Toughening Effect and Oxidation Behavior of MoSi2-ZrO2 Composites

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Toughening Effect and Oxidation Behavior of MoSi2-ZrO2 Composites

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Abstract
Toughening effect of ZrO2-particles in MoSi2-based materials is one of the important toughening mechanism. In this work, the influence of particle size and volume percentage of unstabilized ZrO2-addition on toughening in MoSi2-matrix composites was studied. The measured data revealed that the fine particle size, < 1 μm, with certain volume percentages around 20% gave more effective toughening results. The tested materials were prepared by two different sintering processes: pressure-less sintering (PLS) and PLS + Hipping sintering. The results on sintered density, RT-hardness and RT-toughness indicated that the PLS process could be a practical and economical method for producing MoSi2-ZrO2 composites in industry. Oxidation behavior of MoSi2-ZrO2 composites was also studied in the work. Clearly, the ZrO2-addition made the oxidation resistance of the composites worse than that of monolithic MoSi2, which means that a low ZrO2-addition should be used in the composites, as far as an acceptable toughening effect was reached.

Introduction
Structural materials used under oxidizing and aggressive environments at temperatures above 1000 °C have drawn special attention from materials scientists. The choice of materials is limited to the silicon-based structural materials. And, MoSi2 is presently considered as one of the promising materials due to its high melting point (2030°C) and excellent high temperature oxidation resistance. MoSi2 as an intermetallic material, one major problem, which has impeded its usage as high temperature structural materials, is poor ductility and toughness below brittle-to-ductile transition temperature, around 1350°C [1].

Addition of alloying elements into MoSi2 may lead to solid solution strengthening and improved toughness of MoSi2. Clearly, the alloying effects depend on the solid solubility of the added alloying elements. The solid solubility of transition metal elements in MoSi2 have been systematically studied [2-10] with these alloying process. So, the alloying additions have been found to have a limited toughening effect on MoSi2. Further progress depends on the development of engineered composite materials. At the end of 1980’s, Mcdonnell Douglas Research Laboratories (MDRL) [11] reported that MoSi2-matrix is compatible with most of the selected ceramic reinforcements up to a reasonable application temperature; say 1700 °C. Lately, works [12-22] have clearly demonstrated that ZrO2-toughening effect may be employed to improve MoSi2-based materials significantly. In 1992, Petrovic et al. [18] indicated that the presence of an unstabilized ZrO2 particle phase in MoSi2/ZrO2 composites increased the room temperature indentation fracture toughness by a factor of 3 over that of monolithic MoSi2. Observed composite toughness levels for partially stabilized and fully stabilized ZrO2 were lower than those of unstabilized ZrO2. In our earlier investigation [21], the toughness of MoSi2/unstabilized ZrO2 (UZ) composites was also found to be much higher than for YPSZ composites.
In the present work, the influence of size and volume percentage of ZrO$_2$-particles on toughening effect of the MoSi$_2$-ZrO$_2$ composites was investigated. And, the negative effect of ZrO$_2$-addition on oxidation resistance of the composites was also addressed in the study.

**Experiments**

**Materials and preparation**

In the first step of this work, five different USZ-particle sizes, listed in table 1, were tested in the composites with a composition of MoSi$_2$ – 20 vol.% ZrO$_2$. The composites were prepared by pressure-less sintering (PLS) at 1650 °C in H$_2$ for 1 hr. The commercial Kanthal MoSi$_2$ powders (KT-MoSi$_2$) with average size of 2.2 µm in diameter were used for preparing the specimens.

<table>
<thead>
<tr>
<th>Commercial mark</th>
<th>SF-Extra</th>
<th>DK-1</th>
<th>SF-Premium</th>
<th>DK-2</th>
<th>DK-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average size (µm)</td>
<td>0.74</td>
<td>0.87</td>
<td>0.96</td>
<td>2.13</td>
<td>5.65</td>
</tr>
</tbody>
</table>

The powder mixtures were dispersed by milling in gasoline for 4 hours, and then dried at a temperature below 100°C. The homogeneously mixed powders were processed by crashing and sieving through 400 meshes. The green bodies of 10mm x 10mm x 40mm for pressure-less sintering were produced by a hydraulic press under 306 MPa, and reached a density around 60%. The bulk density of the sintered materials was measured according to ASTM C373. Identities of the tested samples are summarized in Table 2.

