

MoSi₂ AND MoSi₂ - BASED MATERIALS AS STRUCTURAL CERAMICS

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Abstract : MoSi₂, because of its mixed covalent-metallic atomic bonding, is a borderline intermetallic compound which has many attractive properties that can be exploited in high temperature structural applications. Foremost amongst these is its stability in corrosive atmospheres up to about 1600 C. However, there are a few undesirable properties that need to be addressed before it can become a viable material in high temperature applications. Since MoSi₂ forms thermodynamically stable composites with both metals and ceramics, many reinforcing materials are incorporated into the matrix to improve the fracture toughness and creep properties. The low temperature oxidation can be controlled by compaction to high density. Mo(Al, Si)₂, a related ceramic, which also has good high temperature properties besides having better low temperature toughness. However, presence of Mo₅Si₃ phase, which has low oxidation resistance, needs to be controlled. This is being achieved by synthesizing Mo(Al, Si)₂ at as low a temperature as 1300 C. This article summarizes important attempts that are made in improving the properties of MoSi₂ by reinforcement with other materials.

Keywords : ceramics, MoSi₂, reinforcement, mechanical properties

1. INTRODUCTION

With the technological advancement in various fields, the demand on materials which can withstand high temperatures for long durations of time has increased. It is also necessary that these materials should tolerate high stresses in aggressive environments. The two critical requirements that must be satisfied in order for a structural material to be successfully used in elevated temperature applications are (i) high oxidation resistance to prevent degradation during high temperature exposure (ii) attractive combination of mechanical properties. Of the structural ceramics silicides and aluminides are gaining importance because of their corrosion resistance at high temperatures. The intermetallic compound MoSi₂ (with weak metallic bonding between Mo-Mo atoms and Mo-Si strong covalent bonds) has many attractive properties like high melting temperature (2030 C) and moderate density of 6.3 g/cc. It has high oxidation resistance at high temperatures in corrosive atmospheres. Other important and useful properties are,

- Good thermal conductor¹.
- Chemically, MoSi₂ has better resistance towards hot corrosion by NaCl, V₂O₅ and H₂S than best superalloys².
- Has a high Young's modulus of 440 GPa³.
- Undergoes a brittle-to-ductile transition (BDTT) around 1000 C and thus exhibiting plasticity above this temperature⁴.
- Can be machined by electrodischarge machining because of its high electrical conductivity.
- Can form thermodynamically stable alloys and composites with many other ceramics⁵.

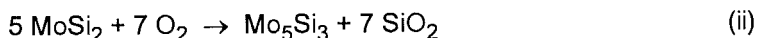
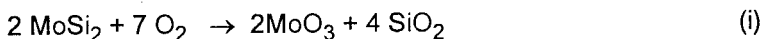
However, MoSi₂ has a few undesirable properties like

1. 'PEST'ing⁶
2. Low fracture toughness at low temperatures.
3. Low creep resistance at high temperatures⁷.

Before MoSi₂ related materials could be used for structural purposes in high performance engines the above shortcomings need to be addressed to. Extensive research to improve these properties is being carried out. In this article the various efforts that are being made will be reviewed.

2. 'PEST'ing

Oxidation in MoSi₂ proceeds as follows:



