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AUTHOR(S) John J. Petrovic
A. K. Vasudevan

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A PERSPECTIVE ON $MoSi_2$ BASED COMPOSITES

J.J. PETROVIC* AND A.K. VASUDEVAN**
*Materials Science and Technology Division, Group MST-4, Los Alamos National Laboratory, Los Alamos, NM 87545
**Office of Naval Research, Code 1222, 800 North Quincy Street, Arlington, VA 22217-5000

ABSTRACT

$MoSi_2$ based composites represent an important new class of "high temperature structural silicides", with significant potential for elevated temperature structural applications in the range of 1200-1600 °C in oxidizing and aggressive environments. The properties of $MoSi_2$ which make it an attractive matrix for high temperature composites are described and the developmental history of these materials traced. Latest results on elevated temperature creep resistance, low temperature fracture toughness, and composite oxidation behavior are summarized. Important avenues for future $MoSi_2$ based composite development are suggested.

INTRODUCTION

$MoSi_2$ based composites are attracting increasing attention as high temperature structural materials [1]. The purpose of the present discourse is to provide a perspective on these silicide-based materials, describing their characteristics, highlighting key recent research results, and suggesting important avenues for further development.

The intermetallic compound $MoSi_2$ was first investigated by Hoenigschmid in 1907 [2]. Due to its excellent high temperature oxidation resistance and brittle characteristics at low temperatures, it was initially used as an oxidation resistant coating material for metals. Later, based on its electrical conductivity, it was employed as a heating element material for electrical resistance furnaces [3]. This heating element application continues to the present.

In the early 1950's, Maxwell first suggested the use of $MoSi_2$ as an elevated temperature structural material [4], and determined some of its high temperature mechanical properties. However, due to the low temperature brittle nature of $MoSi_2$, Maxwell's work was not continued, since the materials community at that time did not possess the tools to deal with brittle structural materials.

In the 1970's, Fitzer began examining $MoSi_2$ composites reinforced with Al_2O_3, SiC, and Nb wire as a means to improve the mechanical properties of $MoSi_2$ [5]. Encouraging results obtained by Fitzer lead to a review article by Schlichting [6], suggesting the use of $MoSi_2$ as a matrix material for high temperature structural composites.

Two key articles were published in 1985. The first was an article by Fitzer and Remmele [7], describing in detail their investigations of Nb wire-$MoSi_2$ matrix composites. In particular, they showed that Nb wire reinforcements significantly improved the room temperature mechanical properties of such composites. The second article was by Gac and Petrovic [8], in which they established the feasibility of SiC whisker-$MoSi_2$

matrix composites, demonstrating improvements in room temperature strength and fracture toughness.

In 1988, Carter et.al. [9] established that submicron SiC whisker-$MoSi_2$ matrix composites exhibited mechanical properties within the range of high temperature engineering applications. This lead to an acceleration of research interest in these materials by industry, academia, and government laboratories. In November 1991, the First High Temperature Structural Silicides Workshop was held at NIST in Gaithersburg, MD under the sponsorship of the Office of Naval Research. Many of the recent research results discussed here were presented at that Workshop.

PROPERTIES OF $MoSi_2$

Of the many known silicide compounds, $MoSi_2$ appears the most promising for elevated temperature structural applications, due to the following combination of properties. $MoSi_2$ possesses a high melting point, 2030 °C, and excellent high temperature oxidation resistance. Although brittle at low temperatures, it exhibits a brittle-to-ductile transition at approximately 1000 °C (compressive deformation of single crystals), with deformation by dislocation plasticity above this temperature. $MoSi_2$ is thermodynamically stable with potential ceramic reinforcements such as SiC, ZrO_2, Si_3N_4, Al_2O_3, TiB_2, and TiC [10], and may also be alloyed with other high melting point silicides such as WSi_2 [11]. $MoSi_2$ is an abundant, low cost material which is non-toxic and environmentally benign. Additionally, due to its low electrical resistivity (10 micron-ohm cm at room temperature), it can be electro-discharge machined, which is a significant benefit for the low cost fabrication of components.

