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SiC – $MoSi_2$ Composites

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by

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ABSTRACT

Previous studies have shown that SiC whisker-reinforced $MoSi_2$ is an excellent candidate material for structural use at elevated temperatures. The yield strength at 1400°C was doubled with the addition of Los Alamos VLS SiC whiskers, and increased by a factor of five with the addition of VS SiC whiskers, despite a non-optimal distribution of the reinforcement resulting from dry blending fabrication procedures. A more optimal wet processing technique, providing a much more uniform distribution of the whisker reinforcement will be discussed. Activities directed at alloying $MoSi_2$ with other silicides to improve the mechanical properties of the matrix material will also be described.

I. INTRODUCTION

Ceramics differ from metals in one very key aspect in that they are brittle, and do not show any yield upon loading at ambient temperatures. This lack of a stress-relieving characteristic, giving ceramics their brittle nature and low tolerance for flaws, has been a major drawback to using them in structural applications. One of the methods of dealing with this mechanical property, which can be referred to as its fracture toughness, has been the development of ceramic composites.

Ceramic composites still pose a challenge to the engineer, since the matrix is very brittle. There is a class of materials, however, which offers the advantages of a ceramic and also some of the beneficial mechanical characteristics of a metal. These materials are intermetallics, which at high temperature, have the excellent properties of a ceramic, but mechanically behave more like a metal, since they show yielding and stress-relieving characteristics. The focus of this work is on an intermetallic, molybdenum disilicide ($MoSi_2$), and composites based on this material.

Molybdenum disilicide has a melting temperature of 2030°C, higher than the aluminides, and has excellent corrosion and oxidation resistance, almost as good as that of silicon carbide (SiC). Its oxidation resistance is due to the formation of a silica (SiO_2) layer, which acts as a protective film at high temperatures.[1] Mechanically, $MoSi_2$ behaves as a metal at high temperatures, since it undergoes a brittle-to-ductile transition at approximately 1000°C. This has the advantage of giving $MoSi_2$ a stress-relieving characteristic, but since it undergoes creep and plastic deformation, its high-temperature strength is reduced. The other disadvantage with $MoSi_2$ is that it is brittle at lower temperatures.

Gac and Petrovic[2] showed that the addition of vapor-liquid-solid (VLS) SiC whiskers as a reinforcing medium may improve the fracture toughness at room temperature when the matrix is brittle, as well as increase the strength at elevated temperatures when the matrix is ductile. This work and others since then[3] have shown this to be correct. The improvements in mechanical properties of this material have been very encouraging. They have provided insight into the toughening and strengthening mechanisms, and also which of these mechanisms may provide the best results in this system. However, the strength and toughness values previously attained have not been attractive for most high-temperature structural applications.

In more recent studies, a new reinforcement for $MoSi_2$ has been examined. This new reinforcement is a vapor-solid (VS) whisker made by the Huber Corporation. It is a much smaller whisker, and it was thought that this may give improved strengthening due to the resultant shorter mean free path. The results from the mechanical testing of this composite will be analyzed to determine what mechanisms are involved and how to best utilize the advantageous properties of this intermetallic.

The non-optimal procedure for fabricating these composites, however, has limited the mechanical properties of this material at both room temperature, and at elevated temperatures. Therefore, a wet blending technique has been developed, and will be used to fabricate samples to be mechanically tested in the near future.

Finally, it has been thought to alloy $MoSi_2$ with other refractory materials, to increase the mechanical properties of the matrix material at elevated temperatures. $MoSi_2$ has been alloyed with WSi_2 in this work, and will be mechanically characterized in the near future.

This paper will summarize results of both past and current studies in $MoSi_2$ composites, and discuss the goals of this research being performed at the Los Alamos National Laboratory. This summary is expanded upon by Carter,[4] where the details of the experiments can be found.

II. PROCEDURE

The materials used were a pure $MoSi_2$ powder,* and 20 vol % of either Los Alamos VLS SiC whiskers** or Huber VS SiC whiskers.*** The main difference between the two whiskers used is their size. In the final hot-pressed samples, the Los Alamos VLS whiskers were generally 100 to 200 microns long, 5 microns in diameter, and had an aspect ratio of between 20:1 and 30:1. The Huber VS whiskers, however, were generally 1 to 5 microns in length, had a diameter of about 0.1 microns, and had an aspect ratio of 10:1.