At lower temperatures (<1000 C) reaction (i) occurs and at high temperatures reaction (ii) becomes prominent. MoO₃ formed because of oxidation volatilizes around 700 C leaving behind a coating of SiO₂ on MoSi₂. The glassy SiO₂ layer does not permit diffusion of oxygen through it to attack the MoSi₂ underneath in the bulk and thus provides an anti-oxidation coating on MoSi₂. However, below 700 C, MoO₃ is still present on the surface of MoSi₂ and the oxide layer is highly porous providing a free passage for oxygen diffusion. Thus, the bulk of MoSi₂ is exposed to oxygen resulting in total oxidation with the disintegration of the compact. This phenomenon is termed as "PESTing"⁶. Pesting is found to be maximum around 500 C. Controlling pesting has been the topic of investigation for many years and extensive research is being carried out. According to some reports, pesting is more in samples with defects like pores, microcracks and intergranular boundaries as pesting is attributed to the accelerated formation of voluminous MoO₃ in the defects. Berztiss et al.⁸ reported that the arc melted MoSi₂ disintegrated to powder at 500 C in 43 h whereas in the HIPed samples cracks started appearing on the surface in 41 h. It was thought that the initial cracks and pores were the sites of internal oxidation which in turn was responsible for the disintegration. Chou and Nieh⁹, in the hot pressed commercial MoSi₂ (with 90% density) found severe pesting in 21h at 500 C. The arc melted samples inherently possess many cracks and pores which assist the oxidation to penetrate into the bulk of the compact. Chou and Nieh¹⁰ from their experiments on MoSi₂-AlN and MoSi₂-Al₂O₃ composites concluded that foreign additives have an adverse effect on the kinetics of the pest disintegration. At the same time Mitra et al.¹¹ found that there was no disintegration of compacts of MoSi₂ + 20 vol% SiC prepared by hot pressing even after 250 h heating at 500 C. Yanagihara et al.¹² noted that the oxidation properties of Mo₅Si₃ improved with the addition of boron.

In order to study effect of density Vs inclusions, Ramasesha and Shobu¹³ prepared high density (> 99% of theoretical density) MoSi₂ compacts with incorporated foreign phases like Mo₅Si₃, SiC and Mo₅Si₃C in addition to SiO₂ (which is invariably present in all MoSi₂ compacts) and attempted studying their effect on the pesting. MoSi₂, Mo(Al, Si)₂ and MoSi₂ + 1 wt% C were *in-situ* synthesized and compacted starting from the elements by hot pressing in argon atmosphere. The pressure was applied at room temperature and heated directly to temperatures in the range of 1700 to 1800 C. Fig. 1 shows the SEM of the samples before subjecting them to prolonged heating at 500 C. The dark spots seen MoSi₂ and Mo(Al, Si)₂ were amorphous silica. The SEM of Mo(Al, Si)₂ showed lighter phase was Mo₅Si₃. The Mo, Si and C mixture produced MoSi₂, Mo₅Si₃C (lighter phase in the SEM) and β - SiC (darker spots). Pesting experiments were carried out at 500 C for 100 h on rectangular samples cut from above compacts and polished with 1 μ diamond paste. After the oxidation test none of the samples disintegrated and crumbled into pieces as reported earlier. Monolithic MoSi₂ did not show any change at all whereas the

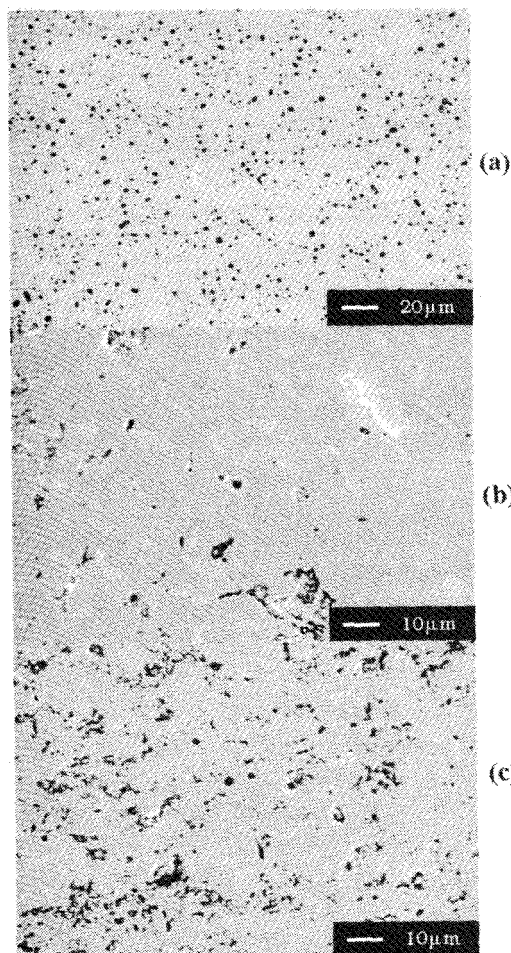


Fig. 1. SEM of high density (a) MoSi₂, the black spots are SiO₂; (b) Mo(AlSi)₂, the lighter islands are the Mo₅Si₃ and the darker phase is SiO₂; (c) MoSi₂ + 1 wt.% C, lighter Mo₅Si₃C and darker SiC phases are observed.

