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Potential of MoSi_2 and $\text{MoSi}_2\text{-Si}_3\text{N}_4$ Composites for Aircraft Gas Turbine Engines

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1. Introduction

It has been expected that gas turbine engines in high temperature environments where aggressive mechanical stresses may occur and a good surface stability is needed should operate more efficiently. So the investigations about the materials which will be able to carry the aviation technology to the next level are beginning to accelerate in this direction. And also it expected that those new materials using in gas turbine engines as a high temperature structural material will exceed the superalloys' mechanical and physical limits. The intended development can only be achieved by providing the improvement of the essential properties of the structural materials such as thermal fatigue, oxidation resistance, strength/weight ratio and fracture toughness. There are two different type of materials which are candidate to resist the operating conditions about 1200°C; first one is structural ceramics such as SiC, Si₃N₄ and the second one is structural silicides such as MoSi₂.

After the propulsion systems with high strength/weight ratio, it observed that development of new materials with high strength and low density was necessary, thus the studies about the intermetallics began. The most important ones of these intermetallic compounds are silicides and aluminides. By the oxide layers in Al₂O₃, it can be used as a protective material in high temperature applications. Moreover, aluminides such as FeAl, TiAl, Ni₃Al, can be suitable for some special applications in low and medium temperatures. In spite of these advantages, they remain inadequate above the temperatures 1200°C for their melting points with 1400-1600°C. Their low strength and creep resistance is not suitable for the temperatures above 1000°C. For this reason, it seems that silicides and aluminides are the proper materials for high service applications (Vaseduvan & Petrovic, 1992).

2. Superalloys and their limitations at elevated temperatures

In aviation applications, advanced gas turbine elements are exposed to several mechanic, thermal and corrosive environments and intensive studies for the developing of these parts are still continuing. However, these alloys are needed to be cooled during the operation of

the turbine engine and the practical temperature limits for metallic alloys remain below 1100°C. But in this situation, the elevation of turbine inlet temperature will be quite difficult and expensive. Because of these given limitations, there is not any important improvements on nickel based superalloys since 1985 (Soetching, 1995).

The basic facts that can directly effect the performance of superalloys in high temperatures are oxidation, hot corrosion and thermal fatigue. These effects cause the superalloy elements' surfaces may react with hot gases easier, and then their surface stability decreases (Bradley, 1988). Furthermore, during operation and stand-by period of turbine, there occurs a oscillation motion in the hot section elements respectively. This causes thermal fatigues on the superalloy parts.

2.1 Oxidation

Oxidation is one of the most serious factors acting on the gas turbine's service life and can be determined as the reaction of materials with oxygen in 2-4 atm. partial pressure (Tein & Caulfield, 1989). Mostly the uniform oxidation is not accepted as a considerable problem in relatively low temperatures (870°C and below). But in temperatures about 1100°C, the aluminum content in the form of Al₂O₃ as a protective oxide can not provide the expected protection in long term periods. For this reason, it is necessary to use the silicide based structural composite materials or to make protective coatings with respect to the segment's location in gas turbine.

2.2 Hot corrosion

The process of hot corrosion contains a structural element and the reactions occurring in its surroundings. In operating conditions at high temperatures there is a possible accelerated oxidation for superalloys. Another name for this reaction is hot corrosion and it consists of two different mechanisms as low temperature (680-750°C) and high temperature (900-1050°C) hot corrosion (Akkuş, 1999).

The basic principle to avoid from the hot corrosion in superalloys is using of the high content of chrome (\geq %20) during the manufacturing of material. But only a few types of nickel based superalloys have this rate for their high proportion of γ' and γ'' structure.

2.3 Thermal fatigue

Heating with non-uniform distribution make interior stresses in the zones hotter than the average temperature of the turbine, and tension stresses in the colder zones. Superalloy turbine vanes are the good examples of elements exposed to thermal fatigue in aeroplane jet engines. During the acceleration, inlet and outlet edges of the turbine vane can heat and expand easier than the medium part under cooling. But in deceleration, inlet and outlet parts can quietly cool off than the medium parts. This case results as fatigue crack at the edges.

3. Physical and mechanical properties of MoSi₂

MoSi₂ is a potential material for high temperature structural applications primarily due to its high melting point (2020°C), lower density (6.3 g/cm³) compared with superalloys,

excellent oxidation resistance, high thermal conductivity, and thermodynamic compatibility with many ceramic reinforcements. However, low fracture toughness at near-ambient temperatures, low strength at elevated temperatures in the monolithic form and tendency to pest degradation at ~500°C have seriously limited the development of MoSi₂-based structural materials. Several recent studies have attempted to address these issues and have shown promising results. For example, pest resistant MoSi₂-based materials have been developed using silicon nitride reinforcement or alloying with Al.

For general polycrystalline ductility five independent deformation modes are necessary. Changing the critical resolved shear stress of the slip systems through alloying may be a way to activate all three slip vectors, and obtain polycrystalline ductility. In fact, solid solution softening has been observed at room temperature in MoSi₂ alloyed with Al and transition metals such as Nb, V and Ta. The mechanism of softening is not clearly understood, although first principles calculations indicate that solutes such as Al, Mg, V and Nb may change the Peierls stress so as to enhance relative to cleavage. Clearly, more work is needed to understand how alloying may influence the mechanical behavior of MoSi₂.

With regard to elevated temperature strengthening of MoSi₂, both alloying with W to form C11b (Mo, W)Si₂ alloys and composites with ceramic reinforcements such as SiC have been tried. A (Mo, W)Si₂/20 vol.% SiC composite was shown to have significantly higher strength than Mar-M247 superalloy at temperatures above 1000°C. However, the strength of the (Mo, W)Si₂/20 vol.% SiC composite dropped by almost an order of magnitude from 1200 to 1500°C; the yield strength at 1500°C was only ~75 MPa. A simpler and more effective way of strengthening MoSi₂ at elevated temperatures is needed where the strength can be better retained with increasing temperature above 1200°C. Our preliminary studies using hot hardness experiments have shown that Re addition to MoSi₂ caused significant hardening up to 1300°C. Further, it has been reported that alloying with Re, perhaps in synergism with carbon, increased the pesting resistance in the temperature range of 500 ± 800°C. In another preliminary study, polycrystalline (Mo, Re)Si₂ alloys exhibited a minimum creep rate of ~5 × 10⁻⁶/s at 100 MPa applied stress at 1400°C as compared with the ~1 × 10⁻⁴/s creep rate exhibited by MoSi₂. No detailed mechanistic study has been performed to understand the effects of Re alloying on the elevated temperature mechanical behavior of MoSi₂. In the present investigation, we have evaluated the mechanical properties, in compression, of arc-melted polycrystalline MoSi₂ and (Mo, Re) Si₂ alloys. We find that significant strengthening is achieved up to 1600°C by only small additions of Re. The mechanisms of elevated temperature solid solution strengthening are elucidated by considering the generation of constitutional Si vacancies that may pair with Re substitutionals to form tetragonally distorted point defect complexes. Characteristics of MoSi₂ make it an interesting material as high temperature structural silicide. Not only it has a low density and a high melting point but also it can excellently resist the free oxygen of air in high temperature environments for a long time period. On the other hand, researchers noticed its potential as a structural material due to its electrical resistance increasing after every use and high modulus of elasticity at high temperatures. This makes MoSi₂ a candidate material for structural high temperature applications particularly in gas turbine engines. MoSi₂ and its composites offer a higher rate of resistance to oxidizing and aggressive environments during the combustion processes with their high melting points.

