The effect of powder processing on the coefficient of thermal expansion of MoSi₂–Si₃N₄ composites

H. Choe *, T. Hsieh, J. Wolfenstine
Department of Chemical and Biochemical Engineering, University of California, Irvine, CA 92697-2575, USA
Received 7 February 1997; received in revised form 29 April 1997

Abstract

The coefficient of thermal expansion (CTE) of MoSi₂–Si₃N₄ (10, 20, 40 vol.%) composites decreases as the volume fraction of Si₃N₄ increases. Analysis of the microstructural variables suggests that the CTE of the composites is independent of MoSi₂-grain size but a function of Si₃N₄ particle size, increasing with decreasing particle size. At the high volume percent (~40%) of Si₃N₄ particulates required in MoSi₂ so that the CTE of the composite is close to that of Mo, Kerner's model provides the closest prediction to the experimental data. Deviation from the prediction is most likely a result of microcracks at MoSi₂/Si₃N₄ interfaces.

Keywords: MoSi₂, Si₃N₄, Composites; Thermal expansion

1. Introduction

Molybdenum is extensively used in the glass manufacturing industry primarily due to its high melting point (2623°C) and high strength at elevated temperature [1–3]. However, significant oxidation of molybdenum occurs at temperatures above 500°C in air. As a result, a protective coating is generally required for Mo when used up to temperatures of about 1500°C required for glass melting. MoSi₂ is considered a prime candidate material as a protective coating for Mo due to its excellent oxidation and corrosion resistance under both air and molten glass environments at elevated temperatures. However, the coefficient of thermal expansion (CTE) of MoSi₂ is higher than that of Mo (8.5 × 10⁻⁶/°C and 5.8 × 10⁻⁶/°C, respectively), leading to transverse cracking within the coating and delamination near or at the coating/substrate interface [2].

One possible method to eliminate this problem is to add low CTE secondary phases (e.g., ceramic particles such as Si₃N₄) into the MoSi₂ matrix, so that the CTE of the composite coating is close to that of the Mo substrate.

It is the purpose of this paper to (i) investigate the CTE of MoSi₂–Si₃N₄ particulate reinforced composites as a function of Si₃N₄ particulate volume fraction and microstructure (e.g., matrix grain size) with the overall goal of identifying which variables exert the most influence on the CTE of the MoSi₂–Si₃N₄ composite, (ii) determine the volume fraction of Si₃N₄ particulates in the MoSi₂–Si₃N₄ composites required such that the CTE of the composite matches the CTE of Mo in the temperature range required for glass melting (1000–1500°C), and (iii) determine which of the existing models for the thermal expansion behavior of composites best describes the experimental data for the MoSi₂–40vol.%Si₃N₄ composites.

2. Experimental procedure

Si₃N₄ was chosen for its similar oxidation resistance at high temperature and its low CTE (3.5 × 10⁻⁶/°C) compared to MoSi₂. Two different methods were used to prepare the MoSi₂/10, 20, and 40 vol.% Si₃N₄ powder mixtures prior to consolidation. In the first method, dry mixing (DM), the MoSi₂ and Si₃N₄ powders were blended in a rotating V-shaped cylinder for 1 h. In the second method, ball milling (BM), the MoSi₂ and Si₃N₄ powders were milled with steel balls for 12 h in a container flushed with argon gas. A total of six different MoSi₂–Si₃N₄ composite samples were prepared for...
Table 1

Microstructural variables

<table>
<thead>
<tr>
<th></th>
<th>Relative density (%)</th>
<th>Grain size (μm)</th>
<th>Particle size (μm)</th>
<th>Particle shape</th>
<th>Particle distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 BM</td>
<td>99</td>
<td>15</td>
<td>5</td>
<td>Spherical</td>
<td>Uniform</td>
</tr>
<tr>
<td>10 DM</td>
<td>68</td>
<td>38</td>
<td>14</td>
<td>Spherical</td>
<td>Non-Uniform</td>
</tr>
<tr>
<td>20 BM</td>
<td>95</td>
<td>8</td>
<td>6</td>
<td>Spherical</td>
<td>Uniform</td>
</tr>
<tr>
<td>40 BM</td>
<td>97</td>
<td>6*</td>
<td>6*</td>
<td>Spherical</td>
<td>Agglomerated</td>
</tr>
<tr>
<td>40 DM</td>
<td>86</td>
<td>7*</td>
<td>8*</td>
<td>Spherical</td>
<td></td>
</tr>
</tbody>
</table>

