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MECHANICAL CHARACTERIZATION OF SiC WHISKER-REINFORCED $MoSi_2$

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ABSTRACT

The mechanical characteristics of an intermetallic matrix with two different reinforcements were studied. The matrix material was $MoSi_2$, with either Los Alamos VLS SiC whiskers or Huber VS SiC whiskers. The purpose of the reinforcement was to provide toughening at ambient temperature and strengthening at elevated temperatures. The VLS whiskers greatly improved the yield strength of the matrix at 1200 °C, and also increased the room temperature fracture toughness of the matrix. The VS whiskers were added because they are much smaller in length and diameter, and therefore decreased the mean free path between whiskers, at the same volume fraction. The VS whiskers improved the toughness of the matrix at ambient temperature, and increased the yield strength of $MoSi_2$ at 1400 °C by 470%. The high strength of this new composite places this material in the realm of attractive engineering materials for high-temperature applications.

INTRODUCTION

Ceramic materials have some outstanding properties, such as high temperature strength, thermal shock and fatigue resistance, corrosion resistance, low density, and low thermal expansion which make them attractive materials for high temperature applications. For instance, if ceramics were used as engine components, the engine could be run at a higher temperature, and thus be much more efficient than it could be with metal components. This has sparked a great deal of interest in studying different ceramics for these types of applications, and has generated a wealth of knowledge of the properties of various ceramics.

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. Many authors[1,2,3] have summarized the mechanisms which may act in toughening ceramic composites. These include the transfer of load from the matrix to the fiber based on elastic modulus, microcracking or prestressing due to a difference in thermal expansion, crack deflection, and phase transformation toughening.

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 2010 °C, higher than the aluminide 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.[4] 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[5] 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[6] 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.

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,[7] where the details of the experiments can be found.

PROCEDURE

The procedure for fabricating both types of $MoSi_2$ composites was the same. The materials used were a pure $MoSi_2$ powder,[a] and 20 vol% of either Los Alamos VLS SiC whiskers[b] or Huber VS SiC whiskers.[c] 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 about 20 to 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.

The powder and whiskers were weighed out and then blended dry for one minute in a small high-speed blender,[d] similar to a coffee grinder. The powder mixture was then placed in a grafoil-lined die for hot-pressing into disks. The disks measured 31.75 mm in diameter by 6.35 mm in thickness.

The samples were hot-pressed in argon at 1700 °C to 30.5 MPa, with a hold time at the peak temperature of about 5 minutes. The resulting densities were very good, typically between 97.5% and 98.4% of theoretical, which is 5.691 g/cm^3.

There was no apparent reaction between the SiC whisker and the matrix, as expected through thermodynamic calculations. The earliest study showed that the whisker was attacked, however this was attributed to iron and aluminum impurities present in the $MoSi_2$. This study also found substantial grain growth in the matrix, and attributed this to the impurities present. In more recent studies, a much purer powder has been used, and so the grain size of both the matrix and the composite were 5 to 10 microns, similar to the starting powder size

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

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

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

d. Ika Werk Model A10, Janke and Kunkle KG Staufen i Breisgau, West Germany

Four-point bend strength and four-point bend Chevron-notched fracture toughness tests have been performed on all three materials at room temperature, 1200 and 1400 °C. Further bend strength tests have been performed on VS SiC whisker-reinforced $MoSi_2$ at 1000, 1100 and 1300 °C. The data points in Figure 5 represents an average of between 2 and 4 samples per data point. The bend samples measured 20 x 5.1 x 2.5 mm.

RESULTS AND DISCUSSION

The impurities present in $MoSi_2$ in an earlier work also caused the formation of a liquid phase at the grain boundaries during hot-pressing. This liquid phase, rich in silicon, aided the powder to completely surround the whiskers, whereas in the pure $MoSi_2$, the $MoSi_2$ powder did not flow evenly around every whisker. The porosity in each study was similar, however the earlier study exhibited a finer distribution of porosity, whereas the pure $MoSi_2$ caused more porosity surrounding individual whiskers. This difference caused the samples with the impure $MoSi_2$ to have a higher fracture toughness than those with the pure $MoSi_2$. The interface between the $MoSi_2$ and the whisker was weaker in the impure $MoSi_2$ samples, thus causing a higher fracture toughness.

Figures 1 and 2 show the $MoSi_2$ matrix and composite with VLS whiskers under polarized light. The size of the whisker is apparent. Also, it is evident that the whiskers break during hot-pressing. It can be seen that some whiskers are surrounded by pores. This occurs especially by two or more whiskers in very close proximity trapping voids, which detract from the strength of the composite. The matrix cannot transfer load to the whisker if there is a pore surrounding the whisker.

Figures 3 and 4 show the composite with Huber whiskers. The whisker clumps, in Figure 3, align in a plane perpendicular to the hot-pressing direction, as expected. There is a large amount of porosity within these agglomerations of whiskers. This 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. It is evident that there is a large amount of SiC particulate along with the whiskers.

Figure 1: $MoSi_2$, Polarized Light

Figure 2: VLS SiC(w) - $MoSi_2$, Polarized Light

Figure 3: VS SiC(w) - $MoSi_2$

Figure 4: VS SiC(w) - $MoSi_2$, Polarized Light

Figure 5: 0.2% Yield Strength as a Function of Temperature

~~The strength of the $MoSi_2$ at elevated temperatures has been increased by the addition of~~ VLS whiskers, but even more dramatically with the addition of VS whiskers.