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* Stock #48108, 99.9% pure $MoSi_2$ powder from Alfa Products, Danvers, MA 01923, a division of Morton Thiokol, Inc.

** Type 4-6A VLS beta-SiC Whiskers, Los Alamos National Laboratory, Los Alamos, NM 87545.

*** "XPW2 Silicon Carbide Whisker" from J. M. Huber Corporation, Borger, TX 79008-2831.

The previously used procedure for dry blending the powder and whiskers is reported by Carter.[4] The new wet processing technique involves a number of steps. The $MoSi_2$ powder is screened to -400 mesh. When fabricating an $MoSi_2$ alloy matrix composite, the second powder, such as WSi_2 is blended with the $MoSi_2$ during this step. The VS whiskers are homogenized and sonicated in a suspension of water at a pH of 9.5. The whiskers above the sedimented layer are collected after 5 minutes of settling. This is to remove the large clumps of whiskers, which were severely detrimental to the mechanical properties. This whisker supernatant is sedimented for 24 hours, and then dried. The whiskers and powder are dispersed in an aqueous medium at a pH of 9.5 while mechanically stirring and ultrasonically dispersing. This dispersion is slip cast in a plaster of paris mold. The slip cast body is then screened to -10 mesh, and hot-pressed at 1800°C to 1900°C in a grafoil lined graphite die. The hot pressing is done in argon, at a hold time at temperature of about 5 minutes.

There was no apparent reaction between the SiC whisker and the matrix, as expected through thermodynamic calculations. Figure 1 shows the microstructure of a wet processed VS SiC whisker $MoSi_2$ matrix composite. The reinforcement is much more evenly distributed in this microstructure than in the samples fabricated previously.[4] These new wet processed samples have not yet been mechanically tested.

Four-point bend strength and four-point bend Chevron-notched fracture toughness tests were performed on all three dry-blended materials at room temperature, at 1200°C, and at 1400°C. Further bend strength tests were performed on VS SiC whisker-reinforced $MoSi_2$ at 1000°C, 1100°C and 1300°C. The bend samples measured 20 x 5.1 x 2.5 mm.

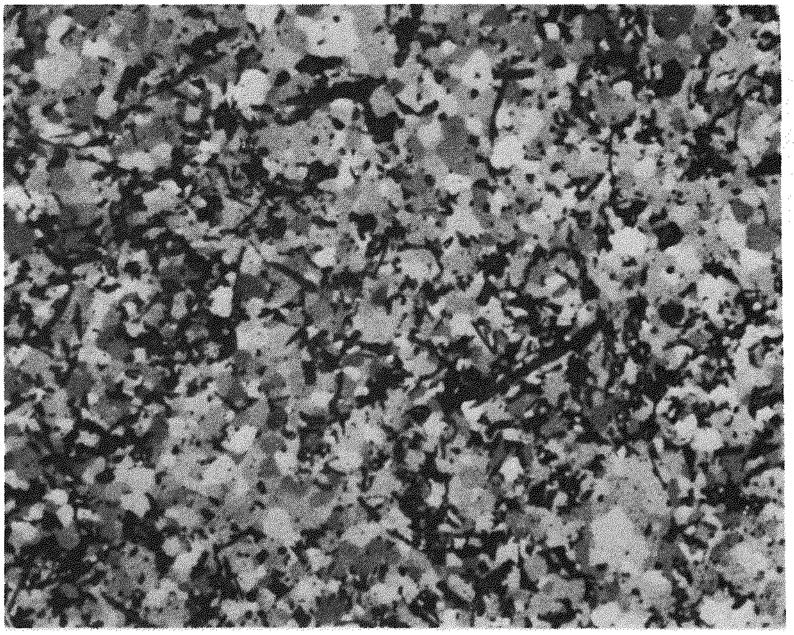

Figure 1: 20 vol % VS SiC(w) + $MoSi_2$ wet processed composite.

III. RESULTS AND DISCUSSION

From the microstructure of the VLS whisker composite, it is evident that the whiskers break during hot-pressing, and that some whiskers are surrounded by pores. This lowers the strength of the composite, since the matrix cannot transfer load to the whisker if there is a pore surrounding the whisker.