*aEstimated.*

The relevant microstructural features of the hipped BM and DM materials are listed in Table 1. From Table 1, three important points are noted. Firstly, all materials except 40 DM had relative densities above 95%. Secondly, the microstructural variables of 10 BM are different than those for 10 DM. 10 BM has both finer Si₃N₄ particles and MoSi₂ matrix grain size than 10 DM. Thirdly, the microstructures of 40 BM and 40 DM are nearly identical except for the difference in relative density.

3. Results

3.1. Microstructure

The relevant microstructural features of the hipped BM and DM materials are listed in Table 1. From Table 1, three important points are noted. Firstly, all materials except 40 DM had relative densities above 95%. Secondly, the microstructural variables of 10 BM are different than those for 10 DM. 10 BM has both finer Si₃N₄ particles and MoSi₂ matrix grain size than 10 DM. Thirdly, the microstructures of 40 BM and 40 DM are nearly identical except for the difference in relative density.

3.2. Thermal expansion coefficient

Fig. 1 is a graph of the thermal expansion coefficient as function of temperature for the 10 BM, 10 DM, 20 BM, 40 BM, and 40 DM materials. Included in Fig. 1 is data for Mo and monolithic MoSi₂ [2]. Several important points are illustrated in Fig. 1. Firstly, it is observed that the CTE of the MoSi₂–Si₃N₄ composites decreases as the volume fraction of Si₃N₄ increases. This is expected since, the CTE of Si₃N₄ is lower than that for MoSi₂. It is somewhat surprising that the CTE for the 10 BM material is higher than or equal to that for monolithic MoSi₂ at temperatures below 650°C. At present reasons for this anomalous behavior are not known. It may be possible that the monolithic MoSi₂ material shown in Fig. 1 may contain impurities or second phases that were present in the starting powders or acquired during powder processing which could reduce its CTE. The chemistry and phase constitution for the monolithic MoSi₂ material shown in Fig. 1 were not reported [2]. Secondly, the thermal expansion of the 10 BM material is significantly higher than that of the 10 DM material, whereas the thermal expansion of the 40 BM material is equal to that for the 40 DM material. Thirdly, the thermal expansion coefficient for the 40 BM and 40 DM materials is close to that for pure Mo, whereas those for the 10 BM, 10 DM, and 20 BM materials are much higher.
Fig. 2. Coefficient of thermal expansion of the MoSi$_2$ Si$_3$N$_4$ composites and Mo [2] as a function of Si$_3$N$_4$ volume fraction.

4. Discussion

4.1. Microstructural effect

It is apparent from Fig. 1 and Table 1 that microstructure does indeed influence CTE. At the high vol.% of Si$_3$N$_4$ (40%) where the microstructural variables except porosity are similar there is no appreciable difference in CTE between the BM and DM materials. From Fig. 2, since the CTE of the 40 DM and 40 BM materials fall almost on the same line with identical microstructures except porosity, it can be concluded that porosity does not have much of an effect on the CTE. This is in agreement with results of Coble and Kingery [5], who observed that the CTE was independent of porosity for anisotropic materials.

In contrast, at low Si$_3$N$_4$ vol.% (10%) where there is a difference in microstructure (grain size and particle size), there is significant difference in the CTE between the 10 BM and 10 DM materials. The effect of grain size and particle size will be examined for the 10 BM and 10 DM materials to determine, if possible, which of these gives the largest contribution to the CTE difference shown in Fig. 1. Unfortunately, due to the fact that both grain size and particle size vary between the 10 BM and 10 DM materials, this determination is not so simple. In order to solve this problem, a model for the effect of grain size on the CTE will be developed that will aid in determining which variable, grain size or particle size has the largest influence on the CTE of the MoSi$_2$ 10vol.%Si$_3$N$_4$ materials.