The crystal structure of $MoSi_2$ is tetragonal, with c = 0.785 nm and a = 0.32 nm. Dislocations in $MoSi_2$ have been observed to have <100>, <110>, and 1/2<111> burgers vectors [12]. Studies of the elevated temperature compressive deformation of single crystals have indicated an onset of ductility at 1000 °C and yield stress levels of 300-800 MPa at 1100 °C and 50-270 MPa at 1500 °C, depending on crystallographic orientation [13]. Bend tests on low oxygen content, large grained, polycrystalline $MoSi_2$ indicate a brittle-to-ductile transition in flexure in the vicinity of 1350 °C, with a flexural yield stress at 1400 °C of 210 MPa [14]. The room temperature fracture toughness of polycrystalline $MoSi_2$ is 3 MPa $m^{1/2}$, and the fracture mode is 75% transgranular and 25% intergranular at room temperature [15]. Its hardness is 9 GPa. The thermal expansion coefficient of $MoSi_2$ is 7-10 x 10^{-6} C^{-1} in the range of 20-1400 °C, and is a reasonably close match to that of Al_2O_3. Its thermal conductivity is 65 W/mK at room temperature and decreases to 30 W/mK at 1400 °C. These conductivity values are intermediate between Si_3N_4 and SiC.

The elevated temperature oxidation resistance of $MoSi_2$ is similar to that of SiC, since it forms a very protective, adherent, and coherent SiO_2 layer. Recent work [16] has shown that the maximum oxidation rate occurs at 500 °C, an intermediate temperature range where oxidation pesting can occur under certain conditions. However, pest behavior is not observed in stress-free single crystals of $MoSi_2$, or in dense polycrystalline

materials. Pest behavior can also be minimized by the addition of $MoGe_2$ [7], which alters the viscosity and thermal expansion coefficient of the oxidation layer.

$MoSi_2$ may be alloyed with other high melting point silicides as a means of improving mechanical properties [11]. It has been shown that solid solution alloying with WSi_2 improves high temperature mechanical properties [17]. A recent interesting observation is the ubiquity of the C40 hexagonal phase in alloys of $MoSi_2$ with other disilicides such as $TiSi_2$ [18]. However, it should be noted that all other disilicides and trisilicides have an oxidation resistance inferior to that of $MoSi_2$.

$MoSi_2$ COMPOSITES

$MoSi_2$ possesses excellent elevated temperature oxidation resistance. However, for $MoSi_2$ to be used as an oxidation-resistant elevated temperature structural material, both its high and low temperature mechanical properties must be significantly improved. This dictates improvements in high temperature strength and creep resistance, and low temperature fracture toughness.

The composite approach with $MoSi_2$ as the matrix can produce such mechanical property improvements. $MoSi_2$ is stable with a large number of carbide, nitride, oxide, and boride ceramic reinforcements, such as SiC, TiC, Si_3N_4, ZrO_2, Al_2O_3, Y_2O_3, TiB_2, and ZrB_2 [1,10]. It is reactive with refractory metals such as Nb, Ta, Mo, and W. $MoSi_2$ also reacts with carbon.

Significant issues for $MoSi_2$ composites include reactivity of reinforcement and matrix, thermal expansion coefficient mismatch, low temperature fracture toughness, elevated temperature creep resistance, and both intermediate and high temperature oxidation resistance. To date, the most extensively studied $MoSi_2$ based composites have been SiC-$MoSi_2$, ZrO_2-$MoSi_2$, C-$MoSi_2$, Al_2O_3-$MoSi_2$, TiB_2-$MoSi_2$, and refractory metal-$MoSi_2$. Key research findings on the properties of selected $MoSi_2$ composites will now be discussed.

COMPOSITE ELEVATED TEMPERATURE CREEP RESISTANCE

Adequate creep resistance is a central issue for high temperature structural materials. The creep behavior of SiC-$MoSi_2$ composites has been examined the most extensively to date [19,20,21]. Observed creep rates are shown in Table I.