There are large whisker clumps of approximately 300 μm in the dry-blended VS whisker composites, as previously reported. There is a large amount of porosity within these agglomerations of whiskers, which is most likely the cause for the low strength of this composite at room temperature. The strength at high temperatures is not as sensitive to these pockets of flaws. These processing defects will be diminished with the new wet-processing technique.

As shown in Figure 2, the strength of the $MoSi_2$ at 1200°C has been doubled by the addition of VLS whiskers, and tripled with the addition of VS whiskers. At 1400°C the VS whiskers increase the yield strength of the matrix by 470%. At elevated temperatures, the 0.2% offset yield strength for the materials is reported, since the samples underwent plastic deformation, as is evident in Figure 3. Ultimate strength values above 1000°C would not be accurate measures of the strength of these materials because of this plastic deformation in bending. At room temperature, the values on Figure 2 are actually the ultimate strengths, since the samples did not yield.

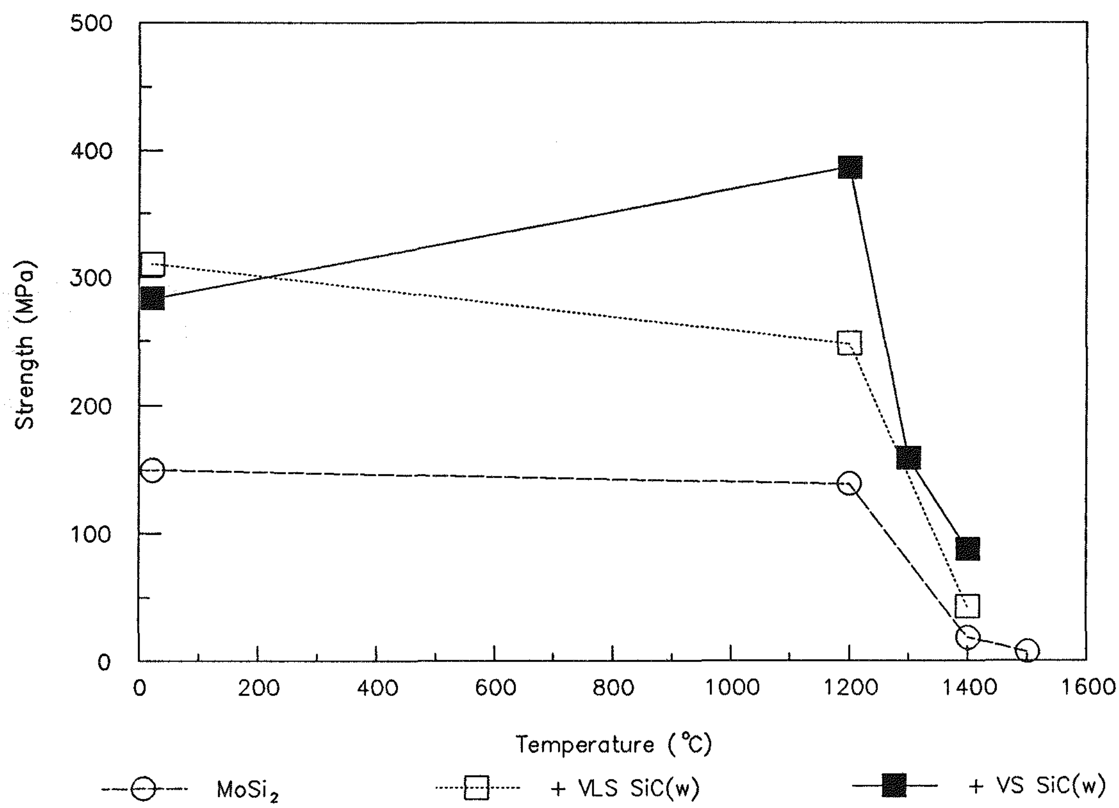

Figure 2: 0.2% yield strength as a function of temperature.

Figure 3: 20 vol % VS SiC(w) + $MoSi_2$ bend test at 1200°C.

$MoSi_2$, like most ceramics, exhibits brittle behavior at room temperature due to the lack of independent active slip systems at room temperature. Neither the strength nor toughness of ceramics is controlled by dislocation motion, as with metals, because dislocations are either immobile, or are not mobile on enough slip systems to influence toughness.[3] Therefore, ceramics are made tougher by modifying the microstructure, and providing resistance to fracture via these microstructural modifications, and not by the movement of dislocations.