4.1.1. MoSi$_2$ grain size effect

It has been reported that in Cu the thermal expansion coefficient of the grain boundaries is about 2.5–5.0 times the thermal expansion coefficient of the lattice [6,7]. The grain size of 10 BM (15 μm) is smaller compared to that of 10 DM (38 μm). As a result, the 10 BM material has a higher number of grain boundaries than the 10 DM material and thus, it is possible that the main CTE difference between the 10 BM and 10 DM materials is related to the grain size difference. A model is developed in the following paragraphs to determine if the grain size difference can explain the CTE difference between the 10 BM and 10 DM materials.

Assuming that the grains are cubic, and the grain size is a side of the cube, then the ratio of the number of grains for a certain volume of 10 BM to 10 DM would then be about 16:1. Therefore, the volume ratio of 10 DM to 10 BM is 16:1, since the ratio of the number of grains for a certain volume of 10 BM to 10 DM is 16:1. The amount of grain boundaries for 10 DM is then $16^{1/3} \times 16^{1/3} \times 6 \times (1/2) = 19.05$, while that of 10 BM is $1 \times 6 \times 16 \times (1/2) = 48$. Hence, the grain boundary ratio of 10 DM to 10 BM is 1:2.5.

Since the thickness of a usual grain boundary is a few atomic spacings while that of a usual grain is on the order of microns, the ratio of the thickness of grain boundary to grain can be approximated as 1:1000 [8]. Based on this assumption, the volume ratio of grain boundary to grain is $(1002^3 - 1000^3)/2:1000^3 \approx 1:333$. Since the CTE of single crystal MoSi$_2$–10vol.%Si$_3$N$_4$ is not known, it is hard to theoretically approximate the CTE of the 10 BM and 10 DM materials. However, it is possible to obtain the CTE difference between 10 BM and 10 DM based on modeling. Assuming the volume ratio of the grain boundary to grain is 1:333 and the 10 DM grain has only one grain boundary then, 10 BM will contain two and a half grain boundaries with a volume of 333. Knowing that the CTE of 10 DM at 200°C is $7.4 \times 10^{-6}/°C$, letting the CTE of the single crystal MoSi$_2$–10vol.%Si$_3$N$_4$ composite be $X$, and the fact that 10 DM has one grain boundary per grain with a volume of 333 leads to the following Eq. (1).

$$X(5)(1)(1/333) = (7.4 \times 10^{-6}) - X \quad (1)$$

From Eq. (1), it is estimated that the CTE of single crystal MoSi$_2$–10vol.%Si$_3$N$_4$ with no grain boundary, $X$, is about $7.3 \times 10^{-6}/°C$. In addition, knowing that the CTE of a grain boundary is about 2.5–5 times that of the matrix [6,7], then the maximum difference in CTE between 10 BM and 10 DM due to grain size is (10 BM has 1.5 more grain boundaries than 10 DM per grain with a volume of 333):

$$7.3 \times 10^{-6}/°C(5)(1.5)(1/333) = 1.64 \times 10^{-7}/°C \quad (2)$$

It is thus concluded that the grain size difference for the case in which the ratio of the grain size of 10 DM to that of 10 BM is about 2.5:1 cannot explain the major CTE difference, since the experimentally observed CTE difference of 10 DM and 10 BM is about $8 \times 10^{-7}/°C$ at 200°C which is about 5 times that predicted ($1.64 \times 10^{-7}/°C$, Eq. (2)), for the case where the CTE of a
grain boundary is assumed to be 5 times that of the matrix. This suggests that the main difference in CTE between 10 BM and 10 DM is most likely related to the 

Si₃N₄ particle size difference.

