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Ta and Nb Reinforced $MoSi_2$ Revision 1.076, 11 April 1990

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ABSTRACT

$MoSi_2$ matrix composites have been recognized lately as potential materials for structural applications at elevated temperatures. Specifically, $MoSi_2$ composites may exhibit useful properties at temperatures to 1400 °C. Previous work improved the yield strength of $MoSi_2$ at 1400 °C by a factor of five through SiC whisker reinforcement. Current research is directed towards increasing the fracture toughness of $MoSi_2$ through the addition of ductile phase reinforcements such as niobium and tantalum. The reaction between Nb and $MoSi_2$ to form $(Mo,Nb)_5Si_3$ proceeds with faster kinetics at hot isostatic press temperatures as low as 1100 °C when compared to the reaction between Ta and $MoSi_2$ to form $(Mo,Ta)_5Si_3$. This reaction product exhibits very poor properties, as evidenced by crack propagation through this layer during fracture. The feasibility of hot working these composites to produce tailored microstructures is examined.

INTRODUCTION

Molybdenum disilicide ($MoSi_2$) has been recognized as a potential material for elevated temperature structural applications. $MoSi_2$ is an intermetallic compound with a melting temperature of 2030 °C. It possesses excellent corrosion resistance and superb oxidation resistance, nearly equivalent to silicon carbide (SiC). This oxidation resistance is due to the formation of a silica (SiO_2) layer which acts as a protective film at high temperatures.

Mechanically, $MoSi_2$ behaves as a metal at elevated temperatures. It exhibits a brittle-to-ductile transition at approximately 1000 °C and above this temperature it deforms through dislocation motion. However, monolithic $MoSi_2$ does not have sufficient mechanical properties for most engineering applications. At room temperature it is relatively brittle, with a fracture toughness of just over 5 $MPa \cdot m^{1/2}$ and a strength of 300 MPa. Its yield strength drops off rapidly above 1200 °C and its creep resistance is relatively poor All of these factors demonstrate the requirement to use $MoSi_2$ as a composite material.

The purpose of this paper is to report on previous work done at Los Alamos with $MoSi_2$-SiC composites and to describe the current research being performed on ductile phase reinforcements of $MoSi_2$. Finally, the approach being used for future composites will be outlined.

BACKGROUND

The purpose of reinforcing $MoSi_2$ in a composite is to improve its fracture toughness, strength and creep resistance. As shown in Figure 1, the creep resistance of $MoSi_2$ is not as good as that of other more common high temperature materials. The $MoSi_2$ tested, however, was not processed under optimum conditions, in that it was less than 100% dense and not phase pure. [1,2]

All previous Los Alamos studies have been on brittle phase reinforcements for $MoSi_2$. The addition of 20 vol% VLS SiC whiskers doubled the strength of $MoSi_2$ at 1200 °C [3]. The room temperature fracture toughness also increased from 5.3 to 8.2 $MPa \cdot m^{1/2}$. In later studies a much smaller VS whisker type was added to decrease the mean free path between reinforcements. This tripled the yield strength at 1200 °C and increased the yield strength at 1400 °C by 470%, as shown in Figure 2. [4,5]

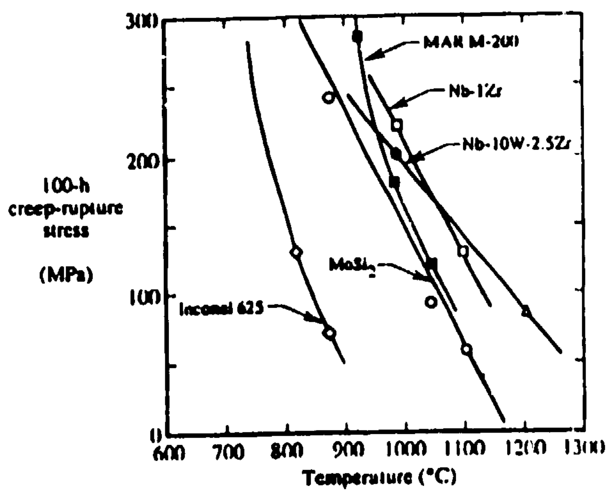

Figure 1: Creep Resistance of High Temperature Materials. (From Ref. 6.)

