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Thermal properties of $MoSi_2$ and SiC whisker-reinforced $MoSi_2$

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The heat capacity, thermal conductivity and coefficient of thermal expansion of $MoSi_2$ and 18 vol% SiC whisker-reinforced $MoSi_2$ were investigated as a function of temperature. The materials were prepared by hot isostatic pressing between 1650 and 1700 °C, the hold time at temperature being 4 h. The heat capacity of $MoSi_2$ showed an increase from about 0.44 $W s g^{-1} K^{-1}$ at room temperature to 0.53 at 700 °C. Whisker reinforcement increased heat capacity by about 10%. Thermal conductivity exhibited a decreasing trend from 0.63 $W cm^{-1} K^{-1}$ at room temperature to 0.28 $W cm^{-1} K^{-1}$ at 1400 °C. Whiskers reduced conductivity by about 10%. The thermal expansion coefficient increased from 7.42 $°C^{-1}$ between room temperature and 200 °C to 9.13 $°C^{-1}$ between room temperature and 1200 °C. There was a 10% decrease resulting from the whiskers. The measured data are compared with literature values. The trends in the data and their potential implications for high-temperature aerospace applications of $MoSi_2$ are discussed.

1. Introduction

Molybdenum disilicide ($MoSi_2$) is an intermetallic compound with very attractive properties for use as a candidate material for high-temperature aerospace applications. It is very refractory with a melting point of 2030 °C. In addition, $MoSi_2$ is highly oxidation resistant. These features, combined with good thermal and electrical conductivities, have led to the application of $MoSi_2$ as a high-temperature heating element. The current concerns about this material are its relatively low strength and fracture toughness, the latter especially below the ductile–brittle transition temperature. The mechanical properties can be enhanced by forming composites of $MoSi_2$ with appropriate reinforcements. This has been demonstrated by Gac and Petrovic [1] as well as by the present authors [2] by incorporating silicon carbide whiskers as the reinforcing agent. The presence of the reinforcing phase, however, affects the thermal properties which determine the heat-transfer characteristics, thermal gradients and the resulting thermal stresses the component will experience. The thermal properties of interest are the heat capacity, thermal conductivity and the coefficient of thermal expansion, all measured as a function of temperature. Published values of these properties for $MoSi_2$ have been discussed in a review by Wehrmann [3] and compiled by the Battelle Memorial Institute [4]. The materials used for these measurements were mostly prepared by hot pressing. For the whisker-reinforced $MoSi_2$, there are no thermal property data available. A programme to measure these properties was, therefore, initiated.

2. Experimental procedure

Both $MoSi_2$ and SiC whisker-reinforced $MoSi_2$ were fabricated by hot isostatic pressing (HIP). The whiskers used as reinforcement were manufactured by Advanced Composites Materials Corporation, grade SC-9 with average diameter of 0.5 μm and length of 80 μm. The starting powder for pure $MoSi_2$ was − 325 in. mesh size. For the reinforced material, $MoSi_2$ was microground to a size of about 10 μm and blended with 18 vol % whiskers. The blending was done by Advanced Composite Materials Corporation using their proprietary method. The powders were filled in tantalum cans which were subsequently evacuated and sealed. The process of HIPing was conducted at 30×10^3 p.s.i. (10^3 p.s.i. $\equiv$ 6.89 $N mm^{-2}$) pressure at either 1650 or 1700 °C, the hold time at temperature being 4 h. Fig. 1a and b show the microstructure of the resulting materials. Some characteristics of the microstructure are summarized in Table I. Samples for the thermal property measurements were cut from the HIPed ingots by electrical-discharge machining. Heat capacity samples were in the form of circular cylinders, 0.58 cm diameter and 0.18 cm high; thermal conductivity samples were rectangular blocks 1.27 cm × 1.27 cm × 0.38 cm while the thermal expansion samples had the dimensions 0.48 cm × 0.48 cm × 5.08 cm.

Specific heat was measured using a standard Perkin–Elmer Model DSC-2 differential scanning calorimeter with a sapphire reference standard. The sample and the standard, both encapsulated in pans, were exposed to the same heat flux and the differential