4.1.2. Si₃N₄ particle size effect

From Table 1, it is observed that the Si₃N₄ particle size in 10 BM (5 μm) is different than in 10 DM (14 μm). As a result, it is possible that this particle size difference could account for the majority CTE difference between the two materials observed in Fig. 2. It has been observed in the past for the case of particles whose CTE is lower than that of the matrix (e.g., similar to the Si₃N₄ particles in MoSi₂) that the CTE of the composite is a function of particle size [9-13], in agreement with the results of this study. The experimental results of the present study reveal that as the particle size increases, the CTE of the composite increases. These results are in agreement with findings of Tummala and Friendberg [13] who observed that the CTE of glass matrix composites reinforced with ZrO₂ particles increased as the ZrO₂ particle size decreased.

4.2. Si₃N₄ volume fraction to match the CTE of Mo at high temperature

Fig. 2 is a plot of the thermal expansion coefficient for the MoSi₂–Si₃N₄ composites as a function of volume percent Si₃N₄ at 1200°C for the 10 BM materials. The 10 BM material was chosen for the graph since three different Si₃N₄ compositions exist. Included in this plot is the CTE for Mo at 1200°C [2]. From this plot, a volume fraction of about 33% Si₃N₄ is required such that the CTE of the MoSi₂–Si₃N₄ composites matches the thermal expansion coefficient of Mo. An identical analysis revealed that, at 1100 and 1300°C, the volume percentage of Si₃N₄ required to match the thermal expansion coefficient of Mo is 32 and 34%, respectively. If the DM materials are used, the vol.% Si₃N₄ required to match the CTE of Mo would be ≈ 31–33% at 1100–1300°C. These results suggest that the volume fraction of Si₃N₄ required in the MoSi₂–Si₃N₄ composite coatings such that the CTE of the coating matches the CTE of Mo substrate at temperatures required for glass melting (≈ 1000–1500°C) is between 30–35 vol.%. 

4.3. CTE predictions

It is the intent of this section to see how well the CTE of the MoSi₂–40vol.%Si₃N₄ composites can be described by the existing CTE models. It is important to determine which of these models best describes the CTE of the MoSi₂–Si₃N₄ composites, so as to be able to obtain a first approximation of the volume fraction of other low CTE ceramic reinforcement particles such as SiC or Y₂O₃ that may be added to MoSi₂ so that the CTE of the ceramic particle-reinforced MoSi₂ composite matches the CTE of Mo at high temperatures required for glass melting. Attention is focused on the 40 vol.% materials rather than the 10 vol.% materials, since the volume fraction of Si₃N₄ required in the MoSi₂–Si₃N₄ composite coatings such that the CTE of the coating matches the CTE of the Mo substrate at temperatures required for glass melting (≈ 1000–1500°C) is between 30 and 35 vol.% (Fig. 2). It is expected that, if other low CTE particles such as SiC or Y₂O₃ are added to MoSi₂, since their CTE is higher than that of Si₃N₄, the volume fraction of these particles required in the MoSi₂ composites to match the CTE of Mo at high temperatures will be closer to 40 than 10 vol.%. 

The existing models for the CTE of a two-phase composite, α_c, are: (i) simple rule of mixtures, (ii) Turner’s model and (iii) Kerner’s model. In the absence of any phase interactions, it is expected that the CTE of a composite should obey the simple rule of mixtures. However, it is often observed that microstresses exist between the phases [14]. As a result, Turner’s and Kerner’s models were developed to take into account the microstresses that exist between the phases. 

1. The simple rule of mixtures is as follows: 

\[ \alpha_c = f_m \alpha_m + f_p \alpha_p \] 

The CTE according to Turner’s model [15] is: 

\[ \alpha_c = \frac{\alpha_m f_m E_m + \alpha_p f_p E_p}{f_m E_m + f_p E_p} \] 

Turner’s model is based on the assumption that only uniform hydrostatic stresses exist in the composite. To account for both the shear and isostatic stresses, Kerner developed a model given in [16]: 

\[ \alpha_c = \frac{\alpha_m f_m + \alpha_p f_p - (\alpha_m - \alpha_p) f_m f_p (E_m^{-1} - E_p^{-1})}{f_m + f_p + \frac{3}{E_m E_p} + \frac{1}{4G_m}} \] 

where \( \alpha \) is the linear coefficient of thermal expansion, \( f \) is the volume fraction of the material, \( E \) is the moduli of the material, \( G \) is the shear modulus, and the subscripts c, m, and p, denote composite, matrix and particulate reinforcement, respectively.