A number of aspects may be noted in Table I. Absolute creep rate values reported by the different investigators are not totally consistent with one another. This may be related to differences in processing of the various materials examined. Reinforcement with SiC whiskers significantly reduces the creep rate by more than an order of magnitude, while incorporating WSi_2 in solid solution with $MoSi_2$ also leads to lower creep rates. Low creep rates are observed in SiC reinforced composites with a $MoSi_2$-WSi_2 alloy solid solution matrix, suggesting additive effects of reinforcement and solid solution on creep rate. Creep rates in tension are higher than in compression. The creep rate of a $<210>$ oriented $MoSi_2$ single crystal is similar to that of polycrystalline $MoSi_2$.

The lowest creep rates observed at 1200 °C and 50 MPa for current $MoSi_2$ based composites are of the order of 10^{-8} s^{-1}. Such creep rate levels would lead to 1% creep strain in approximately 300 hours at this temperature and stress. By way of comparison, the creep rate under these conditions for a MAR-M-509 superalloy is 3×10^{-5} s^{-1}, three orders of magnitude higher than the $MoSi_2$ based composites.

Table I. Creep Rates for $MoSi_2$ Materials at 1200 °C and 50 MPa

Material	Test Type	Creep Rate (s^{-1})	Ref.
$MoSi_2$ HP	Compression	1.5×10^{-6}	19
$MoSi_2$ HP	Compression	9×10^{-6}	20
$MoSi_2$ HIP	Compression	4×10^{-7}	20
50/50 $MoSi_2$-WSi_2 HP	Compression	1.5×10^{-6}	19
50/50 $MoSi_2$-WSi_2 HP	Compression	1.6×10^{-7}	20
20% SiC(w)-$MoSi_2$ HP	Compression	1.6×10^{-8}	19
20% SiC(w)-$MoSi_2$ HP	Compression	1.6×10^{-7}	20
20% SiC(w)-$MoSi_2$ HIP	Compression	1.8×10^{-8}	20
20% SiC(p)-$MoSi_2$/WSi_2 HIP	Compression	6×10^{-8}	20
20% SiC(w)-$MoSi_2$/WSi_2 HP	Compression	5×10^{-9}	21
20% SiC(w)-$MoSi_2$/WSi_2 HP	Tension	2.5×10^{-8}	21
$MoSi_2$ single crystal <210>	Compression	1×10^{-7}	20

HP = hot pressed HIP = hot isostatically pressed

Observed creep parameters for $MoSi_2$ materials are summarized in Table II. The data in Table II provide some initial insight into creep mechanisms in $MoSi_2$ materials. Creep stress exponents are in the approximate range of 2-3. A creep stress exponent of 1 is indicative of viscous flow processes. Exponents in the range of 1-3 suggest a combination of viscous flow and power law dislocation creep. Stress exponents of 3-4 indicate dislocation recovery controlled by self diffusion, while exponents greater than 4 are taken to indicate the glide/climb of dislocations.

The stress exponent results for polycrystalline $MoSi_2$ materials suggest that dislocation processes play a major role in creep deformation. It is also possible that grain boundary sliding with cavitation due to the presence of viscous silica phases at the grain boundaries is an additional creep mechanism in current materials. This may account for the observed creep rate differences in tension and compression. Self diffusion activation energies in $MoSi_2$ are not well known. The activation energy for Si diffusion in $MoSi_2$ is indicated to be approximately 250 kJ/mole [22,23]. Based on creep data, Sadananda et.al. [19] have inferred an activation energy of 350-540 kJ/mole for Mo diffusion in $MoSi_2$,

suggesting that Mo diffusion may be the rate controlling process for dislocation creep mechanisms.

Table II. Creep Parameters for $MoSi_2$ Materials

Material	Test Type	Temp. (°C)	Stress Exponent	Activation Energy (kJ/mole)	Ref.
$MoSi_2$	Compression	1100-1300	1.75	380	19
$MoSi_2$	Compression	1200	3	306	20
50/50 $MoSi_2$-WSi_2	Compression	1100-1300	2.27	540	19
50/50 $MoSi_2$-WSi_2	Compression	1200	3	306	20
20% SiC(w)-$MoSi_2$	Compression	1100-1450	2.63	460	19
20% SiC(w)-$MoSi_2$	Compression	1200	3	306	20
20% SiC(w)-$MoSi_2$/WSi_2	Compression	1150-1225	2.3	312	21
20% SiC(p)-$MoSi_2$/WSi_2	Compression	1200	3	306	20
20% SiC(w)-$MoSi_2$/WSi_2	Tension	1100-1200	3.2	557	21
$MoSi_2$ single crystal	Compression	1200	3	251	20