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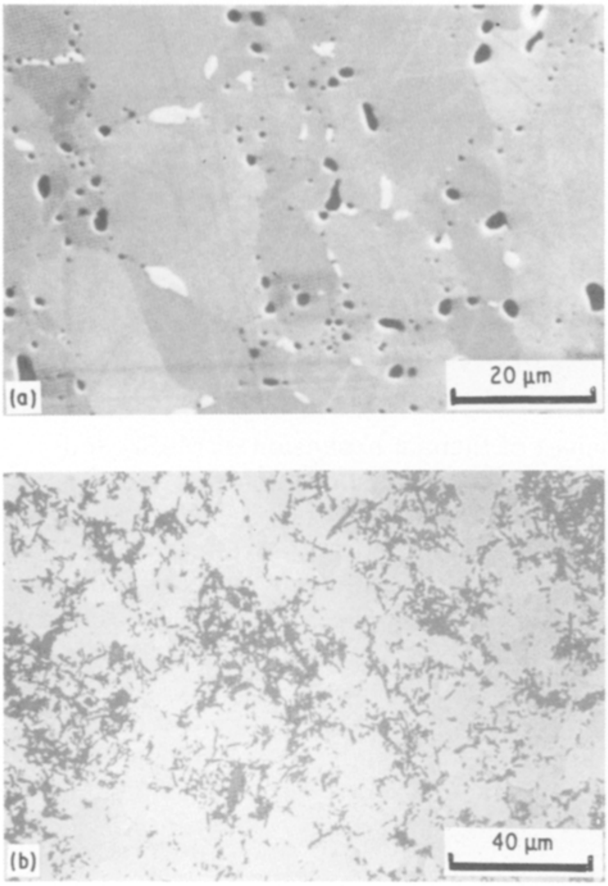

Figure 1 Microstructure of (a) $MoSi_2$ and (b) whisker-reinforced $MoSi_2$.

power needed to heat the sample at the same rate was recorded by a digital data acquisition system. From the known heat capacity of sapphire, the heat capacity of the sample was calculated. Thermal conductivity was calculated from the thermal diffusivity simply by dividing it by the product of density and heat capacity. Thermal diffusivity was determined using a laser flash technique in which the front face of the sample is exposed to a short laser burst and the resulting temperature increase at the rear face is recorded. A dual push-rod dilatometer was used to measure linear expansion. The difference in expansion between the sample and a reference standard was measured as a function of temperature.

3. Results

Heat-capacity data of pure and reinforced $MoSi_2$ as a function of temperature are shown in Fig. 2 together with predicted values of the reinforced material calculated from the data for $MoSi_2$ and SiC. The measurements were made at temperatures up to about 700 °C. Fig. 3 shows thermal conductivity calculated from the thermal diffusivity data. The predicted data for the reinforced material are also included. The temperature range for Fig. 3 extends to 1400 °C. For the calculation of conductivity from diffusivity, values of heat capacity data are required which were only measured to 700 °C. For temperatures above 700 °C, extrapolated values were used. The coefficient of linear thermal expansion is plotted in Fig. 4 which also includes the predicted values of the reinforced material.

4. Discussions

The measured heat-capacity values for $MoSi_2$ in the present work fall within 5% of the values compiled by Battelle [4] and within 2% of values cited in a review by Wehrmann [3]. The differences, however small, probably originate from differences in microstructure. All earlier measurements reported to date were done on hot-pressed samples whereas the present work was conducted on HIPed material which exhibits a more isotropic structure and less porosity.

There are several features of the heat capacity data that are evident in Fig. 2. For electrically non-conducting materials, heat capacity at high temperatures approaches a value of $3R\,\mathrm{g\,at^{-1}\,°C^{-1}}$, where R is the gas constant. This is about $0.52\,\mathrm{Ws\,g^{-1}\,°C^{-1}}$ for $MoSi_2$. The data in Fig. 2 do not show any trend of saturation at this value. This can be understood from the fact that $MoSi_2$ is electrically conducting and, therefore, has an additional electronic contribution to the heat capacity. For the reinforced material, the addition of SiC whiskers has resulted in further increases in heat capacity by about 10%. The reason behind this is clearly the fact that SiC with a molecular weight lower than $MoSi_2$ has, on a per gram basis, higher heat capacity. Values for the reinforced system can be calculated following the rule of mixtures. The calculated results using the heat capacity data for sintered α-SiC [5] at a concentration of 18 vol % are shown in Fig. 1. The measured and calculated values agree fairly well. The use of heat capacity data for

TABLE I Summary of microstructural characteristics

Microstructural parameters	$MoSi_2$	$MoSi_2$ reinforced with whiskers
Average grain size (µm)	30	10
Total porosity (%)	2.5	2
Average pore size (µm)	1–2	1–2
Pore distribution	Grain boundaries	Grain boundaries and whisker clusters
Crystalline phases	Tetragonal $MoSi_2$; 5% hexagonal Mo_5Si_3 at grain boundaries	Tetragonal $MoSi_2$; 5% hexagonal Mo_5Si_3; 18% α-SiC whiskers
Preferred orientation	None	None
Density ($\mathrm{g\,cm^{-3}}$)	6.2	5.6
Reinforcement		
Average diameter (µm)		0.5
Average length (µm)		80

