The effect of Si₃N₄ on the thermal expansion behavior of MoSi₂

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Abstract

The effect of Si₃N₄ particulates on the thermal expansion coefficient (CTE) of MoSi₂ was investigated. It was observed that as the volume percent of Si₃N₄ increases, the CTE of the MoSi₂–Si₃N₄ composites decreases. In the temperature range 1000–1500°C, typical of that required for glass melting, about 30–35 vol% Si₃N₄ particulates are needed in the MoSi₂–Si₃N₄ composites such that the CTE of the composite matches the CTE of Mo.

Keywords: MoSi₂–Si₃N₄ composites; Thermal expansion coefficient; Glass melting

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 [1,2]. 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. Molybdenum disilicide 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 temperature [2–4]. However, the coefficient of thermal expansion (CTE) of MoSi₂ is higher than that of Mo (8.5 × 10⁻⁶C⁻¹ [5] versus 5.8 × 10⁻⁶C⁻¹ [5]), leading to transverse cracking within the coating and delamination near or at the coating/substrate interface [6–8]. 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 Letter to: (i) investigate if the CTE of the MoSi₂–Si₃N₄ particulate reinforced composites decreases as the Si₃N₄ particulate volume fraction increases and (ii) experimentally 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 1000–1500°C, typical of that required for glass melting. Such data is necessary in order to determine which of the existing theoretical models (e.g., rule of mixtures (ROM), Kernèr’s [9] or Turner’s [10]) best describes the CTE of the MoSi₂–Si₃N₄ composites in the temperature range where they are to be utilized as a protective coating for Mo.

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2. Experimental

MoSi₂−Si₃N₄ particulate composites were synthesized from MoSi₂ and Si₃N₄ powders (H.C. Starck Gmbh and Co., Germany). Silicon nitride was chosen for its similar oxidation resistance at high temperature and its low CTE (3.5 × 10⁻⁶C⁻¹ [5]) compared to MoSi₂. The starting size of the MoSi₂ powders was less than 44 μm and the Si₃N₄ powders was less than 30 μm. Ball milling (BM) was used to mix the powders. The MoSi₂ and Si₃N₄ powders were milled with steel balls for 12 h in a container flushed with argon gas. The container was water cooled to maintain the temperature at 25°C. The powder to ball ratio was 1:10. A total of three different MoSi₂−Si₃N₄ composite materials were prepared; containing 10, 20, and 40 vol% of Si₃N₄ (10 BM, 20 BM, and 40 BM, respectively). The mixed powders were then placed in niobium cans, degassed and hot-isostatically pressed (hipped) at 1800°C for 2 h using a pressure of 193 MPa. The hipped material was sectioned into smaller pieces for X-ray diffraction, microstructural examination, and CTE experiments.

The thermal expansion measurements were performed using a theta dilatometer (Dilatamtic II S). A cylindrical sapphire crystal was used for calibration. The CTE of the sapphire crystal was observed to be in excellent agreement with sapphire thermal expansion data found in the literature [11]. For the CTE studies the MoSi₂−Si₃N₄ composites were cut into rectangular parallelepipeds with typical dimensions of 5 mm × 5 mm × 25 mm. The CTE of the samples was measured as they were heated in air from room temperature at a rate of 5°C/min until about 1300°C. At least three samples were tested for each of the three compositions.

3. Results and discussion

The X-ray diffraction patterns of the 10 BM, 20 BM, and 40 BM materials after hipping revealed MoSi₂ (tetragonal phase) and Si₃N₄ (beta phase) as the major phases. A small SiO₂ peak was present in the 10 BM material, but not in the 20 and 40 BM materials. No other Mo−Si phases (e.g., Mo₅Si₃) were observed in any of the three materials. The MoSi₂ and Si₃N₄ peaks in the hipped 10, 20, and 40 BM materials were identical to those observed in the starting powders as well as the ball milled powders. The amount of SiO₂ determined from the diffraction patterns was estimated to be less than 3 vol%.

The major microstructural variables for the densified 10, 20 and 40 BM materials are listed in Table 1. Density measurements revealed that hipping completely densified the powders. The relative density of the hipped 10, 20 and 40 BM materials was 99, 95, and 97%, respectively. Image analysis revealed no apparent porosity in the 10 and 40 BM materials, confirming that hipping produced a fully dense material.