This reasoning cannot be applied to the behavior of $MoSi_2$ at high temperatures. At elevated temperatures this material did not behave as a conventional brittle ceramic. It behaved more as a metal. The bend test specimens bent to a very substantial degree at and above 1200°C. However, the addition of SiC whisker reinforcements improved the material's load-bearing capability. This is apparent in Figure 3, which shows a bend bar of the composite material with 4% plastic strain. Therefore, a different way of examining fracture in $MoSi_2$ must be used to fully understand its behavior, and how to control it. It is proposed that the mode of fracture in $MoSi_2$ at elevated temperatures is plastic deformation through dislocation plasticity.

Transmission electron microscopy is presently being performed on these samples to locate regions of dislocation plasticity, and to provide more direct evidence to support this proposal. Initial studies have shown that there is indeed dislocation motion present in this material.

The explanation for the increase in strength with the VS whisker composite, over the VLS whisker composite at elevated temperatures, follows readily from the model of dislocation plasticity. The mean free path is smaller for the VS whisker composite than for the VLS whisker composite, and thus strengthening due to dispersion strengthening is more effective. The VS whiskers are acting as "pinning sites" to control the dislocation motion.

Dieter[5] gives a summary of the strengthening mechanisms produced by a finely dispersed insoluble second phase in a matrix, which is applicable to this system. The degree of strengthening resulting from second-phase particles depends on the distribution of particles in the ductile matrix. For a constant volume fraction of reinforcement, a decrease in reinforcement size will decrease the average distance between the reinforcing particles, or the mean free path. This was one of the intentions of adding VS whiskers as opposed to VLS whiskers: to reduce the mean free path.

The VLS whisker composite, as would be expected from this discussion, showed a decrease in strength at 1200°C. This is because the large whiskers are ineffective for controlling dislocations, since the mean free path is very large relative to the matrix grain size.

The strength at room temperature is very much dependent on the porosity of the sample, because there is no plastic deformation. The porosity for the VS samples was fairly high within the large groups of whiskers. These large whisker clumps acted as large flaws, and detracted from the composite's room temperature strength. If these large clumps can be dispersed better, both the strength and fracture toughness will be improved, especially at room temperature. Note that it is not necessarily the clumps of whiskers themselves, but rather the porosity within these clusters which detracts from the room temperature strength. The elevated temperature strength is not as sensitive to these pores, because of the large degree of plastic deformation.

The low strength of the VLS composite at room temperature is also due to pores, but in this case the pores are surrounding individual whiskers. The matrix cannot possibly transfer load to the whisker if there are large gaps between the matrix and the whisker. This must detract from the material's strength.

Table 1: Room Temperature Fracture Toughness Data

	$MoSi_2$	$MoSi_2$ + VLS SiC(w)	$MoSi_2$ + VS SiC(w)
$MPa{\cdot}m^{1/2}$ ($ksi{\cdot}in^{1/2}$)	5.32 (4.84)	8.20 (7.45)	6.59 (5.99)

The K_{IC} values are summarized in Table 1. Only the room temperature fracture toughness values can be considered K_{IC} values. At elevated temperatures, the fracture was not linear elastic. Nonlinear fracture mechanics must therefore be applied. The fracture toughness at elevated temperature is not reported as K_{IC} but as work of fracture. The work of fracture values are discussed in detail by Carter.[4] The work of fracture at 1400°C was 46 times higher than the room temperature value.

The fracture toughness results are also encouraging. It has been proposed that particle dispersion strengthening accounts for the dramatic increase in strength for the VS whisker composite at high temperature. Though this is the most important result from this study, the fracture toughness is also important, since it is directly related to the mechanisms of strengthening given above. The strengthening mechanisms discussed lead to an explanation of why the fracture toughness at room temperature was not improved by the VS whiskers as much as with the VLS whiskers.

At room temperature, the matrix is brittle, and so toughening must occur by one or more of the typical ceramic toughening mechanisms, such as crack deflection, crack bridging, or whisker pullout. For any of these mechanisms, the purpose is to interrupt the path of the propagating crack by lowering the stress field around the crack tip, and in front of the crack tip. It is desired to have long thin fibers in order to effectively stop cracks by the aforementioned mechanisms.

The smaller size of the VS whisker is suited for controlling dislocation motion at high temperatures, but cannot provide as much toughening as the VLS whiskers do at room temperature, when there is no dislocation plasticity.

