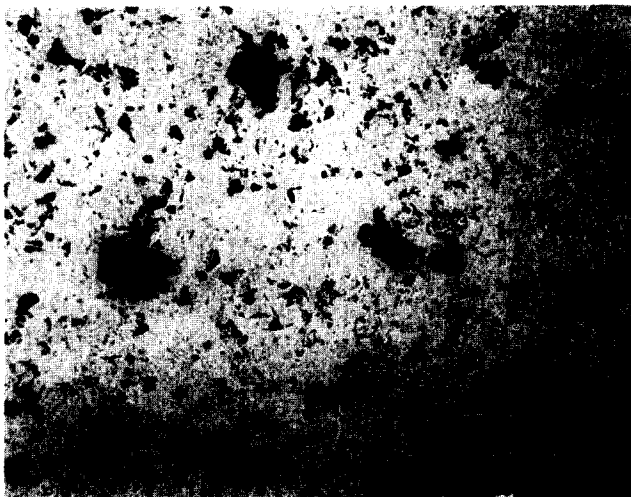


Fig. 12. Microstructures of the MoSi₂–10vol.%TiC composite hot pressed at 1700 °C. The TiC is the dark phase.

paper, when they are tested at low temperatures, below the DBTT. We have applied this model to low-temperature effects of grain boundary strength on the transition between intergranular and transgranular fracture and to low-temperature fracture of script microstructures in eutectics such as those shown in Fig. 9. The results of the simulations give very good agreement with experimental results and will be reported in detail elsewhere. Such simulations allow us not only to determine values of the input parameters to obtain best agreement with experimental observations, but also to make subsequent predictions for modifying microstructural and interface properties to achieve the optimal fracture properties for these systems.

Unfortunately, many of the major problems associated with improvement of the mechanical properties of MoSi₂-based materials involve achievement of plastic flow in one or more microstructural element of the composite. Thus, for example, ductile-phase toughening by molybdenum or niobium in MoSi₂ is attempted for improvement of properties at low temperatures, and the plasticity of MoSi₂ and other phases (such as TiC from our current results) must be accounted for in understanding elevated temperature properties. In the present paper, we describe the results of first attempts to incorporate small-scale plasticity into the elastic mechanics model based on the two-dimensional network of springs. The extended model is initially applied to two simple microstructures—random distributions of ductile particles (molybdenum) in a brittle matrix (MoSi₂) and laminates or lamellar microstructures of a wide brittle layer (MoSi₂) and narrow ductile layers (molybdenum). Subsequent work will utilize input parameters more directly applicable to the Mo₅Si₃, SiO₂, CaO- and TiC-containing composites investigated experimentally in this paper. However, it should be noted that even for the computationally simple Mo–MoSi₂ system, the constitutive behavior (the strain to failure) for molybdenum in the simple geometries simulated is not known. Thus, it is necessary to assume a particular plasticity behavior. Even so, the initial results are encouraging.

We accomplish incorporation of small-scale plasticity into the first-order model by prescribing a non-linear force-displacement relationship for each spring. This procedure is implemented by allowing the equilibrium length of the springs to increase during plastic deformation. On unloading, only the elastic portion of the spring extensions is recovered. The present results are based upon an elastic–brittle MoSi₂ and an elastic–linear–hardening plastic molybdenum phase for which the MoSi₂–Mo interface is assumed to be very strong. In these simulations, molybdenum is modeled to have an infinite strain to fracture. Interface strength, a more realistic constitutive equation for molybdenum

and other composite additions, and plasticity of the MoSi₂ matrix will be utilized as microstructural parameters in future simulations.

Figure 13(a) shows the simulated fracture sequence of a pre-cracked and uniaxially strained MoSi₂ matrix