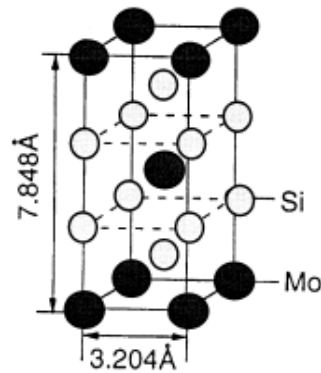


Fig. 1. Unit cell of the body-centered tetragonal C11b structure of MoSi₂. (Misra et al., 1999).

Fracture toughness of the material shows similarities with the other silicon based ceramics and yet it receives a brittle fracture resulted with low toughness. Table 1. shows the considerable characteristics of MoSi₂.

	Metric	English
Density	6.23 g/cm ³	0.225 lb/in ³
Molecular Weigth	152.11 g/mol	152.11 g/mol
Electrical Resistance (20°C)	3.5x10 ⁻⁷ ohm-cm	3.5x10 ⁻⁷ ohm-cm
Electrical Resistance(1700°C)	4.0x10 ⁻⁶ ohm-cm	4.0x10 ⁻⁶ ohm-cm
Thermal Capacity	0.437 J/g-°C	0.104 BTU/lb-°F
Thermal Conductivity	66.2 W/m-K	459 BTU-in/hr-ft ² -°F
Melting Point	2030°C	4046°F
Maximum Service Temp.	1600°C	2912°F
Crystal Structure	Tetragonal	Tetragonal

Table 1. Basic characteristics of MoSi₂.

The figure below shows the tetragonal lattice structure directions, red and blue points indicate silicon and molybdenum atoms respectively.

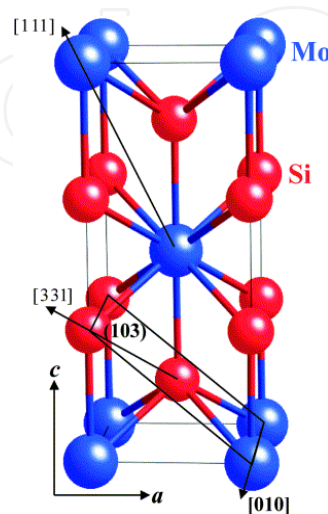


Fig. 2. Tetragonal MoSi₂ lattice structure.

One of the most considerable limitations in MoSi₂ applications is the structural disintegration during the low temperature oxidation which is known as pesting oxidation (Meschter, 1992). Previously, we noted that MoSi₂ has an excellent oxidation resistance above the 1000°C, but at the temperatures about 500°C as it is presented Figure 3., the oxidation mechanism accelerates because of the volume expansion, MoO₃ crystals, amorphous-shaped SiO₂ bulks and MoSi₂ particles residual from the reaction. If the material is porous and the surface accuracy is low, this state can be observed along the cracks or grain boundaries, and granular oxide particles occur as a result.

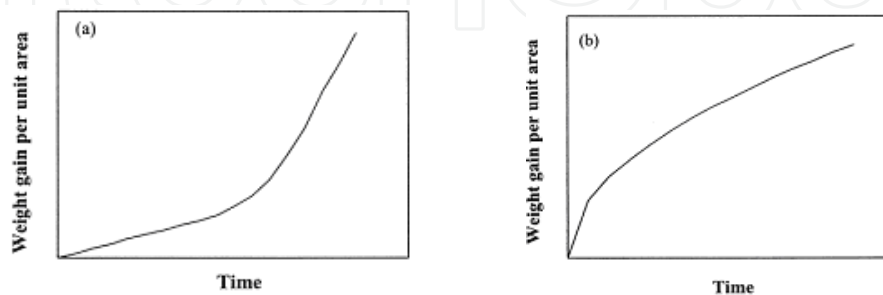


Fig. 3. Isothermal oxidation curves (a) at room temperature, (b) at the temperatures above 1000° C (Liu et al., 2001).

This fact was discovered in 1955 and predicted as the grain boundary fracture due to solution oxygen at the grain boundaries after the short-term cyclic diffusion, even though its complete nature is still a phenomena (Chou & Nieh, 1992, 1993). Methods for preventing from the pest effect are continuing. These methods are; making a protective SiO₂ coating on the material and increasing the relative density of MoSi₂ in the structure (Wang et al., 2003)

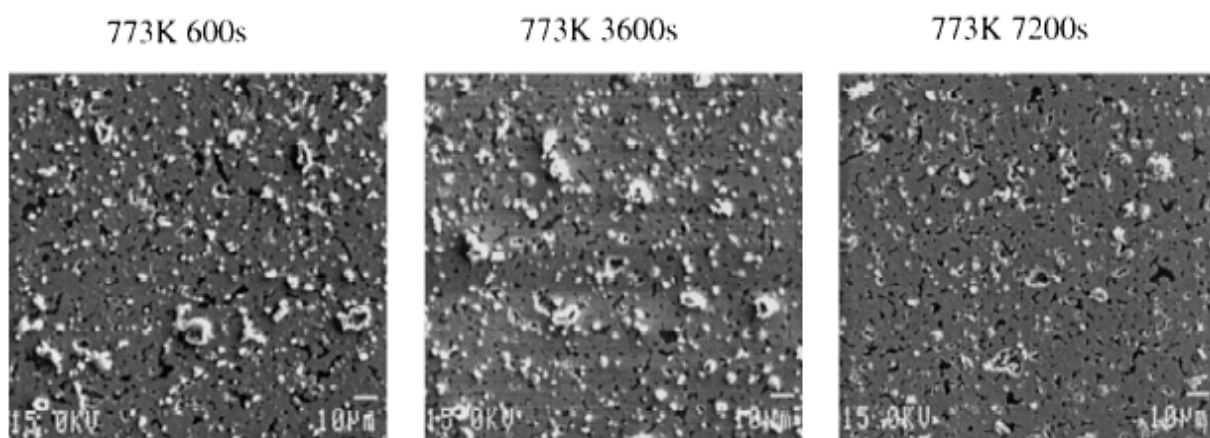


Fig. 4. Surfaces oxidized at 773K for 600-7200s in O₂ (Chen et al., 1999).

During the oxidation reactions above 600°C, no pesting effect can be observed. MoSi₂ based composites have considerably higher isothermal oxidation resistance than any other titanium, niobium or tantalum based composites, intermetallic compounds and nickel based superalloys, MoSi₂ perfectly keeps this condition to 1600°C (Vaseduvan & Petrovic, 1992).

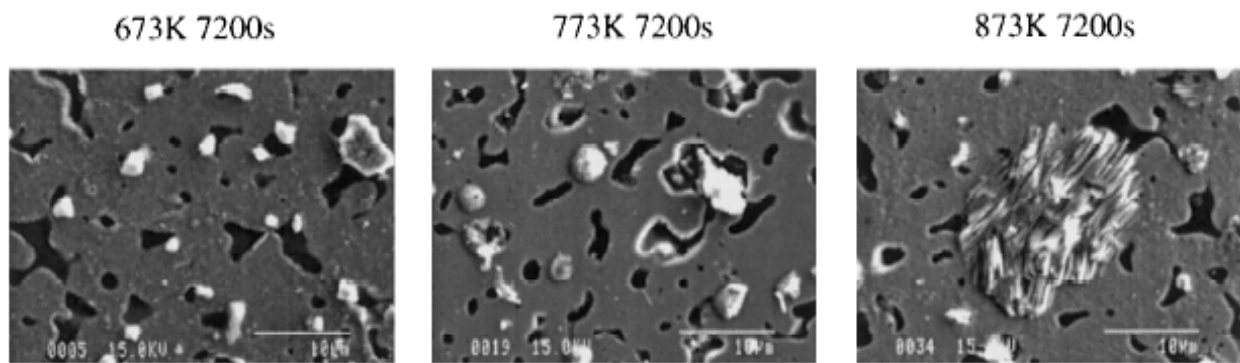


Fig. 5. Surfaces oxidized at 673-873K for 7200s in O₂ (Chen et al., 1999).