Fig. 3 shows the experimental values of the CTE for the 40 vol.% Si₃N₄ materials and the predicted values using the; (i) simple rule of mixtures, (ii) Turner’s model [12] and (iii) Kerner’s model [16]. From Fig. 3 several important points are noted. Firstly, the CTE of the 40 BM and 40 DM materials is below the simple rule of mixtures prediction. These results are in agreement with the experimental results reported in the literature for composite materials which reveal that the CTE often tends to fall below the simple rule of mixtures prediction [15,17–19]. Secondly, the experimental data for 40
BM and 40 DM lies closet to Kerner's prediction. This result is very reasonable, since it is expected that the 40 vol.% materials would have a significant shear contribution to the CTE from the many grain boundaries/interfaces present in these materials as a result of their fine grain size. Kerner's model (Eq. (5)) considers grain boundary/interface shear stresses while Turner's model (Eq. (4)) ignores the shear effects associated with the grain boundaries/interfaces.

Even though, for the 40 vol.% materials, Kerner's model gives the closest fit to the experimental data, it is of interest to note that there is a significant deviation from the prediction. A likely cause of this deviation is the large difference in the CTE between the MoSi, matrix and the Si,N, particles (≈ 5 × 10⁻⁶/°C) leading to microcracking along the MoSi,/Si,N, interfaces during cooling from high temperature. Scanning electron microscopy observations of the 40 vol.% materials did reveal the presence of microcracks at the MoSi,/Si,N, interfaces. The suggestion that microcracks at MoSi,/Si,N, interfaces is responsible for the low experimental CTE of the composites compared to theoretical predictions is in good agreement with previous experimental investigations on two-phase composites with different CTEs for each phase, anisotropic single-phase materials and theoretical predictions, which reveal or predict a decrease in CTE as a result of microcracks which result from the difference in CTE between the phases or anisotropy in single-phase materials [19–24].

5. Conclusions

1. It is observed that the CTE of the MoSi,–Si,N, composites decreases as the volume fraction of Si,N, increases. This is expected since, the CTE of Si,N, is lower than that for MoSi,.

2. Microstructure does indeed influence CTE of the MoSi,–Si,N, composites. At the high vol.% of Si,N, (40) where the microstructural variables are similar there is no appreciable difference in CTE between the BM and DM materials. At low Si,N, vol.% (10) where there is a difference in microstructure (grain size and particle size), there is a significant difference in the CTE between the 10 BM and 10 DM materials. Modeling of the MoSi, grain size effect on the CTE reveals that the CTE of the 10 BM and 10 DM materials is independent of MoSi, grain size over the range investigated. As a result, it is suggested that the major microstructural variable responsible for the CTE difference between the 10 BM and 10 DM materials is the Si,N, particle size. The CTE of MoSi,–Si,N, composites increases with decreasing Si,N, particle size.

3. The volume fraction of Si,N, required in the MoSi,–Si,N, composite coatings, such that the CTE of the coating matches the CTE of Mo substrate at temperatures required for glass melting (≈ 1000–1500°C), is between 30 and 35 vol.%. At the high vol.% (≈ 40) of Si,N, particulates required in MoSi,, so that the CTE of the composite is close to that of Mo, Kerner's model provides the closest prediction to the experimental data. Kerner's model provides the best estimate because it incorporates the effects of interfacial shear stresses which result from many MoSi,/Si,N, interfaces. Deviation from the prediction is most likely a result of microcracks at MoSi,/Si,N, interfaces.

Acknowledgements

The authors wish to acknowledge the University of California Energy Institute for financial support of this research. The authors also would like to thank the reviewer for the excellent comments.

References


Fig. 5. Theoretical and experimental coefficient of thermal expansion vs. temperature for the MoSi,–40vol.%Si,N, composites.