One of the mechanisms of toughening which has been observed in the VLS composite is crack deflection.[6] Other mechanisms are possible, such as crack bowing, branching, bridging, and microcracking. There is no evidence of whisker pullout or debonding at room temperature. The microstructure of the room temperature test specimens shows a brittle fracture, as expected.

Figures 4 and 5 show samples which have been fabricated in this study, but as yet have not been mechanically tested. Figure 4 shows an $MoSi_2/WSi_2$ matrix reinforced with VS SiC whiskers. Since WSi_2 is more refractory than $MoSi_2$, this material should retain a higher yield strength at elevated temperatures.

Figure 5 shows an $MoSi_2$ matrix reinforced with SiC particulate. As discussed previously, the size of the reinforcement is what helped to increase the strength of the VS whisker composite over that of the VLS whisker composite. Therefore, it would be much easier and less expensive to simply add an SiC particulate to reinforce $MoSi_2$.

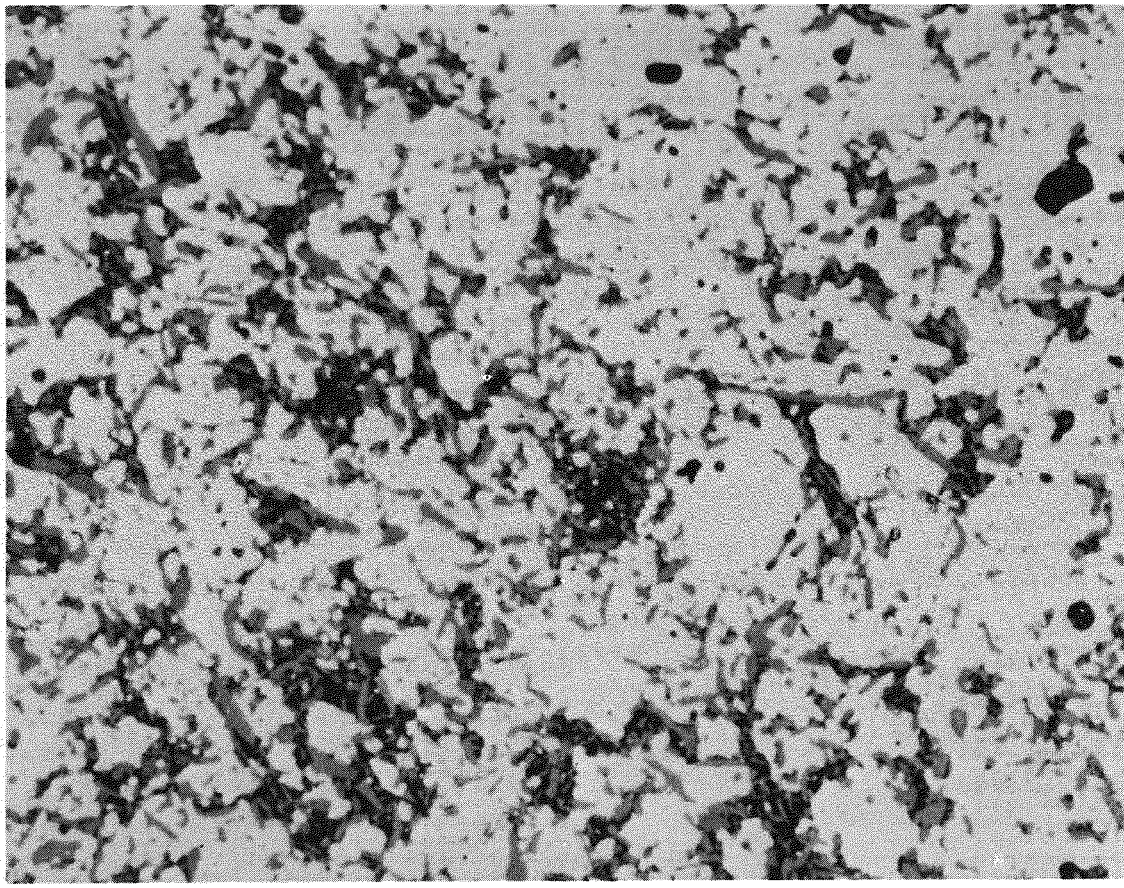

Figure 4: 20 vol % VS SiC(w) + 50/50 mol % $MoSi_2/WSi_2$ composite.