Despite excellent oxidation resistance, high melting point, and low density, the potentials of molybdenum disilicide as a high temperature structural material have not been utilized due to its brittleness at low temperatures and low strength at high temperatures. For example, below 900° C, the fracture toughness of MoSi₂ is in the range of 2–4 MPam^{1/2}, and the 0.2% offset yield strength of MoSi₂ at 1600° C is about 20 MPa. Alloying or reinforcing with a second phase may lower the brittle to ductile transition temperature (BDTT) of MoSi₂. However, ductile-phase toughening with metallic phases has limited applicability in MoSi₂ due to the chemical reaction with silicon to form silicides, and reinforcing with ceramic second phases such as SiC and ZrO₂ has only a modest effect on enhancing plastic flow and increasing toughness.

First principles calculations indicate that alloying of MoSi₂ while maintaining its body-centered tetragonal (C11b) structure may result in improved mechanical properties. For example, Al and Nb may enhance ductility and Re may increase strength. Improvements in both low and high temperature mechanical properties of MoSi₂ have been reported by alloying MoSi₂ with small amounts of Al, Nb, and Re (<2 at.%). During alloying, below the solubility limits of alloying elements in the C11b structure of MoSi₂, Al substitutes for Si, whereas Re and Nb substitute for Mo. The solubility limits of Re, Nb and Al in MoSi₂ have been reported as ~2.5, 1.3 and 2.7 at.%, respectively. Although improvements in the ambient temperature toughness have been reported by alloying of MoSi₂ beyond the solubility limits with Nb and Al, the rates of improvement per fraction of solute are not as considerable as those observed in single phase alloys. Furthermore, the presence of secondary phases with a lower high temperature strength than the matrix alloy would degrade the mechanical properties at high temperature (>1500°C) for which applications MoSi₂ is an excellent candidate. The aim of this investigation was to explore the possibility of obtaining concurrently enhanced room temperature ductility and high temperature strength in single-phase MoSi₂ by combining the high temperature hardening and the low temperature softening effects of Re, Al, and Nb. Hardness testing at room temperature and compression testing at 1600° C are conducted on unalloyed and alloyed MoSi₂ samples in order to study both low and high temperature effects of each alloying composition on the mechanical properties of MoSi₂. (Sharif et al., 2001).

4. Effects of alloying

4.1 Hardness

Microhardness testing performed on stoichiometric samples obtained from melting (Mo, Re or Nb)(Si, Al)_{2.01} samples indicated that unalloyed MoSi₂ had an average Vickers hardness

value of 89968 Hv. Samples containing 2 at.% Al or 1 at.% Nb had average Vickers hardness values of 72928 Hv and 72950 Hv, respectively. 2.5 at.% Re containing samples had the highest hardness value of 103971 Hv. Samples containing 1 at.% Re+2 at.% Al had an average hardness value of 74230 Hv, slightly higher than Al containing samples but significantly lower than both MoSi₂ and (Mo, 1 at.% Re)Si₂ samples. Slip lines were observed around indentations in all samples except the unalloyed MoSi₂ and (Mo, 2.5 at.% Re)Si₂ samples. Samples containing 1 at.% Nb+2 at.% Al did not exhibit any improvements in the mechanical properties and were excluded from further considerations.

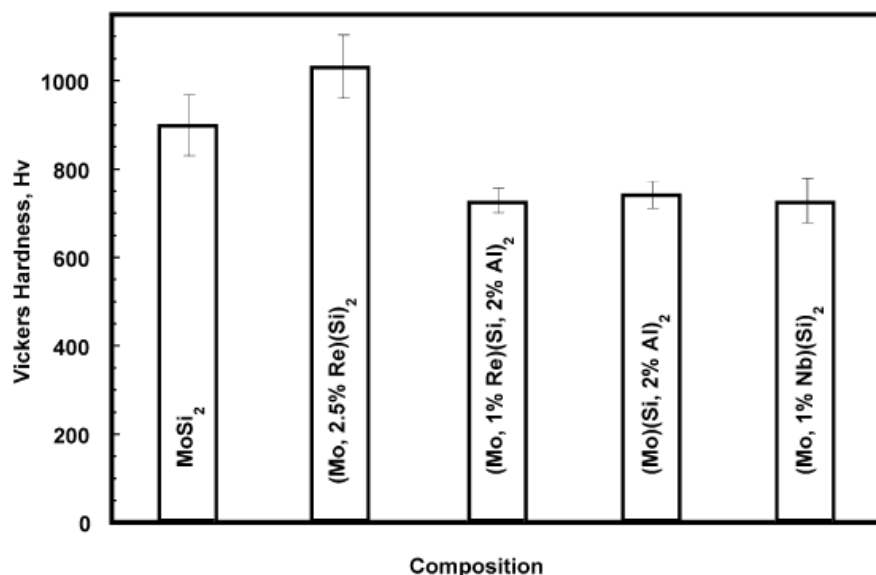


Fig. 6. Vickers hardness values for polycrystalline samples of all composition under investigation. Hardness of polycrystalline Al containing samples is also compared to the values obtained on monocrystalline Al containing samples on (100) and (001) surfaces of the crystal.

4.2 Yield strength

Compression testing at room temperature and at 1600°C was used to determine the 0.2% offset yield strength for all polycrystalline samples. Unalloyed MoSi₂ and 2.5 at.% Re containing samples could not be deformed plastically below 900 and 1200° C, respectively. Below these temperatures, the aforementioned samples would undergo brittle fracture during compression testing. The addition of 2.5 at.% Re increased the BDTT, in compression, of MoSi₂ by about 300° C while increasing its yield strength from 14 MPa to 170 at 1600° C. Among alloying elements investigated here, 2.5 at.% Re was most effective in increasing strength at 1600° C. The addition of 2 at.% Al was effective in both increasing the high temperature strength to 55 MPa and lowering the BDTT to 425° C. Mo(Si, 2 at.% Al)₂ samples exhibited the lowest room temperature yield strength of 415 MPa. Addition of 1 at.% Re+2 at.% Al combined the beneficial effects of both alloying elements and resulted in enhanced ambient temperature compressive plasticity and high temperature strength compared to the unalloyed samples.

However, the improvements in room temperature plasticity was less than that of samples alloyed with 2 at.% Al alone as evident from the value of the room temperature yield

strength of (Mo, 1 at.% Re)(Si, 2 at.% Al)₂ alloy, 670 MPa. Similarly, the enhancement in high temperature strength was less than that of only Re containing samples but greater than that of only Al containing samples. The effects of 1 at.% Nb as an alloying element by itself in lowering BDTT and enhancing high temperature strength of MoSi₂ was more pronounced than the combined effects of 1 at.% Re and 2 at.% Al. The room temperature yield strength of (Mo, 1 at.% Nb)Si₂, 500 MPa, was higher than that of 2 at.% Al containing samples and lower than that of (Mo, 1 at.% Re)(Si, 2 at.% Al)₂ samples. The 0.2% offset strength of (Mo, 1 at.% Nb)Si₂ samples at 1600°C, 143 MPa, was an order of magnitude greater than that of unalloyed MoSi₂ (Sharif et al., 2001).