COMPOSITE FRACTURE TOUGHNESS

Since $MoSi_2$ is a brittle material below its brittle-to-ductile transition temperature, composite approaches to improve low temperature fracture toughness generally follow those employed for structural ceramic materials. Evans [24] has recently summarized such approaches, indicating that composite toughening mechanisms decrease in effect in the following order: continuous fibers, metal dispersed particles, transformation toughening, whiskers/platelets/particles, microcracking.

Table III. Room Temperature Fracture Toughness of $MoSi_2$ Based Composites

Type of Reinforcement	Highest Fracture Toughness (MPa $m^{1/2}$)	Ref.
Refractory metal (Nb,W,Mo) wires	Greater than 15	7, 25
20 vol. % Ta particles	10	26
20 vol. % ZrO_2 particles	7.8	27
20 vol. % SiC whiskers	4.4	28
20 vol. % SiC particles	4.0	29
Polycrystalline $MoSi_2$	3	15

Current low temperature fracture toughness results for $MoSi_2$ based materials are summarized in Table III. It is evident from Table III that $MoSi_2$ composites can possess significantly higher room temperature fracture toughness than polycrystalline $MoSi_2$.

Refractory metal wires and particles have exhibited the highest toughness levels to date. However, the oxidation resistance of such composites can be poor. In addition, $MoSi_2$ is not thermodynamically stable with the refractory metals, and thus coatings are required on refractory metal reinforcements in order to minimize reaction effects. Concerning such effects, Maloney and Hecht [25] have observed that oxide "plugs" form over the refractory metal fibers of W-3%Re fiber reinforced $MoSi_2$ composites when exposed to air at 1400 °C, which protect the fibers from further oxidation. They have employed Al_2O_3 coatings on the fibers to minimize reaction effects with $MoSi_2$.

ZrO_2 transformation toughening effects can produce substantial toughening in $MoSi_2$ based materials. Highest toughness levels to date have been obtained with unstabilized ZrO_2, and appear to be associated in part with microcrack toughening mechanisms. A very intriguing additional aspect occurring in unstabilized ZrO_2-$MoSi_2$ composites is the "pumping" of dislocations into the $MoSi_2$ matrix as a result of the volume change associated with the spontaneous ZrO_2 tetragonal-to-monoclinic phase transformation [27]. Upon cooling from the fabrication temperature (1700 °C), this transformation initiates in the vicinity of 1175 °C. The unstabilized zirconia transformation temperature is above the brittle-to-ductile transition of $MoSi_2$, and so dislocation "pumping" occurs as a result of the spontaneous ZrO_2 transformation strains. R-curve behavior and synergistic toughening effects with combined ZrO_2-SiC reinforcements have also been observed [27]. Presence of ZrO_2 does not significantly degrade the elevated temperature oxidation resistance of ZrO_2-$MoSi_2$ composites [30].

Only moderate room temperature toughening effects are derived from submicron SiC whiskers and particles. Toughening levels for these reinforcements are similar to those observed in ceramic matrix composites [31], and are associated with mechanisms such as crack deflection and crack bridging.

A very important recent observation is that grain boundary silica phases, resulting from oxygen on the surfaces of commercial $MoSi_2$ powders, have a detrimental effect on the elevated temperature fracture toughness of polycrystalline $MoSi_2$ materials [32,33]. This occurs because presence of the silica phase promotes grain boundary sliding deformation mechanisms. When the grain boundary silica is removed by reaction with carbon additions, fracture toughness increases with increasing temperature, due to the operation of dislocation plasticity mechanisms. The fracture toughness of polycrystalline $MoSi_2$ containing 2 wt.% carbon has been reported to be 11.5 MPa $m^{1/2}$ at 1400 °C, with a "graceful failure" stress-strain response due to plasticity effects [33].