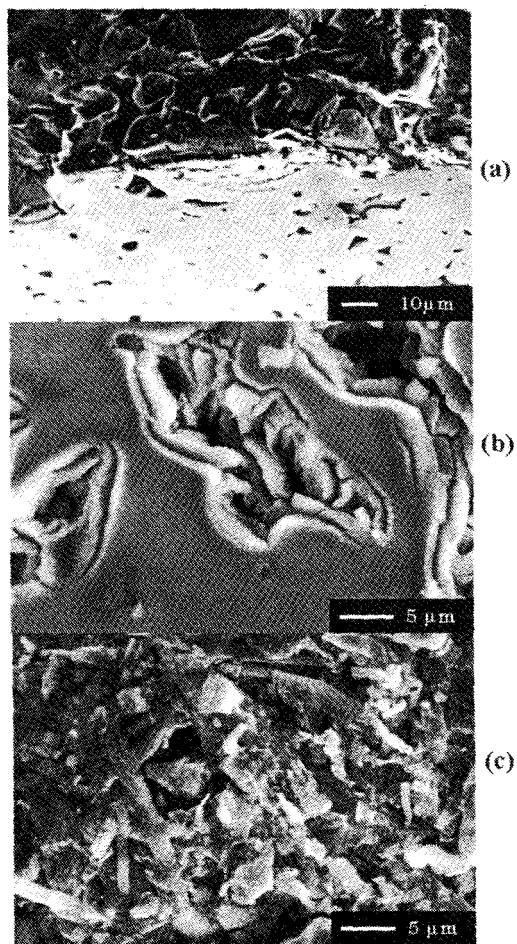


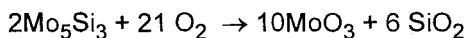
Fig. 2. SEM of the samples after oxidation experiment (a) MoSi₂, at the edge of the fractured surface. No visible oxidation on either surface; (b) the open blisters on the surface of Mo(Al, Si)₂. MoO₃ rods are seen inside the open blisters; (c) MoO₃ rods are seen on the surface of MoSi₂ + 1 wt.% C.

Mo(Al, Si)₂ and MoSi₂ + 1 wt% C specimens were covered with deep bluish green layer. Fig. 2 shows the SEM of samples after oxidation test. Samples were fractured intentionally at the center to see if any changes had taken place in the bulk. The polished top surface as well as the fractured bulk surface were observed under the SEM. The micrograph of MoSi₂ taken at the edge of the fractured surface showed both the surfaces. There was no indication of any MoO₃ or more silica spots than before the oxidation experiment. Mo(Al, Si)₂ surface had many open blisters containing rod like MoO₃ in them and the surface of the blister was still Mo(Al, Si)₂ implying that there is no oxidation of Mo(Al, Si)₂ confirming the observation of Maruyama and Yanagihara¹⁴. Mo₅Si₃ that was present before heating was no longer present in the oxidized samples. It seems likely that the Mo₅Si₃ is preferentially oxidized as Mo₅Si₃ has poor oxidation resistance than MoSi₂. The oxidation of Mo₅Si₃ proceeds as,

Table I. Compatibility of reinforcements with intermetallic and ceramic matrices⁵.

Matrix	Compatibility with the following reinforcement materials							
	SiC	Si ₃ N ₄	Al ₂ O ₃	TiC	TiB ₂	ZrB ₂	Y ₂ O ₃	Nb
MoSi ₂	C	C	C	C	C	C	C	R
CoSi ₂	C	C	C	C	C	C?	C/WR	R
Cr ₃ Si	C	C	C	C	C	R	C	R
Ti ₅ Si ₃	R	R?	C	C	C	R	C?	C
NiAl	C/WR	C/WR	C	C/WR	C/WR	C/WR	C/WR	R
Ni ₃ Al	R	R?	C	R	R	C/WR	C/WR	R
TiAl	R	R?	C/WR	R	C/WR	R	C/WR	R
Ti ₃ Al	R	R?	C/WR	R	R	R	C/WR	R
SiC	C	C	R	C	C	R	R	R

C : chemically compatible with no interfacial reactions; *C/WR* : chemically compatible with interfacial reactions; *R* : chemically unstable with the (a) formation of one or more interface reaction products; or (b) diffusion of one or more elements into the matrix; ? : possible estimates.