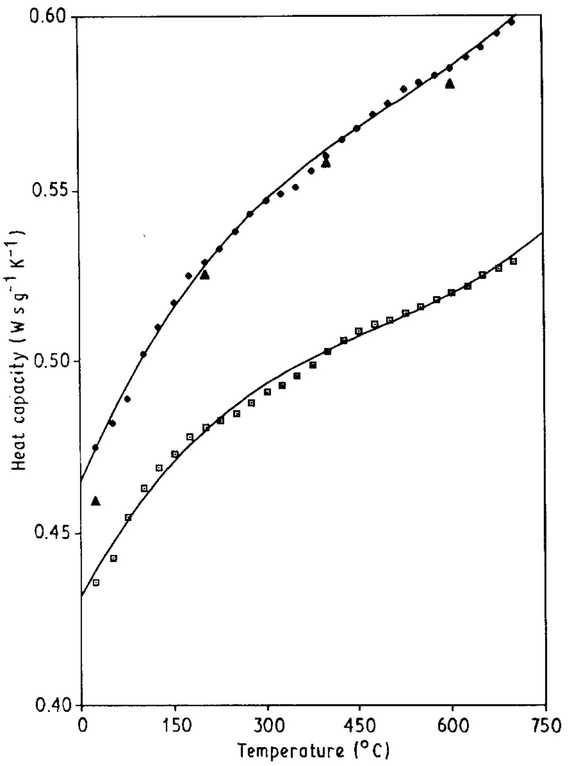

Figure 2 Heat capacity of $MoSi_2$. (□) Pure $MoSi_2$, (◆) reinforced $MoSi_2$, (▲) predicted values.

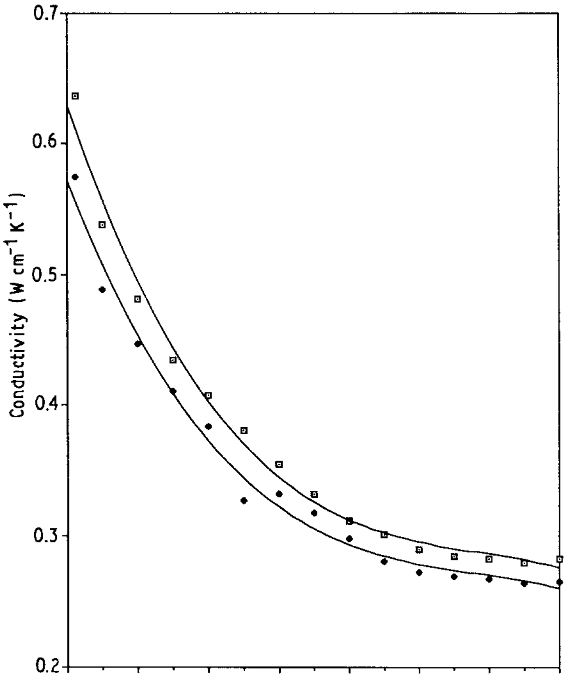

Figure 3 Thermal conductivity of (□) pure and (◆) reinforced $MoSi_2$.

polycrystalline α-SiC, which is isotropic, is justified, especially in the absence of similar data on whiskers, because the microstructure and the whisker orientation of the HIPed material in the present study do not exhibit any preferred orientation which normally occurs in hot-pressed materials.

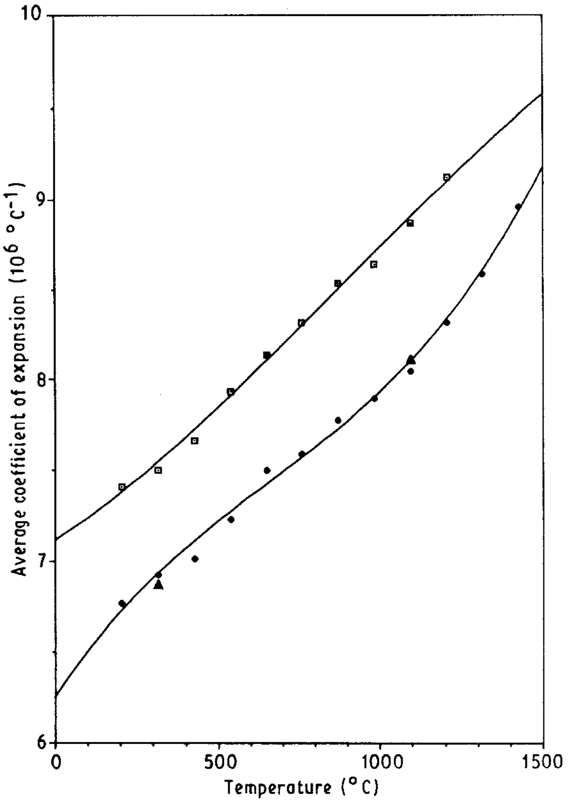

Figure 4 Coefficient of linear thermal expansion coefficient of (□) pure and (◆) reinforced $MoSi_2$. (▲) Predicted values.