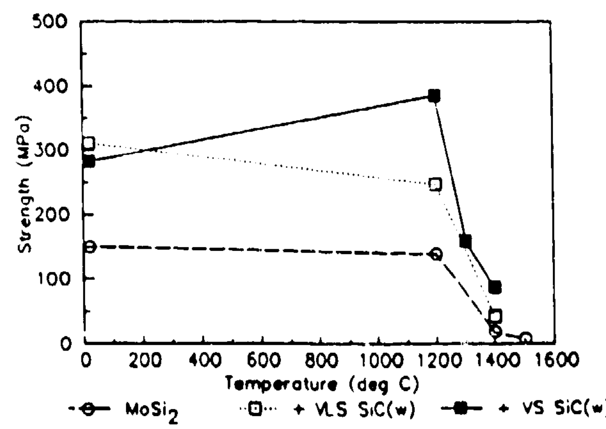

Figure 2: 0.2% yield strength as a function of temperature. (From Ref. 4,5.)

Ductile phase reinforcements may also lead to an improvement in properties. The problem with pure metallic elements used for reinforcements is that none of the refractory metal candidates (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W) are fully compatible with $MoSi_2$ [7]. The formation of an Me_5Si_3 interface reaction layer by silicon diffusion into the metal is detrimental to the composite's mechanical properties, since this interface layer is extremely brittle. The parabolic rate constants for growth of Me_5Si_3 between the metal (Me) and $MoSi_2$ are shown in Figure 3, as compiled by Fitzer and Schmidt [8].

Ductile phases, such as continuous wires, have been shown to lead to a dramatic increase in both room temperature and elevated temperature strength and fracture resistance. Early work in this area was performed in Germany where it was demonstrated that Ta and Nb are both candidates for reinforcing $MoSi_2$. Fitzer and Remmele demonstrated that additions of 40 vol% Nb wires leads to a flexural strength of 700 MPa, and an increase in impact resistance of 700%. [9] Their results are shown in Figure 4. The addition of 10-50 mol% $MoGe_2$ to the matrix to decrease the viscosity of the silica formed on the surface has been shown to improve the oxidation resistance, decrease the "pest" oxidation problem, and improve the thermal expansion compatibility between the oxide and the matrix. [9,10]

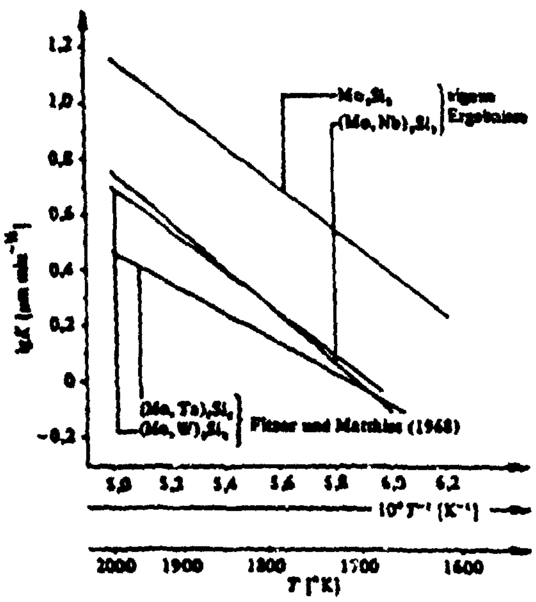

Figure 3: Growth Rate Coefficients of Me_5Si_3. (From Ref. 8.)

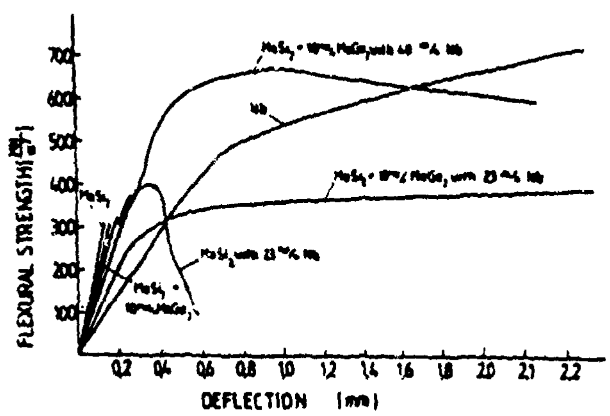

Figure 4: Stress-deflection curves of pure and Nb wire-reinforced $Mo(Si,Ge)_2$. (From Ref. 9.)

RESULTS AND DISCUSSION

The purpose of current research is to further improve the mechanical properties (fracture toughness, strength, and creep resistance) through the addition of ductile phase reinforcements. There are two goals of the current work. The first is to examine the compatibility of various ductile phases with $MoSi_2$ at elevated temperatures. The second goal is to look at hot-working these composites to further improve their properties. Hot-working has not yet been considered as a method to process $MoSi_2$ composites, however it may prove to be a valuable tool to fully densify the composite as well as to produce desired shapes and orientations of the reinforcement/toughening phase. Hot-working has been used in other intermetallic systems to improve their low temperature properties [11].