The change in volume could be responsible for the formation and opening up of the blisters. No such blisters were observed in MoSi₂ + 1 wt% C which had only MoO₃ whiskers and SiO₂ on the surface. It is possible that the passage of oxygen through Mo₅Si₃C is more difficult than Mo₅Si₃. Hence blisters are not formed underneath the top surface to burst. Mo₅Si₃C reacts with oxygen to form MoO₃, SiO₂ and CO₂. MoO₃ and SiO₂ are seen on the surface of the oxidized sample.

None of the samples, as seen by the SEM of fractured surfaces, showed any indication of oxidation in the bulk. Though the Mo(Al, Si)₂ and MoSi₂ + 1 wt% C samples exhibited severe surface oxidation, the fractured surface SEM did not show any oxidation inside the body of the specimen. The oxidation was very superficial. If the grain boundaries are the sites for the oxide formation, then the disintegration has to be more in hot pressed samples as the area of grain boundaries per unit volume is higher in them than in arc melted sample. Maruyama and Yanagihara¹⁴ made a significant observation that in the cross-section of the oxidized samples, one grain had more oxygen than another in the neighborhood did. Some grains did not have any oxygen at all indicating that the grain boundary may not be the prime site for oxidation. The disintegration would occur due to the oxide formation in the pre-existing defects. The volumetric change associated with the decomposition of MoSi₂ is more than double which would extend the cracks. Hence for complete pesting large number of pores and cracks are needed which are present in low-density compacts. No oxidation was observed in the high density monolithic MoSi₂ compacts made by Ramasesha and Shobu¹³ whereas very superficial oxidation with no penetration into the bulk was present in high density MoSi₂ with foreign phases. Hence the high density of the samples had prevented the diffusion of oxygen providing evidence to the hypothesis that presence of small amounts of impurities is not as detrimental for pesting failure of the compacts as presence of defects like cracks and pores. Hence pesting problem can be overcome by having compacts of high density (i. e. >95%).

Table II. Fracture toughness, hardness and flexural strength of hot pressed and spray deposited monolith of MoSi₂ and its composites.

Sample	Sample condition	Fracture toughness (MPa m ^{1/2})	Hardness (GPa)	Flexural strength (MPa)
MoSi ₂	Hot pressed ¹⁵ As sprayed ¹⁶	2.58 - 5.1 ~ 4.7 (S.D) ~2.7 (P.S.D)	8.6 - 10 ~10.3	225 - 280 280
	Sprayed + HIP ¹⁶	~3.6 (S.D) ~3.2 (P.S.D)	~10.06	364
MoSi ₂ + Al (2.5 - 8.1 wt.%)	Hot pressed ¹⁵	3.6 - 4.3	7.9 - 8.3	-
MoSi ₂ + Ta (10 - 20 wt.%)	As sprayed ¹⁶	~6.9 (S.D) ~4.4 (P.S.D)	~8.65	
	Sprayed + HIP ¹⁶	~5.9 (S.D) ~4.9(P.S.D)	~7.86	
MoSi ₂ + Nb (20 - 25 vol.%)	Hot pressed ^{18,19,20}		8.2 - 8.75	
	Particles	~7.5		
	Fibres Foils	15.2 ± 2.2 15.2 ± 1.3		
MoSi ₂ + Al ₂ O ₃	Laminate ²¹	8.57		220 - 240
	Fibres ²²	9.02		
MoSi ₂ + ZrO ₂ (PSZ) (10 - 30 vol.%)	Hot pressed ²³	6 - 7.5	8.49	
MoSi ₂ + TiC	Hot pressed ²⁴	5.0		125.3
MoSi ₂ + TiB ₂	As sprayed ²⁵	6.1	~10.6	380
MoSi ₂ + SiC (1 - 4wt.%)	Hot pressed ²⁶	4- 6	10 - 14	
MoSi ₂ + SiC (10 - 40 vol.%)	Hot pressed ^{27,28}			
	Particles	4.7 - 8.7	~11.5	350
	whiskers	4.5 - 7.5	~10.7	
	As sprayed ²⁹	5.4	~12.03	300
	Sprayed + Heat treated ²⁹	7.8	~11.37	410