An optical micrograph of a typical MoSi₂−Si₃N₄ microstructure is shown in Fig. 1. In this case, the 20 vol% Si₃N₄ material exhibited a lamellar microstructure, which is typical for these materials. The CTE results are shown in Fig. 2. The CTE values increase with increasing Si₃N₄ content, as expected.
BM material is shown. The Si₃N₄ particles are black, whereas the MoSi₂ phase is white. From Fig. 1 it is observed that ball milling resulted in a uniform distribution of Si₃N₄ particles. A similar result was observed for the 10 and 40 BM materials. The Si₃N₄ particulate shape was nearly spherical and the same diameter (5–6 μm) for all three compositions.

In all three materials the MoSi₂ matrix grains were equiaxed. From Table 1 it is observed that as the volume fraction of Si₃N₄ increases from 10 to 20%, the MoSi₂ grain size decreases from about 15 to 8 μm. However, as the volume fraction of Si₃N₄ increases from 20 to 40% there is very little change in MoSi₂ grain size (8 to 6 μm).

Hence, the only other variables which could affect the CTE of the three materials besides the difference in Si₃N₄ volume fraction are: (i) porosity difference, (ii) MoSi₂ matrix grain size difference and (iii) presence of the SiO₂ phase in the 10 BM material. Coble and Kingery [12] have shown that the CTE is independent of porosity thus, eliminating this as a variable. The major difference between the 20 and 40 BM materials is in the amount of Si₃N₄. However, between these two materials and the 10 BM material there is a difference in MoSi₂ grain size and the presence of the SiO₂ phase. In a first approximation without sufficient data available we will assume that these effects on the CTE are small in comparison to the effect of Si₃N₄ on the CTE behavior and hence, neglect them in this paper. As a consequence, it will be assumed that any difference in the CTE behavior between the three materials is only a result of the difference in Si₃N₄ volume fraction. Future work will determine if this assumption is justified.

Fig. 2 is a graph of the thermal expansion coefficient as function of temperature for the 10, 20, and 40 BM materials. Included in Fig. 2 is data for monolithic MoSi₂ [5]. From Fig. 2 it is observed that the CTE of the MoSi₂–Si₃N₄ composites decreases as the volume fraction of Si₃N₄ increases. That is, the 40 BM material has the lowest CTE whereas the 10 BM material has the highest. 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. 2 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. 2 were not reported [5]. In any case, the important trend shown in Fig. 2 is that the CTE of the MoSi₂–Si₃N₄ composites decreases as the amount of Si₃N₄ particulates increases.

Fig. 3 is a plot of the thermal expansion coefficient for the MoSi₂–Si₃N₄ composites as a function of volume percent Si₃N₄ at 1200°C. Included in this plot is the CTE for Mo at 1200°C [5]. From this plot, a volume fraction of about 33% Si₃N₄ is required such that the CTE of the MoSi₂–Si₃N₄ composite 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

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**Table 1**

Microstructural variables for the MoSi₂–10, 20 and 40 vol% Si₃N₄ materials

<table>
<thead>
<tr>
<th>Material (vol% Si₃N₄)</th>
<th>Relative density (%)</th>
<th>MoSi₂ grain size (μm)</th>
<th>Si₃N₄ particle size (μm)</th>
<th>Si₃N₄ particle shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>99</td>
<td>15</td>
<td>5</td>
<td>spherical</td>
</tr>
<tr>
<td>20</td>
<td>95</td>
<td>8</td>
<td>6</td>
<td>spherical</td>
</tr>
<tr>
<td>40</td>
<td>97</td>
<td>6</td>
<td>6</td>
<td>spherical</td>
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</tbody>
</table>
the thermal expansion coefficient of Mo is 32 and 34\%, respectively. These results suggest that the volume fraction of Si$_3$N$_4$ required in the MoSi$_2$–Si$_3$N$_4$ 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 volume \%.

4. Conclusions

It was observed that the addition of Si$_3$N$_4$ does indeed decrease the thermal expansion coefficient of MoSi$_2$. As the volume percent of Si$_3$N$_4$ increases, the thermal expansion coefficient of the MoSi$_2$–Si$_3$N$_4$ composites decreases. In the temperature range 1000–1500°C, typical of that required for glass melting, about 30–35 vol\% Si$_3$N$_4$ particulates are needed in the MoSi$_2$–Si$_3$N$_4$ composites such that the CTE of the composite matches the CTE of Mo. Based on these experimental results it would be of interest to determine which of the existing theoretical models for CTE (e.g., ROM) best describes the CTE behavior of the MoSi$_2$–Si$_3$N$_4$ composites.

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References