The thermal conductivity of $MoSi_2$ measured in the present investigation is roughly twice that of typical superalloys at low temperatures and decreases to half that at high temperatures. It falls within the band of data compiled by Battelle [4] and matches to within 7% of values cited in Wehrmann's review [3]. Again, the differences are likely due to differences in microstructure, particularly the amount of porosity. The porosity in the samples in [4] ranged between 2% and 6% compared with 2.5% in the present study. The temperature dependence of thermal conductivity, Fig. 3, shows a decreasing trend with temperature, unlike metals. In this respect $MoSi_2$ follows ceramic materials which typically exhibit a decreasing thermal conductivity with increasing temperature. The difference in behaviour between metals, particularly superalloys and $MoSi_2$ arises because in metals and alloys, carrier scattering distances are primarily controlled by defects and, therefore, are not strongly temperature dependent. As a result the thermal conductivity follows somewhat the temperature dependence of heat capacity. In $MoSi_2$, however, carrier scattering occurs through interaction with phonons. The scattering distances are expected to be strongly inversely temperature dependent. This dependence more than offsets the increase in heat capacity with temperature, resulting in the thermal conductivity decreasing with increasing temperature. For the reinforced material the addition of SiC has resulted in a decrease in thermal conductivity as is seen in Fig. 3, despite the fact that SiC has higher thermal conductivity than $MoSi_2$. One possible explanation would be that the whiskers have a greater effect on scattering lengths than on heat capacity. The reduction on scattering length more than offsets the increase in heat capacity. The system, therefore, cannot be modelled by a rule of mixtures. Further analysis is required to understand the details of the effect of SiC on thermal conductivity.

The coefficient of thermal expansion of $MoSi_2$ measured in the present study agrees very well with the values reported by Long [6] which are cited in the review by Wehrmann [3] and agree, on the average, to within 5% of the data compiled by Battelle [4]. Microstructure, again, is thought to play a key role in the difference, particularly because of the fact that $MoSi_2$ is inherently anisotropic. The coefficient lies halfway between that of typical ceramics, such as SiC, and cobalt-based superalloys. The average thermal expansion coefficient decreases with temperature, Fig. 4. The addition of SiC whiskers lowered the expansion coefficient by about 10%. This is because SiC itself has a lower thermal expansion coefficient. Values for the expansion coefficient of the reinforced material have also been calculated by using the rule of mixtures and are shown in Fig. 4. There is good agreement between the calculated and experimental values. The thermal expansion of composite bodies has been modelled by Kingery *et al.* [7] taking into account the residual strains generated because of thermal expansion mismatch among the various phases of the composite. The final equations involve terms containing the bulk and shear moduli of the phases in addition to the rule of mixtures term. In the present study, the close agreement between the rule of mixtures and the measured values indicates that the residual strains induced by thermal expansion mismatch are small, possibly because of the small size of the whiskers, the strain being proportional to the whisker dimension. The implications of the magnitudes of the thermal properties of $MoSi_2$ and the whisker-reinforced $MoSi_2$ relative to the traditionally used nickel- and cobalt-based superalloys, is worth considering. Superalloy components survive in the thermal environment of the hot section of gas turbine engines because of effective cooling facilitated by the good thermal conductivity of these alloys. Because the thermal conductivity of $MoSi_2$ is, on average, comparable to that of the superalloys, it can also be effectively cooled. However, higher melting point and better oxidation resistance of $MoSi_2$ would favour less cooling requirement, if any, than for the superalloys. Whisker reinforcement reduces thermal conductivity by about 10%. However, the mechanical properties improve significantly. It is, therefore, unlikely that whisker-reinforced $MoSi_2$ will require any additional cooling.

The thermal expansion coefficient of $MoSi_2$ is lower than that of the superalloys. The expansion mismatch may be a concern at regions where $MoSi_2$ is attached to metallic components. Innovative design and strain isolation would be required to reduce the resulting stresses. A 10% reduction in thermal expansion occurs on whisker reinforcement. This would make the material less susceptible to thermal shock, because the thermal stress is proportional to the expansion coefficient.

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