S. D. — Measured along the sprayed direction; P. S. D.— Perpendicular to the sprayed direction

3. MECHANICAL PROPERTIES

MoSi₂ undergoes brittle to ductile transition around 1000 C. Below this temperature MoSi₂ has low fracture toughness while high temperature strength is governed by plastic flow. To improve the mechanical properties of MoSi₂ it is necessary to reinforcement it with other materials as it is well known that the properties of the composite are better than individual components. Unlike many high temperature structural ceramics including SiC, MoSi₂ is compatible with most of the stable ceramics (Table I).

Improvement in fracture toughness was found by the reinforcement of ductile as well as ceramic phases. Fracture toughness of MoSi₂ is in the range of 2.6 to 5.1 MPa m^{1/2} at room temperature^{15, 16}. Fracture toughness was found to increase with decrease in grain

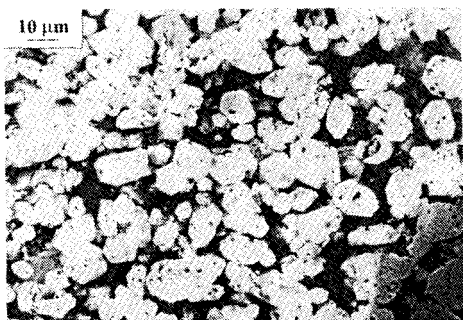


Fig. 3. 85% density MoSi₂ preform infiltrated with aluminium at 1200°C and annealed at 1600°C for 10 min. the Mo(Al,Si)₂ (lighter phase) particulates exhibiting hexagonal morphology. the dark phase is aluminium.

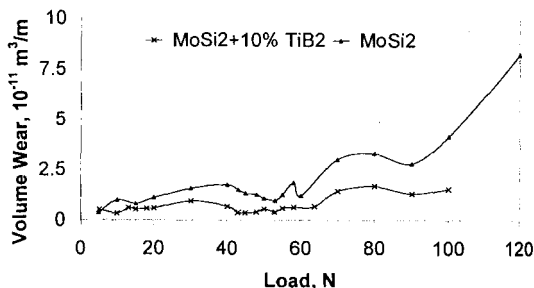


Fig. 4. Volume wear as a function of load for monolithic and 10 wt.% TiB₂ reinforced MoSi₂.

temperature strength was observed. Many other oxide and non-oxide ceramics has been reinforced in order to enhance the fracture toughness of MoSi₂. Table II summarizes the results obtained. The toughness of the SiC composite was found to be a function of volume fraction of SiC^{27, 28, 30}. In the SiC particulate reinforcement maximum toughness was obtained with 20 vol% SiC. The reinforcement of partially stabilized zirconia (PSZ) into MoSi₂ matrix was found to improve the mechanical properties of MoSi₂ due to its low temperature transformation toughening³¹. In the neighbourhood of the crack tip stress field, the tetragonal particles transform to the monoclinic structure with an associated volume increase of ~ 4%. This crack induced structural phase transformation shields the crack from external stress thereby improving the toughness. The increase in the toughness with SiC and ZrO₂ double reinforcement was greater than that with ZrO₂ alone. 3 mol% Y₂O₃ stabilised ZrO₂ (3Y-ZrO₂) reinforcement was also attempted. In this system the microstructure consisted of MoSi₂ matrix with Mo₅Si₃C and well crystallized ZrSiO₄. The glassy silica at the grain boundaries reacted with ZrO₂ to form crystalline zircon. The fracture strength was found to be maximum (~1050 MPa) with reinforcement of >15 mol% 3Y-ZrO₂ and the fracture toughness improved to about 4.5 MPa m^{1/2}.