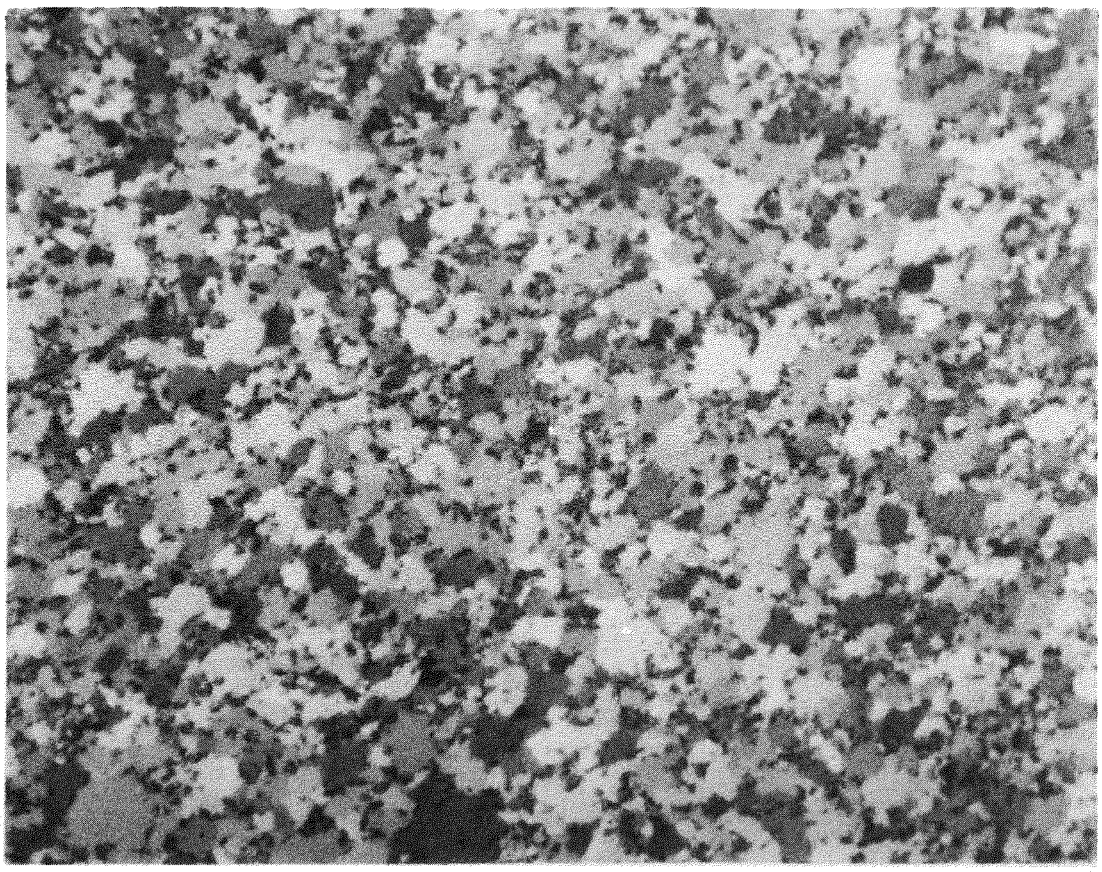

Figure 5: 20 vol % SiC particulate + $MoSi_2$ composite.

IV. CONCLUDING REMARKS

The most important result from this study is the improvement in strength of $MoSi_2$ due to the VS whisker reinforcement. It has been found that the decreased mean free path with the VS whisker reinforcement as compared to the VLS whisker reinforcement served to increase the high temperature strength of $MoSi_2$ by 470%. The reason for this is that at elevated temperatures the mode of failure of $MoSi_2$ is through dislocation plasticity, and the small VS whiskers acted in a dispersion strengthening mechanism to inhibit this dislocation motion.

Future studies include characterizing the materials fabricated using the new wet processing technique. Also, the creep behavior of these materials must be determined. Finally, the oxidation resistance at intermediate temperatures must be characterized to determine the effect of the $MoSi_2$ "pest" oxidation.

It has been shown that $MoSi_2$ composites may indeed be useful materials for engineering applications at elevated temperatures. Substantial gains have been made in the understanding of the strengthening mechanisms important in $MoSi_2$ at high temperatures and also the relevant toughening mechanisms at room temperature.

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