The new composite, using VS whiskers instead of VLS whiskers, improved the yield strength at 1200 °C, as shown on Figure 5. At elevated temperatures, the 0.2% offset yield strength for the materials are reported, since the samples underwent plastic deformation. Ultimate strength values above 1000 °C would not be an accurate measure of the strength of these materials because of this plastic deformation. At room temperature, the values on Figure 5 are actually the ultimate strengths, since the samples did not yield.

~~The strengthening provided by the VS whiskers is due to an entirely different mechanism~~ than that which the VLS whiskers provide. Load transfer is a plausible model for high temperature strengthening by VLS whiskers, but not by VS whiskers. Recall that the VLS whiskers are at least twenty times longer than the VS whiskers. The important point is that the load transfer model requires a critical aspect ratio for optimum strengthening. This was calculated to be 12 for the purely elastic case, and 53 for the plastic case. This was found by applying a simple "rule of mixtures" to the elastic modulus, assuming the strain in the matrix and the strain in the fibers were equivalent.[8] The VS whiskers are much shorter, relative to the grain size of $MoSi_2$, and also have a smaller aspect ratio, and therefore are not long enough to provide adequate strengthening due to load transfer.

$MoSi_2$, 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 temperature. At elevated temperatures this material did not behave as a conventional brittle ceramic. It behaved more as a metal, in that it underwent plastic deformation, and exhibited creep and stress relaxation.

The bend test specimens bent to a very substantial degree at and above 1200 °C. However, the addition of SiC whisker reinforcement improved the materials load-bearing capability. 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 motion. This could be due to either grain boundary sliding or dislocation plasticity.[9]

Very often in a two phase system such as this, one indication of grain boundary sliding, or diffusional creep, would be large void formations at boundaries between the two phases. Through SEM studies, there is no direct evidence of void formation at the grain boundaries.

Therefore, it is proposed that the deformation is due to classical dislocation plasticity, rather than grain boundary sliding, or diffusional creep. 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.

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[10] 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 composites 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. Figure 6 shows this porosity quite clearly. 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.

Figure 6: VLS SiC(w) - $MoSi_2$, Tested At Room Temperature, 2KX

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,[7] and so need not be reported here.

Table 1: Room Temperature Fracture Toughness Data

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

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 critical length to diameter ratio has been calculated by Gac et al.[8] and is close to that of the~~ VLS whiskers.

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.[11] 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 show a brittle fracture, as expected.

When the whisker is surrounded by the matrix, the bond is normally very strong. This is shown explicitly in Figure 6. The crack propagated straight through the large horizontal whisker, leaving each half of the whisker bonded to the matrix. A strong bond is good for strengthening of many metal and polymer composites, but too strong of a bond is not good for the toughness of most ceramic composites since most reinforcements have a modulus on the same order as the matrix. Therefore the propagating crack would not be deflected, or the whisker would not show any debonding or pullout if the bond strength was too high.

At high temperature, the toughening mechanism provided by the VS whiskers is related to its strengthening mechanism. Since the fracture at high temperature is through plastic deformation rather than through brittle fracture, the control of dislocation motion will give a higher work of fracture than the toughening mechanisms designed for brittle fracture. Therefore, the work of fracture is much higher for the VS whisker composite than for the VLS whisker composite or the matrix because the VS whiskers control the dislocation motion more efficiently.

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 $MoSi_2$ more than 450%. 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.

Since there is little or no dislocation motion in $MoSi_2$ at room temperature, the small whiskers had little effect on the mechanical properties at room temperature, specifically its fracture toughness. Though the VS whiskers did improve the fracture toughness slightly, the larger VLS whiskers are much better suited for the typical ceramic toughening mechanisms such as crack deflection.

In conclusion, the results from the mechanical tests performed in this work are extremely significant. 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. These results are also very useful, in that they clearly dictate the logical path for future work on this system.

FUTURE WORK

First, it has been shown that a dramatic improvement in high temperature strength was obtained by utilizing a smaller whisker, and thus a shorter mean free path. A similar effect should be attained by the addition of fine SiC powder. This would enable a better control of the size of reinforcement. The clumps of whiskers introduced pores, which acted as flaws, and substantially decreased the room temperature strength. One solution would be to improve the method of processing to disperse these clumps of whiskers by using a wet-blending process, or one could simply add fine SiC powder instead.

Secondly, the VLS whiskers provided a better source of toughening at room temperature than the VS whiskers, because of their much larger size. Typical ceramic toughening mechanisms are dominant at room temperature, and so the composite must be designed with this in mind. The stress field at a crack tip must be minimized by alterations of the microstructure, rather than relying on inhibitors to dislocation motion, since dislocation plasticity does not exist at room temperature.

Therefore, the logical reinforcement for $MoSi_2$ would be a combination of VLS whiskers and fine SiC powder, which would take advantage of the relevant strengthening or toughening mechanisms at room temperature and at high temperatures.

There are other possible approaches which can be drawn from this work to improve the mechanical behavior of $MoSi_2$. First of all, the processing methods could be improved a great deal. Dry-blending is quick and easy, but does not give optimum properties. Also, one might attempt to increase the VLS whisker loading, which would probably necessitate a wet-blending technique. An increased whisker loading would help to decrease plastic deformation at high temperature, and also may help increase the fracture toughness at room temperature.

It may be more useful, however, to alter the composition of the composite. For instance, to further reduce the plastic deformation of $MoSi_2$ at high temperature, and thus improve its creep resistance, one might alloy the $MoSi_2$ with a more refractory material, such as tungsten disilicide.

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