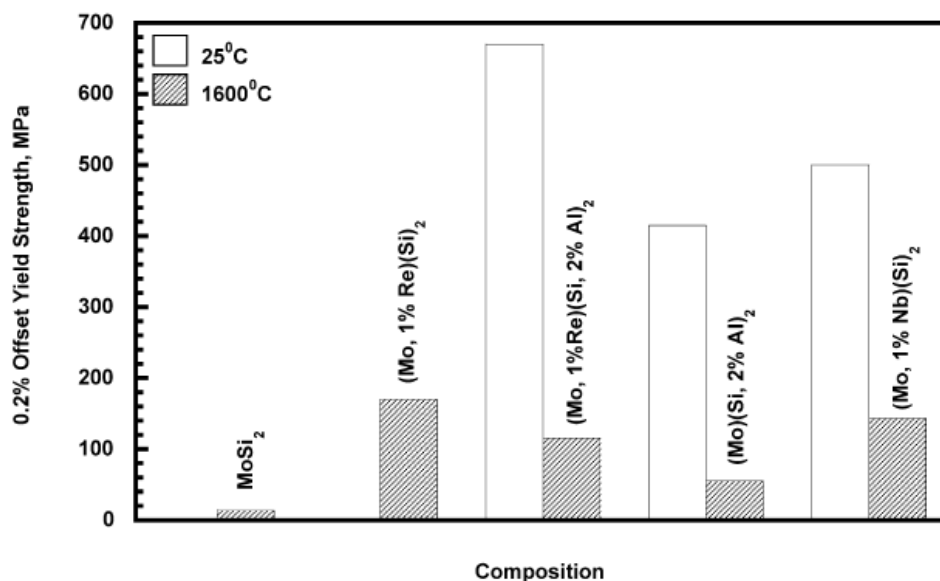


Fig. 7. Effects of alloying on the room temperature and high temperature (1600°C) strength of MoSi₂.

4.3 Ductility

Molybdenum disilicide crystallizes in an ordered body centered tetragonal structure with $a=0.320$ nm and $c=0.785$ nm, formed by alternate stacking of single Mo and double Si (001) layers. With its high temperature ductility and exceptional resistance to corrosion and fatigue crack growth, MoSi₂ combines the toughness of a metal with the strength of a ceramic and is a promising candidate to replace nickel alloys in the next generation of high-temperature gas turbines. Unfortunately, it undergoes a ductile-brittle transition (DBT) at 1200°C, with the fracture toughness dropping to 2–3 MPa m^{1/2}, well below the minimum of 20 MPa m^{1/2} required for engine applications. This brittleness at low temperature means that MoSi₂ must be formed by costly electro-discharge machining and places a severe limitation on its potential technological utility. However, there is a reasonable chance that the DBT in MoSi₂ may be manipulated or even eliminated. Many of the slip systems in MoSi₂ are ductile and it is only for a stress axis near [001] that a DBT is observed.

It is desirable therefore, to alter the properties of MoSi₂ in very specific ways. This can be, and has in the past been, attempted by heuristically changing the composition or structure of the material and studying experimentally the effect of these changes. It will be argued in this paper that advances in the theory of bonding in solids, based on quantum mechanical

density functional calculations, offer an alternative route which can be used as a cost-effective precursor to experiment. The need, in the case of MoSi₂, is for an element or elements which can be introduced at microalloy levels (less than 5%) and which will perturb the brittle-ductile behavior in favor of ductility without adversely affecting the advantageous physical properties. While the method of choice would normally be an atomistic calculation, bonding in MoSi₂ is known to have hybrid metallic and covalent character. Determination of the effects of alloying on such bonding requires accurate quantum mechanical treatment of the electrons, and generation of reliable interatomic potentials, which are an essential prerequisite to atomistic methods, is impractical. Instead, use is made of recent advances in the theory of dislocation nucleation and mobility which provide approximate links between these properties and the generalized stacking fault energy surface, which can be calculated accurately using first principles quantum mechanical techniques. A similar approach has been used successfully by two of the present authors to investigate the DBT in silicon. Even with these gross approximations, the numerical work is intensive. The calculations are restricted to small supercells, with correspondingly large alloy content, and the effects of true microalloying must be estimated by interpolation. An overview of the experimental background will be presented in the next section.

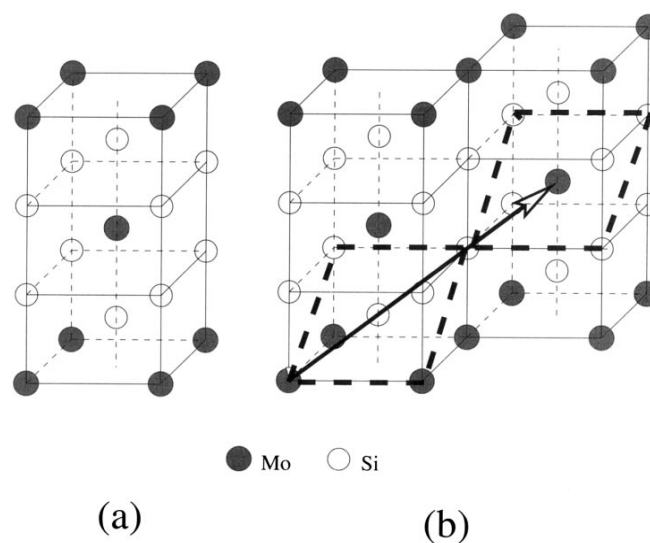


Fig. 8. Crystal structure of MoSi₂. (a) Unit cell for the body centered C11b structure; solid circles represent Mo atoms and open circles represent Si atoms. (b) (013) plane and the Burgers vector for {013}<331> slip systems (Waghmare et al., 1999).

4.4 Creep

The creep behavior of MoSi₂-based materials has been extensively studied. It has been observed that the grain size has a large effect on creep resistance of monolithic MoSi₂. Reinforcing with SiC also refined grain size that enhanced creep rates overshadowing any beneficial effects of reinforcement. Increased creep resistance has been noted only when volume fractions of SiC are above 20%. Another important factor strongly affecting the creep strain rate of MoSi₂ is the presence of silica particles (SiO₂). During high temperature deformation, the SiO₂ particles at the grain boundaries flow to form intergranular film, which slides or cracks. A high volume fraction of SiO₂ and reduction in grain size, both

enhance creep rates; but it is of interest to examine how the two are interrelated. Alloying of polycrystalline MoSi_2 with Al and C converts SiO_2 to Al_2O_3 and SiC , respectively, which leads to the enhancement in creep resistance. When C is added, oxygen is got rid off in the form of CO or CO_2 , which may leave behind fine pores, which are difficult to close. When Al is added, the reaction between Al and SiO_2 forms Al_2O_3 and Si. The Si may remain in elemental form or react with Mo_5Si_3 particles that are present in small volume fractions. These particles form due to partial oxidation of MoSi_2 during hot pressing, particularly when vacuum is low. The probability of the reaction between free Si and residual Mo_5Si_3 in the present study is high, as free Si has been observed in the microstructure only very rarely. The figure below presents the effect of alloying of single and polycrystalline MoSi_2 with Al, on the creep rates at 1300°C . The single crystals of $\text{Mo}(\text{Si}_{0.97}\text{Al}_{0.03})_2$, with hexagonal C40 or hP9 (Pearson's symbol) structure, have shown higher creep rates, compared to those of single crystals of MoSi_2 along the $[0\ 15\ 1]$ orientation of stress axis. However, the trend reverses with change of stress-axis to $[001]$ direction. On the other hand, polycrystalline MoSi_2 -5.5Al alloy has shown improvement in creep resistance, compared to polycrystalline MoSi_2 at 1300°C . Unlike $\text{Mo}(\text{Si}_{0.97}\text{Al}_{0.03})_2$, the matrix phase of MoSi_2 -5.5Al has tetragonal, C11b structure.