Thermodynamic Compatibility

The samples in Figures 5-8 were fabricated by dry blending 50 vol% of the reinforcing phase with pure (99.9%) $MoSi_2$*, cold isostatically pressing the powder, and finally hot isostatically pressing the compact at 1100 °C for 1 hour at 30 ksi in a Ta can. Metallographic and semi-quantitative examination was used to reveal the reaction between the metal and the $MoSi_2$ powder.

Fine Nb particulate, approximately 5 μm in diameter was added to $MoSi_2$ powder and compacted. As shown in Figure 5, there was a strong reaction between the Nb and the $MoSi_2$ at 1100 °C to form a reaction layer, determined to be $(Nb,Mo)_5Si_3$ through

*Lot # , 99.9% pure $MoSi_2$ powder from Alfa Products, Danvers, MA 01923.

Figure 5: $MoSi_2$ + 50 vol% fine Nb particulate; HIP at 1100 °C/1 hr/30 ksi

Figure 6: Fracture surface of $MoSi_2$ + 50 vol% fine Nb particulate

Figure 7: $MoSi_2$ + 50 vol% coarse Nb particulate; HIP at 1100 °C/1 hr/30 ksi

Figure 8: $MoSi_2$ + 50 vol% Ta; HIP at 1100 °C/1 hr/30 ksi

EDS analysis. Many of the particles were completely consumed. A cylinder of this composite was compressed to fracture. The resulting fracture surface is shown in Figure 6. As expected, the crack occurred in the $(Nb,Mo)_5Si_3$ layer almost exclusively.

Figure 7 shows a composite with a coarser Nb particulate, approximately 50 μm in diameter, added to minimize the percentage of the reaction product. It is evident that there is still a substantial reaction layer, again determined to be $(Nb,Mo)_5Si_3$. A Ta particle was inadvertently introduced into the composite, and this is shown in Figure 7 as the lighter particle near the center. The surprising part of this experiment is that there appears to be no reaction layer, and under closer inspection under the SEM, no evidence of $(Ta,Mo)_5Si_3$ was found. This is contradictory to the data from Figure 3, which predicts that the formation of $(Nb,Mo)_5Si_3$ should be slower than that of $(Ta,Mo)_5Si_3$ at 1100 °C.

A composite consisting of 50 vol% Ta particulate and $MoSi_2$ was fabricated, and is shown in Figure 8. As expected from the previous experiment, no reaction layer of $(Ta,Mo)_5Si_3$ was detected.

Hot Working

The purpose of the following experiments was to look at the strain rate sensitivity of $MoSi_2$, with the eventual goal of hot working these composites. The samples were HIPed at low temperatures in order to minimize the reaction between the Ta and the $MoSi_2$; completely dense composites were not used. A composite of 20 vol% Ta particulate was added to $MoSi_2$ and HIPed at 1200 °C at 30 ksi for 1 hour. The resulting composite was approximately 65% dense. This composite was then compressed at 1300 °C in two stages; the first to 10%, and the second to a total of approximately 22% at an engineering strain rate of approximately $2 \cdot 10^{-4}$ sec^{-1}. The resulting microstructure is shown in Figure 9.

A composite of $MoSi_2$ + 20 vol% Ta was HIPed at 1300 °C at 30 ksi for 1 hour. The resulting composite was approximately 65% dense. A strain rate sensitivity test was performed on this material at 1400 °C. The material was compressed at true strain rates of 10^{-4}, 10^{-3} and 10^{-2} sec^{-1}. The resulting microstructures are shown in Figure 10.

There were a number of reasons for performing this test; i) to attain full density in the composite, ii) to determine the strain rate sensitivity of the material, and iii) to determine if the Ta particles could be deformed to platelet shapes.

From the micrographs, it appears as though the composite did not fully densify. However there is some question as to whether or not the surface is actually showing pores or pullout. Some related work has indicated that the number of these voids decreases with extended times or different techniques of polishing, indicating that these voids are indeed pullouts. Figure 10(c) shows many of these voids localized around the Ta particles. This implies that the $MoSi_2$ did not flow evenly around the Ta. It could also mean that the reaction zone $(Ta,Mo)_5Si_3$ formed around the surface of the Ta, and this very brittle phase pulled out during polishing. At higher magnification, it is evident that there are voids in the $MoSi_2$ matrix, indicating that even the matrix did not fully densify.