Many workers are investigating aluminum reinforcement into MoSi₂ matrix. Fracture toughness increased with increase in aluminum content in the matrix. This was attributed to the formation of a more ductile Mo(Al, Si)₂ phase with C40 structure. Mitra et al.³² have varied the Al content from 1. 5 to 5 wt% in MoSi₂ matrix. It was found that the Al reduced SiO₂ content in MoSi₂ to form Al₂O₃. The surplus Al reacted with MoSi₂ to form Mo(Al, Si)₂. Hence the compacts with high Al content had three phases, namely, MoSi₂, Mo(Al, Si)₂ and α - Al₂O₃. The fracture toughness increased to 6.4 MPa m^{1/2} in 5 wt % Al.

Since Mo(Al, Si)₂ is found to have good oxygen resistance and also good fracture toughness it is drawing a lot of attention in recent times. Ramasesha and Shobu³³ made Mo(Al, Si)₂ - Al composites by reactive infiltration technique. Here a preform of MoSi₂ with different densities was infiltrated with Al. During infiltration Al reacts with MoSi₂ to form Mo(Al, Si)₂. The infiltration could be achieved at as low a temperature as 1050 C and density of the preform as high as 85 %. Another interesting thing observed was that after infiltration if the specimen was annealed around 1600 C for short duration of 10 min. the Mo(Al, Si)₂ particulates attained hexagonal morphology (Fig. 3). Since the infiltration

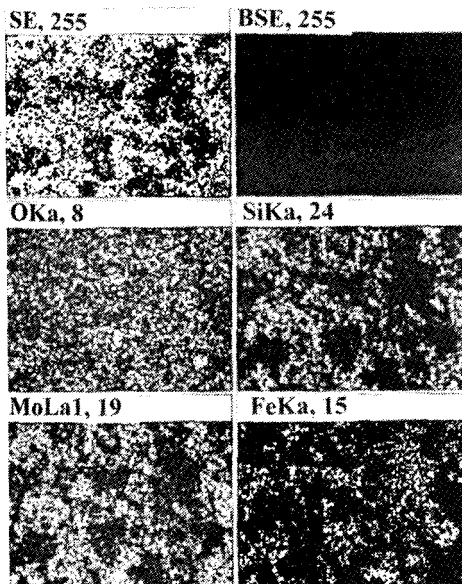


Fig. 5. X-ray mapping of MoSi₂ pin surface after the wear experiment showing the presence of Fe and O.

could be obtained at low temperatures it may be possible to synthesize Mo(Al, Si)₂ at low temperatures. It was attempted by Zhang et al.³⁴ by taking MoSi₂, Mo and Al. The room temperature bending strength was found to be 310 MPa and fracture toughness of 3 MPa m^{1/2}, when hot pressed for 10 min. However, their samples contained two different types of particles with different Al content.

In order to obtain single phase Mo(Al, Si)₂, Mo, Si and Al were taken in required proportion and hot pressed at different temperatures. It was found that single phase Mo(Al, Si)₂, in the absence of excess Al, is formed in the temperature range of 1300 to 1400 C³⁵. The sample synthesized at 1500 C contained many impurity lines of Mo₅Si₃ in the x-ray diffraction pattern. The SEM of the sample synthesized at 1300 C showed a single type of particles. Thus, Mo(Al, Si)₂ is a MoSi₂ related ceramic which may have good mechanical properties for structural applications and these properties are currently under study.