COMPOSITE OXIDATION BEHAVIOR

It is important that $MoSi_2$ composite development avenues lead to materials with acceptable oxidation behavior at both elevated and intermediate temperatures. The oxidation of $MoSi_2$ based composites has recently been investigated by Cook et.al. [34],

for composites synthesized by the XD™ process with various types of reinforcements. Cyclic oxidation results from this study are summarized in Table IV.

Table IV. 72 Hour Cyclic Oxidation of $MoSi_2$ Composites at 1200 °C and 1500 °C

Material	1200 °C Weight Gain (mg/cm^2)	1500 °C Weight Gain (mg/cm^2)
$MoSi_2$	0.1	0.4
30% SiC-$MoSi_2$	0.01	0.5
30% TiB_2-$MoSi_2$	0.6	2.8
30% HfB_2-$MoSi_2$	0.7	2.0
30% ZrB_2-$MoSi_2$	2.7	7.3

These cyclic oxidation results indicate that SiC-$MoSi_2$ composites possess the best elevated temperature oxidation resistance in comparison to pure $MoSi_2$, and that TiB_2-$MoSi_2$ and HfB_2-$MoSi_2$ also possess reasonable oxidation resistance.

Cook et.al. [34] also performed intermediate temperature oxidation studies at 500 °C, for both static and cyclic conditions. With the exception of the SiC reinforcement, none of the materials in Table IV exhibited oxidation pest behavior. Pest behavior was not observed either statically or after 1200 °C.cycling for the SiC-$MoSi_2$ composites, but was observed after 1500 °C cycling. The occurrence of pest behavior was attributed to the large particle size of the SiC reinforcement, since particles on the order of 50 microns were present in the composite matrix. It is likely that these large particles in combination with the thermal expansion mismatch between SiC and $MoSi_2$ lead to thermal stress-induced cracking and associated pesting.

These intermediate temperature oxidation results make it clear that thermal expansion coefficient mismatch and reinforcement size effects must be kept in view in $MoSi_2$ based composite development. For SiC reinforcements, this dictates that the size of the SiC phase should be kept as small as possible, so as to eliminate thermally induced cracking. It may also indicate the use of pest inhibiting additives such as $MoGe_2$ [7] in developmental composite approaches.

IMPORTANT AVENUES FOR FUTURE $MoSi_2$ BASED COMPOSITE DEVELOPMENT

Important aspects of future $MoSi_2$ based composite development can be roughly divided into the three general areas of materials, processing, and properties. Key research avenues for each area are indicated in Table V. In pursuing the various aspects of $MoSi_2$ based composite development indicated in Table V, it is important to keep in view the fact that $MoSi_2$ is a borderline intermetallic compound, due to its mixed metallic/covalent/ionic atomic bonding state. This material possesses ceramic-like brittleness at room temperature, and metal-like plasticity at elevated temperatures. In addition, $MoSi_2$ composites require significant volume fractions of ceramic reinforcements, and both ceramic and metal

processing techniques are important for their development. All the above factors dictate that the optimization of $MoSi_2$ based composites will require the combined skills of both ceramists and metallurgists.

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Table V. Key Research Areas for $MoSi_2$ Based Composite Development

Materials

- O Elimination of $MoSi_2$ grain boundary silica phases
  - o Higher quality starting powders (submicron, high purity, low oxygen content)
  - o Removal with carbon additions
- O $MoSi_2$ alloying with other high melting point silicides
  - o Binary and ternary silicide phase diagrams
- O Investigations of $MoSi_2$ single crystals
  - o Basic information on mechanical behavior, diffusion, oxidation

Processing

- O Development of important $MoSi_2$ composite processing technologies
  - o Discontinuous fiber/particle, continuous fiber, layered composites
  - o Pressureless sintering
  - o HIP, Sinter/HIP
  - o Plasma spraying
  - o Hot working
  - o Osprey process
  - o In-situ composites
  - o Mechanical alloying
  - o Require fine, uniform dispersions of second phase constituents

Properties

- O Improve $MoSi_2$ composite mechanical properties while retaining elevated and intermediate temperature oxidation resistance
  - o Improve elevated temperature strength/creep resistance
  - o Increase low temperature fracture toughness
  - o Lower brittle-to-ductile transition temperature
  - o Improve thermal shock/thermal fatigue resistance
  - o Optimize mechanical fatigue behavior

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