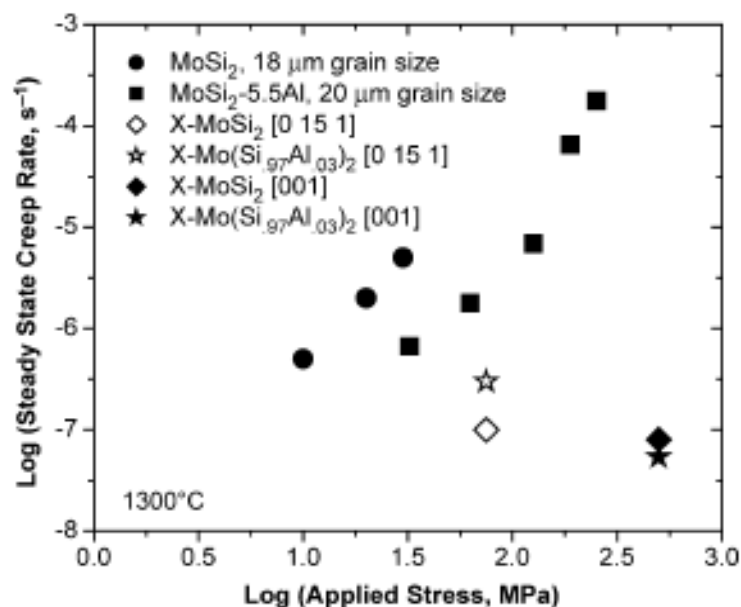


Fig. 9. Comparison of steady state creep rates, measured at 1300°C on MoSi_2 and MoSi_2 -5.5Al alloy, as well as single crystals of MoSi_2 and $\text{Mo}(\text{Si}_{0.97}\text{Al}_{0.03})_2$ tested with $[0\ 15\ 1]$ and $[001]$ orientations. Single crystals are marked as X (Mitra et al., 2004).

As expected, the creep rates of polycrystalline MoSi_2 and MoSi_2 -5.5Al alloy are higher compared to those of single crystals at 1300°C , because of the role of grain boundaries at $0.68\ \text{Tm}$: In the present investigation, samples of MoSi_2 with varying grain sizes and SiO_2 contents, as well as those of MoSi_2 -20 vol% SiC composite and MoSi_2 -Al alloys have been creep tested at 1200°C and their behaviors analyzed. The values of activation volume and threshold stress have been calculated. These provide an insight into the ratecontrolling and strengthening mechanisms. The creep behavior of the above materials has also been compared with deformation behavior under constant strain rate tests.

4.5 Plastic deformation

Monolithic MoSi₂ exhibits only a modest value of fracture toughness at low temperatures and inadequate strength at high temperatures. Thus, many of recent studies on the development of MoSi₂-based alloys have focused on improving these poor mechanical properties through forming composites with ceramics and with other silicides. These properties have recently been reported to be significantly improved in composites formed with Si₃N₄ and SiC. However, the volume fraction of Si₃N₄ and SiC ceramic reinforcements in these MoSi₂-composites generally exceeds 50%. Further improvements in mechanical properties of these composites will be achieved if those of the MoSi₂ matrix phase are improved. The present study was undertaken to achieve this by alloying additions to MoSi₂. Transition-metal atoms that form disilicides with tetragonal C11b, hexagonal C40 and orthorhombic C54 structures are considered as alloying elements to MoSi₂. These three structures commonly possess (pseudo-) hexagonally arranged TMSi₂ layers and differ from each other only in the stacking sequence of these TMSi₂ layers; the C11b, C40 and C54 structures are based on the AB, ABC and ADBC stacking of these layers, respectively. W and Re have been known to form a C11b disilicide with Si and they are believed to form a complete C11b solid-solution with MoSi₂, although recent studies have indicated that the disilicide formed with Re is an off-stoichiometric (defective) one formulated to be ReSi_{1.75} having a monoclinic crystal structure. The details of our crystal structure assessment for ReSi_{1.75} as well as phase equilibria in the MoSi₂±ReSi_{1.75} pseudobinary system will be published elsewhere. Large amounts of alloying additions are possible for these alloying elements, and high temperature strength is expected to be improved through a solid solution hardening mechanism since the hardness of both WSi₂ and ReSi_{1.75} is reported to be larger than that of MoSi₂. The yield strength of MoSi₂ powder compacts is greatly increased when WSi₂ is alloyed with MoSi₂ by more than 50 vol%. In addition, our previous study on single crystals of MoSi₂±WSi₂ solid solutions has indicated that the compression yield stress above 1200° C greatly increases when the WSi₂ content in the solutions exceeds 50 vol.%. However, low temperature deformability may be declined upon alloying with these elements because of the increased strength. Indeed, the room temperature hardness of both MoSi₂± WSi₂ and MoSi₂± ReSi_{1.75} solid solutions is reported to monotonically increase with the increase in either WSi₂ or ReSi_{1.75} content.

V, Cr, Nb and Ta have been known to form a C40 disilicide with Si. Al is also known to transform MoSi₂ from the C11b to the C40 structures by substituting it for Si. Of the five slip systems identified to be operative in MoSi₂, slip on {110}<111> is operative from 500°C. 1/2<111> dislocations of this slip system are reported to dissociate into two identical 1/4<111> partials separated by a stacking fault. The stacking across the fault is ABC and resembles the stacking of (0001) in the C40 structure. Hence, the addition of elements that form a C40 disilicide may cause the energy difference between C11b and C40 structures to decrease so that the energy of the stacking fault would also be decreased, although the solid solubility of these alloying elements in MoSi₂ has been reported to be rather limited to the level of a few atomic %. From this point of view, we may expect that the deformability of MoSi₂ at low temperatures increases upon alloying with elements that form a C40 disilicide. This is consistent that V and Nb may enhance the ductility of MoSi₂. Indeed, room temperature hardness of MoSi₂ polycrystals decreases upon alloying with Cr, Nb, Ta and Al and similar observations were made for Al-bearing MoSi₂ polycrystals. Compression deformation experiments made so far on ternary MoSi₂ single crystals containing these

elements have focused attention to the high temperature deformation behavior. The yield stress of MoSi_2 increases upon alloying with Cr above 1100°C . A similar observation was made for Nb-bearing MoSi_2 at 1400°C . However, since these compression experiments were made only at high temperatures above 1100°C , almost nothing is known about the low temperature strength and deformability of these ternary MoSi_2 single crystals. V, Cr, Nb and Al that form a disilicide with the C40 structure and W and Re that form a disilicide with the C11b structure as alloying elements to MoSi_2 , and investigated the deformation behavior of single crystals of MoSi_2 containing these elements in a wide temperature range from room temperature to 1500°C . The crystal orientations investigated were the $[0\ 15\ 1]$ orientation, in which slip on $\{110\}\langle 111\rangle$ is operative, and the $[001]$ orientation, in which the highest strength is obtained at high temperatures for binary MoSi_2 .