<table>
<thead>
<tr>
<th>Mark of sample</th>
<th>Starting powder</th>
<th>Sintering process</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS – 1</td>
<td>KT-MoSi$_2$ + SF-Extra</td>
<td>Pressure-less sintered</td>
</tr>
<tr>
<td>PLS – 2</td>
<td>KT-MoSi$_2$ + DK-1</td>
<td>as above</td>
</tr>
<tr>
<td>PLS – 3</td>
<td>KT-MoSi$_2$ + SF-premium</td>
<td>as above</td>
</tr>
<tr>
<td>PLS – 4</td>
<td>KT-MoSi$_2$ + DK-2</td>
<td>as above</td>
</tr>
<tr>
<td>PLS – 5</td>
<td>KT-MoSi$_2$ + DK-3</td>
<td>as above</td>
</tr>
<tr>
<td>PLS – 6</td>
<td>KT-MoSi$_2$</td>
<td>as above</td>
</tr>
</tbody>
</table>

Afterwards, a second group of composites were produced for evaluating the influence of volume percentage of ZrO$_2$-particles in the materials on toughening effect. Five different composites with the volume percentages of ZrO$_2$ in a range of 10-30 vol.% were prepared. The used ZrO$_2$ particles are commercial C208 with an average diameter of 0.64 µm. The green bodies of composite specimens were PL-sintered at the first for a high density over 95%, and then sintered by HIPping without capsule under 200 MPa at 1600°C for 4 hours to a near-full density. The sample identities were given in Table 3.

<table>
<thead>
<tr>
<th>Mark of sample</th>
<th>Starting powder (vol. %)</th>
<th>Sintering process</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIP-1</td>
<td>90 vol. %KT-MoSi$_2$ + 10 vol. % C208</td>
<td>Hot Isostatic Press</td>
</tr>
<tr>
<td>HIP-2</td>
<td>85 vol. %KT-MoSi$_2$ + 15 vol. % C208</td>
<td>as above</td>
</tr>
<tr>
<td>HIP-3</td>
<td>80 vol. %KT-MoSi$_2$ + 20 vol. % C208</td>
<td>as above</td>
</tr>
<tr>
<td>HIP-4</td>
<td>75 vol. %KT-MoSi$_2$ + 25 vol. % C208</td>
<td>as above</td>
</tr>
<tr>
<td>HIP-5</td>
<td>70 vol. %KT-MoSi$_2$ + 30 vol. % C208</td>
<td>as above</td>
</tr>
</tbody>
</table>

The room temperature hardness and fracture toughness of the tested materials were determined by using Vickers' indentation technique. The morphology of indentation cracks and their propagation were investigated by optical microscopy. 20 Vickers indentation tests were performed on each
The applied indentation load was 10 Kg. The impression size and the radial crack length were carefully measured. The fracture toughness of these composites was calculated by using Anstis' equation [23]. The applied elastic modules of the composites for calculation was estimated by a rule of mixtures from the volume fraction of MoSi₂ and ZrO₂ using $E_{MoSi_2} = 440 \text{ GPa} \ [30]$ and $E_{ZrO_2} = 210 \text{ GPa} \ [31]$.

**Oxidation Tests**

Oxidation test carried out less than 1400ºC for 100 hours. Surface stability under high temperatures should be one of the important characteristics of the MoSi₂-based alloys. Therefore, the influence of 20 vol. % ZrO₂-addition on oxidation resistance of the MoSi₂-matrix composite was also investigated in this study. A monolithic MoSi₂ sample was tested as a reference. In the study, surfaces of the testing specimens were ground and polished before the oxidation procedure. And after the procedure, the oxidized specimens were examined by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) to identify the phase constitution.