Beyond BDTT, the MoSi₂ undergoes plastic deformation and the creep deformation increases with increasing temperature. Also the presence of silica at the grain boundary enhances the deformation at high temperatures. The reinforcement of Mo, W, C and SiC significantly improved the creep resistance of MoSi₂²¹. Creep of SiC-MoSi₂ composites has been widely studied. SiC particulates and whiskers have been used. Creep rate in monolithic MoSi₂ was found to be around 10⁻⁶ to 10⁻⁴ /s for stresses up to 10³ MPa. The addition of 40 vol % SiC decreased the creep rate to about 10⁻⁸ /s for the same stress

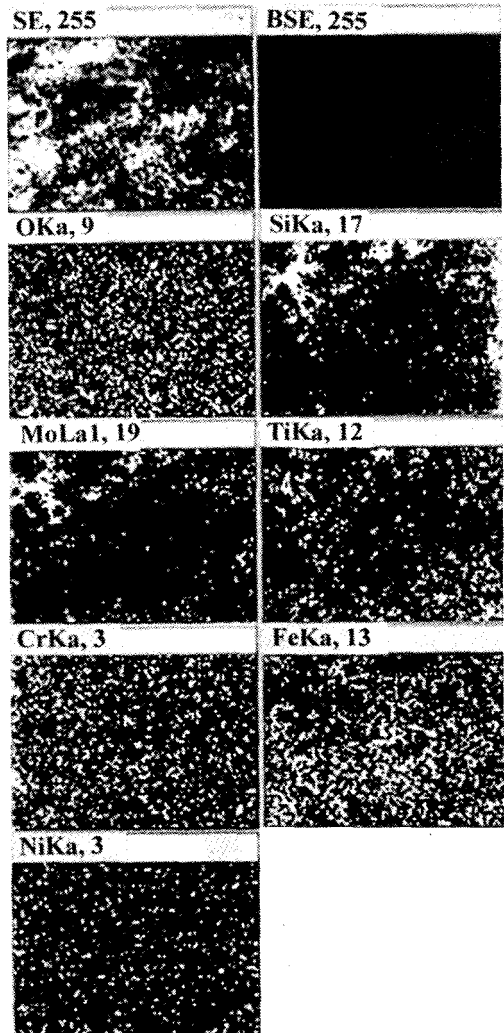


Fig. 6. X-ray mapping of MoSi₂ + 20 wt.% TiB₂ pin surface after wear experiment displaying the presence of Fe, Cr, Ni and O.

ranges³⁶. SiC whisker reinforcement improved the creep properties further as found in MoSi₂ - WSi₂ with 20 vol% SiC(w) where the creep rate was 10⁻⁹ to 10⁻⁷ /s²³.

Wear experiments on MoSi₂ were carried out on pin-on drum apparatus with 150 grit garnet and 150 grit SiC cloth. These experiments indicated that as the hardness of the abrasive increased relative to the hardness of MoSi₂, volume wear increased. Niobium (both fibers and particles) reinforced MoSi₂ exhibited almost 50 % less volume wear than the monolith on garnet³⁷. Wear experiments on 10 and 20 wt% TiB₂ reinforced MoSi₂ have been carried out with pin-on-disc arrangement on EN 24 disc³⁸. It was found that the volume wear in the composite was less than that in the monolith Fig. 4. Ploughing on the disc was evident. A thin reddish brown coating was observed on both monolithic and the reinforced specimens. EDX analysis of the coating showed the presence of Fe, Ni, Cr and O. During wear experiments, because of the friction at the contact area of the specimen and the disc, its temperature increases which would lead to oxidation of the wearing surfaces. The coating in this case could be Fe₂O₃ and Cr₂O₃. Figs. 5 and 6 show the x-ray mapping of monolithic and 20 wt. % TiB₂ reinforced MoSi₂ specimens after the wear experiments. Though monolithic MoSi₂ also showed the presence of Cr and Ni on the surface after the wear experiment, it is not included in Fig. 5. Analysis of these results is in progress.

Thus, MoSi₂ has many attractive properties like good oxidation resistance, high hardness, high temperature ductility etc. Because it can form thermodynamically stable composites with other materials, the undesirous properties like low fracture toughness and creep properties can be improved in order to make MoSi₂ a useful high temperature structural ceramic. Having high density compact can also control the low temperature pesting problem. The major attraction in developing MoSi₂ for applications over other silicon-based ceramics is that it can be machined by the electrodischarge machining because of its high electrical conductivity and hence machining complicated shapes can be inexpensive.

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