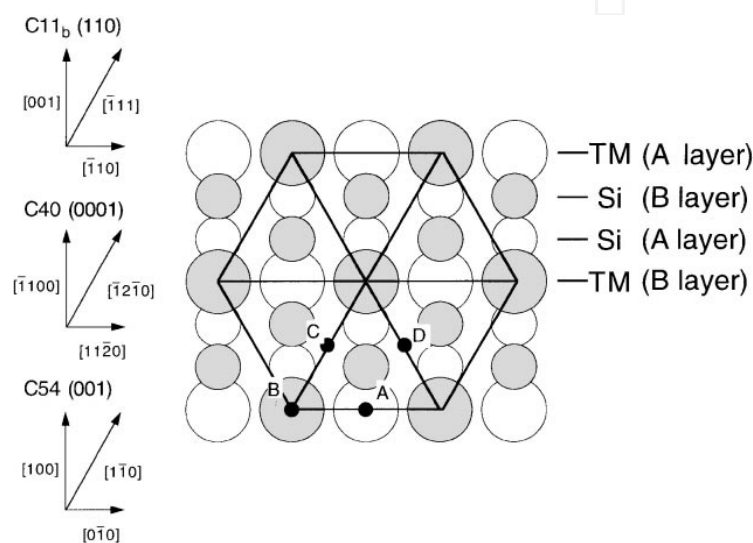


Fig. 10. Atomic arrangement on TMSi_2 layers corresponding to $\{110\}$, (0001) and (001) planes in the C11b, C40 and C54 structures, respectively. The stacking positions of $A\pm D$ and crystallographic directions with respect to these three structures are indicated (Inui et al., 2000)

5. Development of $\text{MoSi}_2 - \text{Si}_3\text{N}_4$ composites

Interest in fiber reinforced ceramic matrix composites (FRCMCs) has increased steadily over the past 15 years, and several refined silicon-base composite systems are now being produced commercially. These composites offer very good structural stiffness, high specific strength to weight, and good high temperature environmental resistance. Industrial applications include, hot gas filters, shrouds, and combustor liners. In addition, silicon-base ceramic composites are being considered for gas turbine hot gas flow path components, e.g. combustors transition pieces, and nozzles. The manufacturers of liquid rocket engines are also looking to ceramic composites in hopes of obtaining better efficiency in the next generation of designs. Applications include inlet nozzles, fuel turbopump rotors, injectors, combustion chambers, nozzle throats, and nozzle extensions. In order to maximize properties, materials developers have now begun to pay more attention to engineered interfaces between the matrix and the fiber reinforcement. If the interfacial debonding energy and sliding resistance is low, the fibers can pull away or out of the matrix and form bridges behind the advancing crack front which renders these otherwise brittle materials

acceptably compliant. Unfortunately, most of the incremental toughening and attended fiber pullout occurs at engineering strains that exceed the strain which occurs at the ultimate strength of the material, and the toughening benefit is, therefore, not useful for design purposes. Thus, the degree of incremental toughening that occurs during the inelastic portion of the stress-strain curve up to the ultimate strength will have to be improved before increased use of FRCMCs can be realized.

It has also been shown that MoSi₂ offers the potential of combining the effects of second phase reinforcements with metallurgical alloying to improve mechanical properties without degrading oxidation resistance. For example, high temperature (1200°C) creep was reduced by a factor of 10 by alloying with WSi₂ and by another factor of 10–15 with the addition of SiC whiskers. Additions of carbon and zirconia have also proven to be beneficial. Carbon reacts with the oxygen impurities in MoSi₂ to improve the toughness at high temperatures by removing SiO₂, and leaves behind a compatible SiC phase. Zirconia, which is thermochemically stable with MoSi₂, can also be used to increase fracture toughness. A 20 v/o loading of particulate ZrO₂ increased the low temperature fracture toughness of MoSi₂ by a factor of four. The toughening transformation occurs above the ductile–brittle transition and therefore enhances the low temperature properties. In an attempt to reinforce MoSi₂ with SCS-6 silicon fibers, it was discovered that the large thermal expansion difference between the matrix and fiber introduced matrix cracking upon cooling from the densification temperature. This problem was solved by adding Si₃N₄ to form a two phase composite matrix with a coefficient of expansion that more closely matches the fiber. There is no reaction between Si₃N₄ and MoSi₂, even at fabrication temperatures as high as 1750°C. No gross cracking occurs on cool down, although some microcracking has been observed and is a function of grain size. The critical particle size below which microcracking will not occur was calculated to be 3 μm. Coarse phase MoSi₂- Si₃N₄ composites also exhibit higher room temperature toughness than fine phase material, reaching values of 8 MPam^{1/2}. Fracture toughness also increases with temperature and the trend is quite significant above 800°C with toughness values exceeding 10 MPam^{1/2}.

However, the fine phase materials are stronger than the coarse phase materials with bend strengths reaching 1000 MPa. The MoSi₂- Si₃N₄ composites have also been shown to exhibit R-curve behavior, and crack deflection and particle pullout have been observed. Molybdenum disilicide does not have good creep resistance at high temperatures above its brittle-to-ductile transition. When high volume fractions of Si₃N₄ are added, creep is improved significantly and the activation energy is comparable to monolithic silicon nitride.

Additions of carbon can also improve creep resistance as well as toughness. In situ processing with carbon additions have produced material with creep resistance comparable to Ni-base superalloys. The silicon-base composite systems of current interest typically utilize carbon or silicon carbide fibers and silicon nitride or silicon carbide matrices. A popular designation is to display the fiber first followed by the matrix phase, e.g. C/SiC, SiC/SiC, and SiC/Si₃N₄. Mixtures composed of MoSi₂ and Si₃N₄ form two phase composites that are also candidates as matrices in C or SiC fiber reinforced composite systems. The combination of a fiber reinforced composite with a composite matrix becomes a little confusing, but can be represented by SiC/ MoSi₂- Si₃N₄.

The matrix properties for several silicon-base composite systems and their fiber properties are presented below. The high coefficient of thermal expansion of SCS-6, i.e. $4.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$, indicates that this fiber will have a larger expansion coefficient than the matrix phase for SiC/SiC and SiC/ Si_3N_4 fiber reinforced composite systems. It is generally more difficult to weave and fabricate structural components from large diameter fibers. The size can also influence properties. For example, toughness scales directly with fiber radius while the matrix cracking strength is inversely proportional to the radius. The properties for MoSi_2 - Si_3N_4 compare quite favorably with both SiC and Si_3N_4 . The fracture toughness is slightly above the middle range for SiC and comparable to Si_3N_4 . The highest matrix toughness values are on the order of $10 \text{ MPam}^{1/2}$ for in situ toughened silicon nitride. The toughness for all the candidate matrix materials will depend upon processing conditions and microstructure. It is anticipated that in situ toughening of the silicon nitride phase in the two phase MoSi_2 - Si_3N_4 composites should yield further improvements for this matrix candidate.

The onset of nonlinear behavior is often found in tension tests marked by a distinct load drop, indicating the initiation of matrix cracking, whereas in flexure, this important feature may go undetected. It is the region between matrix cracking and fiber bundle failure at maximum load where matrix enhancement can make the greatest contribution. Many FRCMC composites exhibit much of their toughness beyond this point, because as the fibers pull away from the matrix, they bridge cracks and impose traction forces that retard crack growth. Pullout toughening extends life after failure, and adds a margin of safety from the catastrophic nature of failure often found in brittle materials, but this phenomenon is not useful as a design property. Three of the composites exhibit matrix cracking stresses in the range of 150–175 MPa. Of the four systems, the SiC/ Si_3N_4 has the highest matrix cracking stress, which is near 350 MPa. This composite also has the largest coefficient of thermal expansion mismatch, CTE, with the fiber having the larger value.