**Results**

**Sintered Density, RT-Hardness and RT-Toughness**

The measured density, room temperature hardness and toughness of the tested specimens were given in Table 4 and Table 5, respectively. The data in parenthesis are the relative densities by calculation, assuming the densities of MoSi₂, m-ZrO₂ and t-ZrO₂ are 6.25, 5.56, and 6.05 g/cm³, respectively. Due to a small amount of heavy Mo₅Si₃-phase always existed on the MoSi₂ matrix, the calculated relative densities in the tables should be only considered as references.

**Table 4. Sintered density, RT-hardness and Toughness of MoSi₂ – 20vol.%ZrO₂ composites by PLS process**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sintered density (g/cm³)</th>
<th>RT-Hardness (Hv, GPa)</th>
<th>RT-toughness (MPam¹/₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLS-1</td>
<td>6.07 (98%)</td>
<td>7.82 ± 0.41</td>
<td>5.79 ± 0.49</td>
</tr>
<tr>
<td>PLS-2</td>
<td>6.13 (99%)</td>
<td>7.80 ± 0.46</td>
<td>6.89 ± 0.47</td>
</tr>
<tr>
<td>PLS-3</td>
<td>6.08 (98%)</td>
<td>7.48 ±0.41</td>
<td>5.63 ± 0.41</td>
</tr>
<tr>
<td>PLS-4</td>
<td>6.02 (97%)</td>
<td>6.97 ± 0.27</td>
<td>4.61 ± 0.42</td>
</tr>
<tr>
<td>PLS-5</td>
<td>5.89 (95%)</td>
<td>6.01 ±0.25</td>
<td>4.06 ± 0.21</td>
</tr>
<tr>
<td>PLS-6</td>
<td>6.07 (97%)</td>
<td>9.19 ± 0.16</td>
<td>3.09 ± 0.19</td>
</tr>
</tbody>
</table>

**Table 5. Sintered density, RT-hardness and Toughness of five different ZrO₂- content composites prepared by PLS + HIP processes**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Sintered density (g/cm³)</th>
<th>RT-Hardness (Hv, GPa)</th>
<th>RT-toughness (MPam¹/₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIP-1</td>
<td>6.31 (100%)</td>
<td>9.76 ± 0.20</td>
<td>4.50 ± 0.35</td>
</tr>
<tr>
<td>HIP-2</td>
<td>6.34 (100%)</td>
<td>9.64 ± 0.22</td>
<td>4.60 ± 0.35</td>
</tr>
<tr>
<td>HIP-3</td>
<td>6.17 (99.5%)</td>
<td>9.13 ± 0.25</td>
<td>5.65 ± 0.54</td>
</tr>
<tr>
<td>HIP-4</td>
<td>6.16 (99.5%)</td>
<td>8.96 ± 0.15</td>
<td>6.13 ± 0.41</td>
</tr>
<tr>
<td>HIP-5</td>
<td>6.16 (99.5%)</td>
<td>9.00 ± 0.20</td>
<td>5.79 ± 0.24</td>
</tr>
</tbody>
</table>

**Analytical Work on the Oxidized Materials**

The cross-sections in Fig.1 show the typical microstructures of the oxidized composite and monolithic specimens. The oxidized composite has a thick surface oxide layer and an internal oxidation zone with thickness of 110 µm and 200 µm respectively, see Fig.1a. In contrast, the monolithic MoSi₂ exhibits an excellent oxidation resistance due to a protective silica scale with an average thickness 25 µm, which is under one fourth of that in the composite counterpart. No internal oxidation occurs in the sub-interface region, see Fig.1b. And, XRD estimation showed that crystalline phases of oxide layer in the composite is consisting of 70 wt% tetragonal ZrSiO₄ and 30
wt% of tetragonal SiO₂. Obviously, this loose layer is un-protective, and most parts of it were spalled off from the substrate during cooling.