Figure 9: $MoSi_2$ + 20 vol% Ta
Hot worked 22% at 1300 °C; $\dot{\epsilon} \sim 2 \cdot 10^{-4}$ sec^{-1}

Figure 10 (a): $MoSi_2$ + 20 vol% Ta
Hot worked 50% at 1400 °C; variable $\dot{\epsilon}$

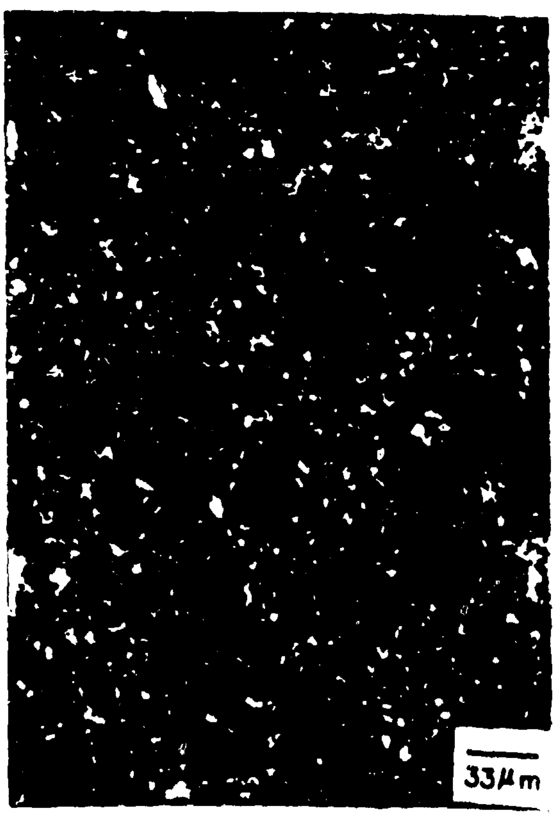

Figure 10 (b): $MoSi_2$ + 20 vol% Ta
Hot worked 50% at 1400 °C; variable $\dot{\epsilon}$

Figure 10 (c): $MoSi_2$ + 20 vol% Ta
Hot worked 50% at 1400 °C; variable $\dot{\epsilon}$

From this early experiment it is evident that $MoSi_2$ deformed under the applied strain rates, and did not crack. The initial work is encouraging since it has snown that $MoSi_2$ can be hot worked at rates as high as 10^{-2} sec^{-1} at 1400 °C.

The Ta particles do not appear to have been deformed in any way. The material started out at only 65% dense, and it was compressed 50%. It is possible that not enough work was put into the composite to have an effect on the Ta reinforcements.

GOALS FOR FUTURE WORK

Hot-working will be used to further improve the properties of $MoSi_2$ composites which have traditionally been processed through powder metallurgy techniques.

Secondly, a ductile reinforcement phase which is more stable than Ta in $MoSi_2$ at elevated temperatures should be introduced. One example would be a high strength Ta alloy. $MoSi_2$ composite components will most likely need to withstand longer times at elevated temperatures, eliminating pure Ta as a candidate for reinforcement, because of the possible formation of $(Ta,Mo)_5Si_3$. Research is presently being undertaken to examine the compatibility of various alloys in $MoSi_2$.

Thirdly, a coating for the reinforcement may be required, depending on the environmental and mechanical requirements of the application.

Finally, different morphologies of reinforcements will be introduced. Though Ta particulate composites are easy to fabricate, a laminant or wire-reinforced composite will have much better mechanical properties, including strength, fracture toughness, and creep resistance.

The optimum $MoSi_2$-based composite will most likely be some combination of reinforcements, including SiC particulate, for elevated temperature strength, and a ductile phase wire or laminant, for improved fracture resistance.

CONCLUDING REMARKS

Molybdenum disilicide is an attractive material for elevated temperature applications, due to its excellent oxidation resistance and high melting temperature. However, its mechanical properties still need to be improved before it can be introduced as a viable engineering component for elevated temperature applications.

It has been shown previously that fine SiC particulate and small SiC whiskers greatly improve the elevated temperature strength of $MoSi_2$. It has also been shown previously that Nb wires greatly improve the impact resistance of $MoSi_2$. The goal of this project is to further improve $MoSi_2$ through the addition of various ductile phase reinforcements, as well as SiC, and also to attempt to hot-work the composites.

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