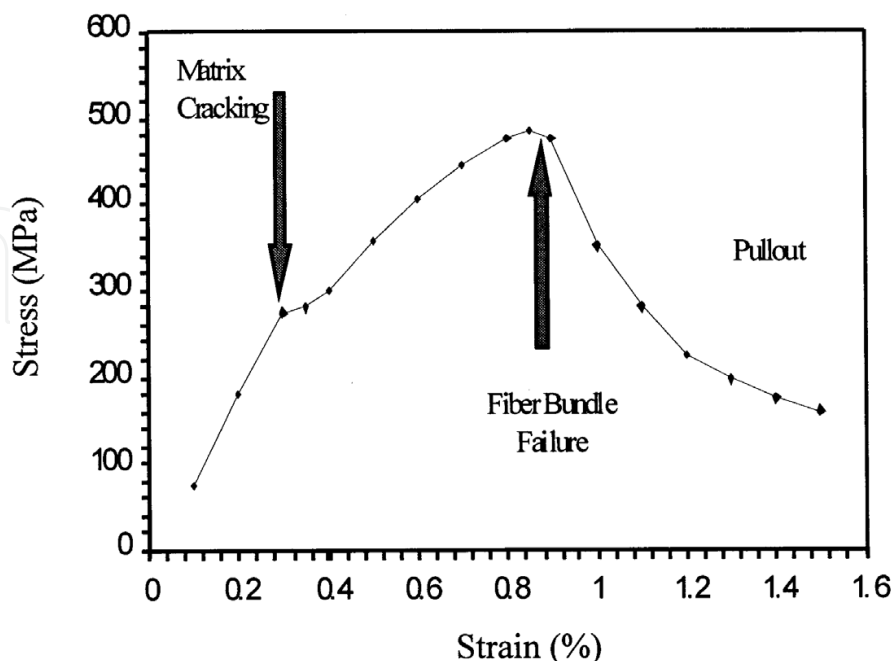


Fig. 11. Stress-strain behaviour for ceramic fiber reinforced: ceramic matrix composites.

Upon cooling from the consolidation temperature, the fiber can theoretically contract and debond from the matrix unless there is enough surface roughness for asperity contact. Upon reloading, the matrix will not efficiently transfer stress to the fiber unless it is in intimate contact. However, the high elastic modulus, as indicated by the stress-strain curve, suggests that good load transfer is occurring in this system. Inelastic behavior starts at about 350 MPa, but the ultimate is reached at about 450 MPa which is well below the expected fiber bundle failure. The ultimate strength for the Silcomp matrix composite is on the order of 650 MPa and is in reasonable agreement with bundle fiber failure, as is the MoSi₂-0.5Si₃N₄ matrix composite.

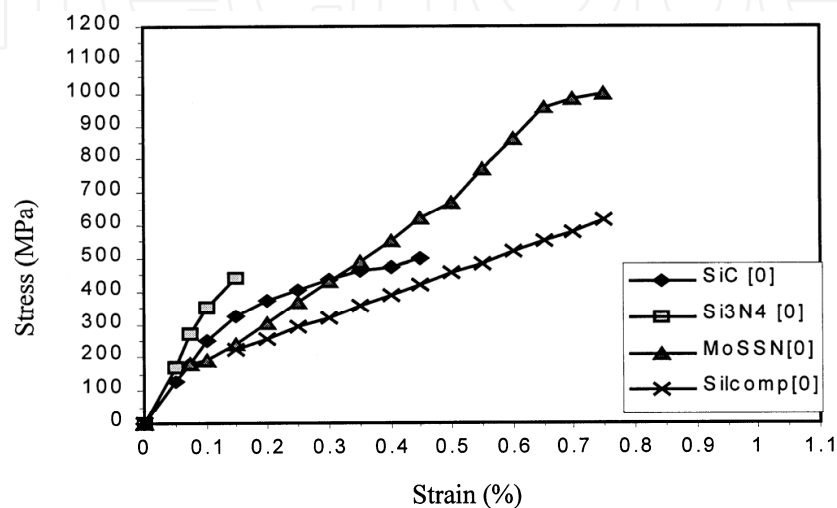


Fig. 12. Tensile stress-strain curves for uniaxial SCS-6 reinforced silicon-base composite systems (Courtright, 1999).

A number of composite approaches have been developed to toughen brittle high temperature structural ceramic materials. Many of these approaches have also been applied to high temperature structural silicides.

The MoSi₂-Si₃N₄ composite system is an interesting and important one. Si₃N₄ is considered to be the most important structural ceramic, due to its high strength, good thermal shock resistance, and relatively high (for a structural ceramic) room temperature fracture toughness. Si₃N₄ and MoSi₂ are thermodynamically stable species at elevated temperatures.

Property	MoSi ₂	Si ₃ N ₄
Density(g/cm ³)	6.2	3.2
Thermal expansion coefficient (10 ⁻⁶ /°C)	7.2	3.8
Thermal conductivity (W/mK)	65	37
Melting point(°C)	2030	2100
Creep resistance (°C)	1200	1400
Toughness	Low	Low
Oxidation resistance	Good	Excellent
Structural stability	Good	Good
Intricate machinability	Good	Difficult
Cost	Low	High

Table 2. Some physical and thermal properties of MoSi₂ and Si₃N₄ (Nathesan & Devi, 2000).

When composites were synthesized with elongated Si_3N_4 grains toughness can reach to 15 $\text{MPa m}^{1/2}$ (Nathal & Hebsur, 1997).

Designation	Microstructure
MS-60	Fully dense $\beta\text{-Si}_3\text{N}_4$, with long whisker-type morphology
MS-70	Fully dense $\beta\text{-Si}_3\text{N}_4$, with long whisker-type morphology
MS-80	Not fully dense $\beta\text{-Si}_3\text{N}_4$, with blocky morphology
MS-50	Fully dense $\alpha\text{-Si}_3\text{N}_4$, with blocky morphology
MS-40	Not fully dense $\alpha\text{-Si}_3\text{N}_4$, fine grained MoSi_2 and blocky $\alpha\text{-Si}_3\text{N}_4$

Fig. 3. Microstructures of different $\text{MoSi}_2\text{-Si}_3\text{N}_4$ composites.

However, a drawback of transformation toughening is that toughness decreases with increasing temperature, due to the thermodynamics of the phase transformation. Discontinuously reinforced ceramic composites have typically employed ceramic whiskers or particles as the reinforcing phases. An example is SiC whisker reinforced Si_3N_4 . Toughening mechanisms here are crack deflection and crack bridging. Discontinuous ceramic composites can reach toughness levels of 10 $\text{MPa m}^{1/2}$. One important variant of this approach is the in-situ toughening of Si_3N_4 due to the presence of elongated Si_3N_4 grains. By way of comparison to structural ceramics, the room temperature fracture toughness of polycrystalline MoSi_2 is approximately 3 $\text{MPa m}^{1/2}$, while the room temperature fracture toughness of equiaxed polycrystalline Si_3N_4 which is densified without densification aids is also 3 $\text{MPa m}^{1/2}$ (Petrovic, 2000). For comparison, two monolithic ceramics SiC and Si_3N_4 are also included in the figure. Further improvement in room temperature fracture can be achieved by microalloying MoSi_2 with elements like Nb, Al an Mg or by randomly oriented long whisker type $\beta\text{-Si}_3\text{N}_4$ grains (Hebsur, 1999).