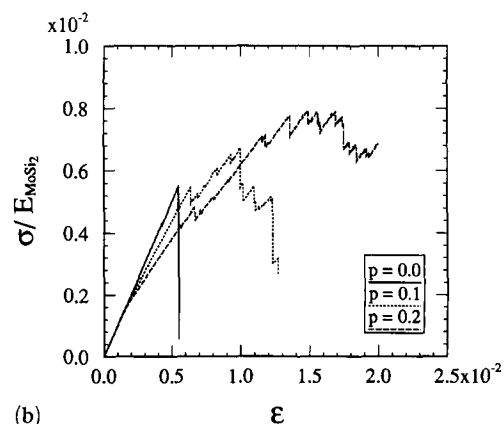
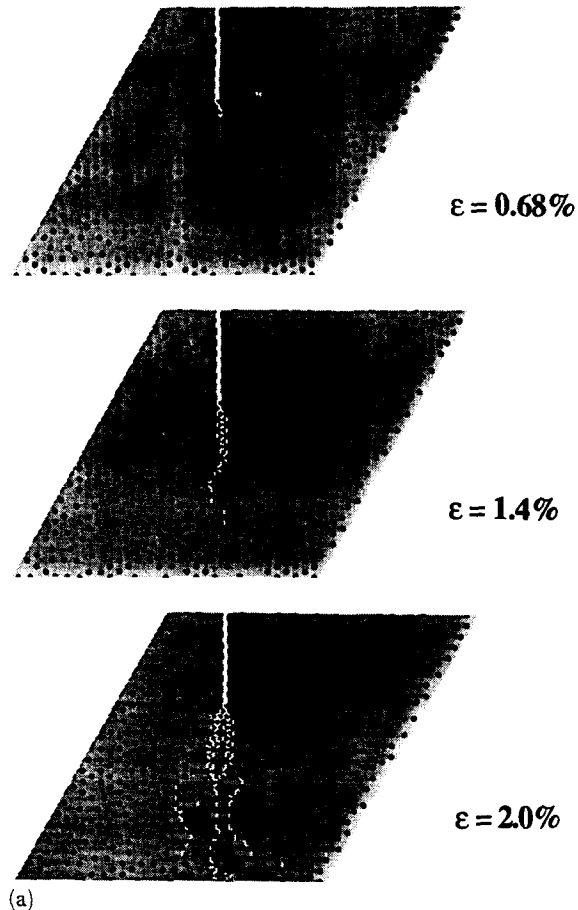
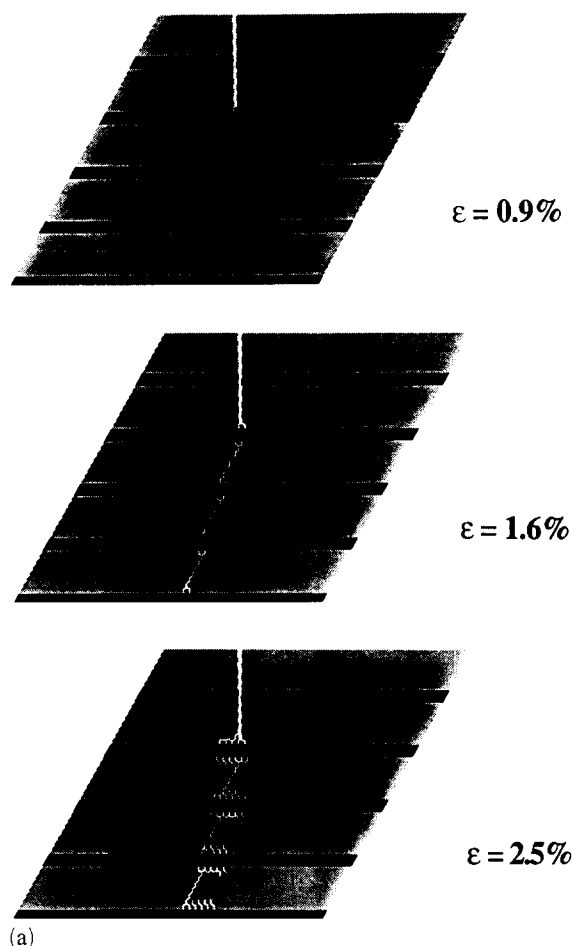


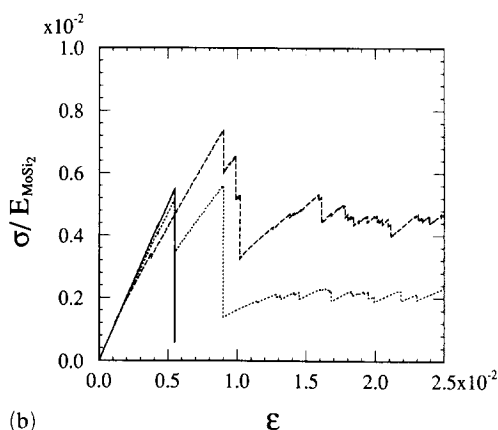
Fig. 13. (a) A fracture sequence in brittle MoSi₂ (gray) containing a random dispersion of 20 vol.% ductile Mo particles (black). The crack path is shown in white. The tensile stress is applied normal to the initial crack plane. (b) Stress–strain curves for pure MoSi₂ (—), MoSi₂ containing 10 vol.% ductile Mo particles (····), and MoSi₂ containing 20 vol.% ductile Mo particles (---). p is the volume fraction.

which has been toughened by a random dispersion of 20 vol.% small molybdenum particles. The propagation of the main crack is accompanied by additional cracking in the brittle matrix as the particles intersected by the crack plastically deform. Eventually, the composite is held together by the ductile particles, which are assumed not to fracture. Figure 13(b) gives the stress-strain behavior for this composite, along with those for the unreinforced MoSi₂ and a composite with 10 vol.% Mo particles. The stress-strain curve for the composite continues to large strains at a slowly decreasing stress level owing to a combination of the small strain hardening coefficient assumed for the molybdenum particles and additional damage accumulation in the MoSi₂. Increasing the volume fraction of molybdenum particles increases both the strength and ductility of the composite, even though the yield strength of molybdenum is below the fracture strength of MoSi₂.