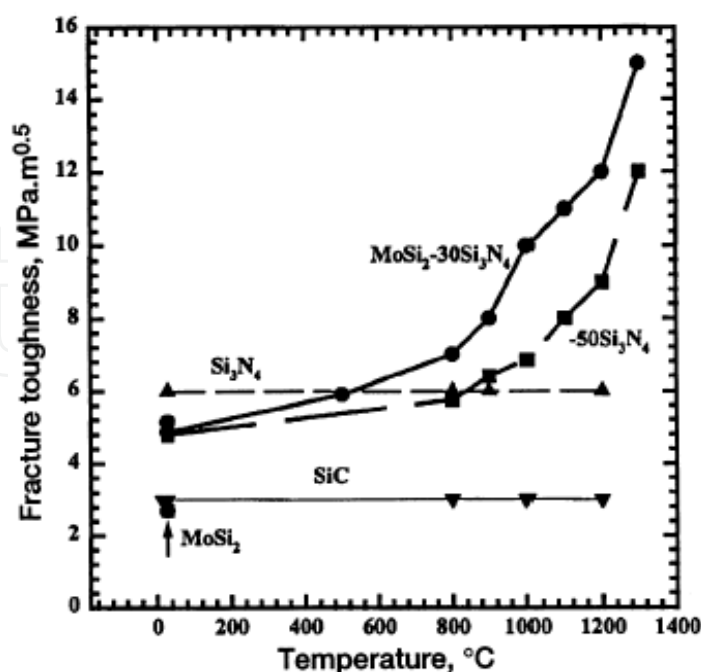


Fig. 13. Temperature dependence of fracture toughness of MoSi_2 -based materials compared with ceramic matrices (Hebsur, 1999).

MoSi₂-Si₃N₄-SiC hybrid discontinuous particle-continuous fiber composites have been developed with excellent room temperature fracture toughness, thermal shock resistance, and thermo-mechanical impact behavior. These hybrid composites consist of MoSi₂-Si₃N₄ particulate composites which form the matrix for SiC continuous fibers. The MoSi₂-Si₃N₄ portion of the hybrid composites has two functions. First, additions of 30-50.% Si₃N₄ to the MoSi₂ completely eliminates the oxidation pest behavior at the intermediate 500°C temperature. Second, the Si₃N₄ addition aids to match the thermal expansion coefficient of the matrix to that of the SiC fibers. This prevents thermal expansion coefficient mismatch cracking in the hybrid composite matrix.

Figure 14.(a) shows a SEM back scattered image of a fully dense MoSi₂-βSi₃N₄ composite (MS-70). During processing, the original α-Si₃N₄ powder particles are transformed into randomly oriented whiskers of β-Si₃N₄. These long whiskers are well dispersed throughout the material and appear to be quite stable, with very little or no reaction with the MoSi₂, even at 1900°C. In some isolated areas, the Mo₅Si₃ phase is visible. Figure 14.(b) shows a back scattered image of MoSi₂-βSi₃N₄ (MS-80) with the β-Si₃N₄ exhibiting a blocky aggregate-type morphology.

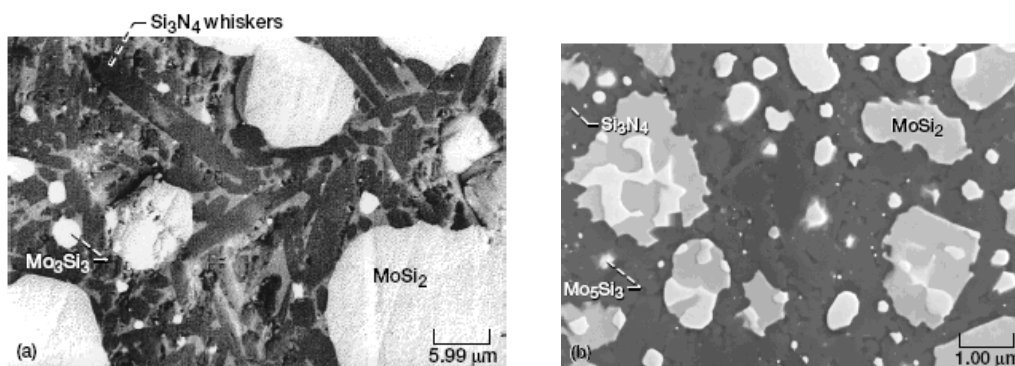


Fig. 14.(a) randomly oriented in-situ grown long whiskers of β-Si₃N₄ and large MoSi₂ particle size, (b) Si₃N₄ has a blocky particulate structure (Hebsur et al., 2001).

Density of (MS-70) is 4.57±0.01g/cm³ and Vickers microhardness is 10.7±0.6GPa. Figure 15. shows the coefficient of thermal expansion as a function of temperature for (MS-70). From this data the average coefficient for expansion of this composite material is about 4.0ppm/°C.

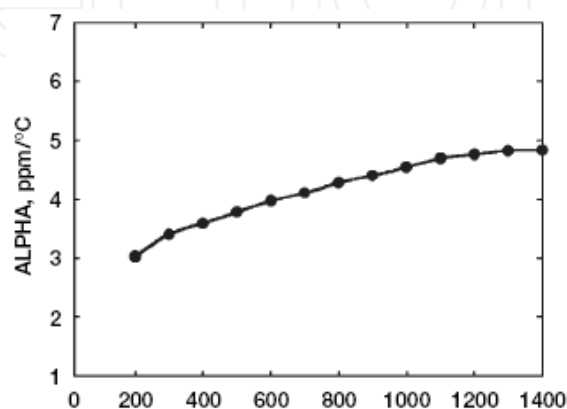


Fig. 15. The coefficient of linear expansion for MoSi₂-βSi₃N₄ (Hebsur et al., 2001).

The oxidation behaviour of a MoSiB alloy is also included for comparison. 500°C is the temperature for maximum accelerated oxidation and pest for MoSi₂-base alloys. There is interest in this alloy, over MoSi₂, for structural aerospace applications due to its attractive high temperature oxidation resistance (Bose, 1992; Berczik, 1997).

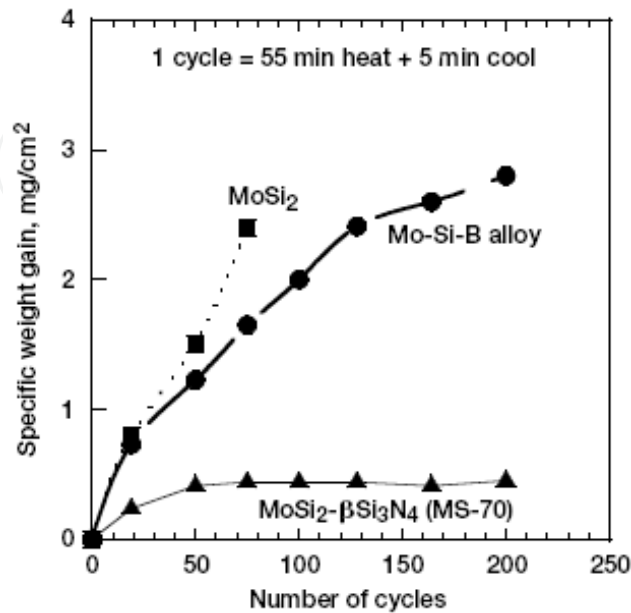


Fig. 16. Specific weight gain versus number of cycles of (MS-70) at 500°C (Hebsur, 2001).

However, the (MS-70) shows very little weight gain compared to binary MoSi₂ and the MoSiB alloy, indicating the absence of accelerated oxidation. In contrast the binary MoSi₂ and MoSiB alloys exhibit accelerated oxidation followed by pesting.

6. Conclusion

Based on the cyclic oxidation properties at 900°C, the family of MoSi₂-Si₃N₄ composites show promise for aircraft applications. The composites do not exhibit the phenomena of pesting, and the weight gain after 500h is negligible and superior to base line hybrid composites.

A wide spectrum of mechanical and environmental properties have been measured in order to establish feasibility of an MoSi₂ composite with Si₃N₄ particulate. The high impact resistance of the composite is of particular note, as it was a key property of interest for engine applications. Processing issues have also been addressed in order to lower cost and improve shape making capability. These results indicate that this composite system remains competitive with other ceramics as potential replacement for superalloys.

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