Figure 14(a) gives similar results for the simulated fracture sequence when molybdenum in the Mo-MoSi₂ composite is present as the ductile reinforcement of a microlaminate microstructure consisting of alternate layers of MoSi₂ and molybdenum, where the molybdenum layers are one quarter as thick as the MoSi₂ layers. These simulations apply qualitatively to the arc-melted MoSi₂-Mo₅Si₃ composites of Fig. 9 in which MoSi₂ exhibits some plasticity at 1200 °C and 1300 °C (Fig. 4). In Fig. 14(a), the microlaminate has been pre-cracked and loaded in tension parallel to the layers. The molybdenum layers are tough, and the crack propagates through the MoSi₂ until it reaches a molybdenum layer. The molybdenum plastically deforms, and a new crack subsequently forms in the MoSi₂ layer on the other side of the molybdenum layer. The crack eventually propagates through all of the MoSi₂ layers until the remaining load is carried predominantly by the plastically deforming molybdenum layers. Substantial damage accumulation occurs in the MoSi₂ immediately adjacent to the Mo-MoSi₂ interface because the interface is assumed to be very strong. For microlaminates, we have also performed simulations for which the Mo-MoSi₂ interfaces are relatively weak. In these cases, the fracture damage of the brittle phase adjacent to the interface is replaced by interfacial fracture and sliding. The stress-strain behavior for the microlaminate with the strong interface is included in Fig. 14(b), along with results for unreinforced MoSi₂ and a microlaminate for which the MoSi₂ is twice as thick. For thick MoSi₂ layers, the stress-strain curve shows an initial load drop due to the onset of crack propagation followed by a more substantial load drop when the crack propagates through the remaining MoSi₂ layers. Once all the MoSi₂ layers are cracked, substantial ductility is



(a)



(b)

Fig. 14. (a) A fracture sequence in a MoSi₂ (gray)/Mo (black) microlaminate. The crack path is shown in white. The tensile stress is applied normal to the initial crack plane. (b) Stress-strain curves for pure MoSi₂ (—), the MoSi₂/Mo microlaminate of Fig. 14 (a) (---), and one in which the MoSi₂ layers are twice as wide as those in Fig. 14 (a) (·····).

achieved owing to the plastic deformation of the molybdenum layers and the subsequent damage accumulation in the MoSi₂. The final fracture behavior cannot be analyzed until a better plasticity law is determined and used for the ductile layers.

4. Summary and conclusions

The deformation of MoSi₂ and its composites with Mo₅Si₃, SiO₂, CaO and TiC particulate reinforcements at temperatures of 1000–1300 °C and strain rates of 10⁻⁶–10⁻⁴ s⁻¹ involves contributions from dislocation creep (glide and climb) and diffusional creep processes.

For composites formed by hot pressing of powders, the addition of 15 vol.% Mo₅Si₃ to MoSi₂ improves the high temperature strength. Increasing the Mo₅Si₃ loading to 30 vol.% reduces the strength owing to dynamic grain refinement.

The addition of erbium to arc-melted MoSi₂-Mo₅Si₃ composites refines the eutectic microstructure and increases the hardness at 25–1300 °C. Crack deflection processes at 25 °C are more effective in erbium-refined microstructures than in untreated coarser eutectics.

MoSi₂-SiO₂ composites with coarse SiO₂ particles at MoSi₂ grain boundaries exhibit very poor creep resistance at high temperatures owing to low viscosity of the SiO₂ at MoSi₂ grain boundaries. Comparably coarse particles of CaO effect modest strengthening at the same temperatures. The very large CTE of CaO and large CTE mismatch of CaO with MoSi₂ may be effective in promoting strengthening of these composites, in spite of microstructural degradation associated with CaO particle disintegration.

As a composite reinforcement, TiC does not significantly interact with MoSi₂ and appears to cause reduced strength and some plasticity enhancement at temperatures of around 1200 °C, probably owing to dislocation pumping mechanisms at MoSi₂-TiC interfaces.

Microstructural modeling of the mechanical behavior of linear elastic-brittle MoSi₂-based composites and elastic-plastic ductile-phase toughened MoSi₂ has been successful in initial model system investigations. The modeling approaches will be applied more directly

to the experimental results in the present investigation in future simulations.

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