Discussion

In the work, MoSi₂-20vol.%ZrO₂ (USZ) composites using five different sizes of ZrO₂-particles in a range of 0.74 – 5.65 μm were prepared by PLS process. The sintered densities of the prepared composites in Table 4 revealed that the high sintered densities, 95% or even higher, were related to the addition of ZrO₂-particles. It seems that the ZrO₂-addition worked as a sintering agent for a high sintered density of the composites due to the reaction between the thin layer of SiO₂-glassy phase on MoSi₂-particles and the added ZrO₂-particles [17, 21]. And, it could also help to understand that the composites with fine ZrO₂-particle addition showed higher sintered density and hardness due to a better dispersive distribution of ZrO₂-particles and more homogeneous interface-reaction, Table 4. For the HIPed specimen, HIP-3 of the same composition is higher than the pressure-less sintered specimens due to an applied external pressure. The room-temperature hardness (RT-Hv) of the pressure-less sintered composites reinforced by the fine ZrO₂-particles (PLS-1, PLS-2 and PLS-3) was also higher than the composites contained the large ZrO₂-particles (PLS-4 and PLS-5).

The measured toughness data of PLS-specimens in Table 4 showed that the USZ-particles with sizes of less than 1 μm generated a better toughening effect, compared to the large size particles. Claussen [24] also indicated that a critical particle size range for ZrO₂ exists, within which tetragonal particles can be transformed. It means that the optimum toughening effects should be in the case when the particles are large enough to transform but only small enough to cause limited micro-crack development.

The measured hardness data in the same table also showed that the composites with ZrO₂-particle sizes of less than 1 μm have higher hardness values than the large ZrO₂-particle added composites. So far, it can be clearly concluded that the small ZrO₂-particles, less than 1 μm in size, are necessary to produce MoS₂-ZrO₂ (USZ) composites for better hardness, toughness and sintered density.

It seems that the external pressure during the sintering obviously increased hardness of the composite, but not so much influence on sintered density and toughness. Therefore, the phenomenon should be related to the interfacial connection between the sintered particles.

To evaluate the influence of volume percentage of unstabilized ZrO₂-particles in the composites on toughening effect, five composites with the volume percentages of ZrO₂, as 10, 15, 20, 25, and 30 vol.%, were prepared by PLS + HIP processes. The used ZrO₂ particles are commercial C208 in an average diameter of 0.64 μm. It was supposed that the sintered materials have a full-density and the best interfacial bonding between MoSi₂-matrix and ZrO₂-particles. In fact, the materials really showed higher hardness after Hipping process, compared to the PLSed materials, see Table 5 and 4. The measured RT-toughness data in Table 5 showed that the composites containing 15 – 25 vol.% USZ-particles have a better toughening effect, compared with the composites having 10 or 30 vol.% particles.

In general, the diffusion rate of Si determines the oxidation behavior of MoSi₂ and MoSi₂-matrix composites [25, 26]. In the present study, oxidation of the composite involved two reactions under 1400°C. Mo₅Si₃ and SiO₂ were formed at first, and then the resultant SiO₂ reacted with ZrO₂ in the matrix to form ZrSiO₄. The reactions can be described as following:

$$5\text{MoSi}_2 + 7\text{O}_2 \rightarrow \text{Mo}_5\text{Si}_3 + 7\text{SiO}_2$$  (1)

$$\text{SiO}_2 + \text{ZrO}_2 \rightarrow \text{ZrSiO}_4$$  (2)

When the reactions (1) and (2) take place simultaneously, a composite oxide layer of SiO₂+ZrSiO₄ will be formed. Since ZrO₂ and ZrSiO₄ are more stable thermodynamically with oxygen compared with Si/SiO₂. It will be difficult for them to establish a continuously protective scale [35]. If the scale contains mostly ZrSiO₄, the resultant scale will consequently porous and un-adhesive, this will
lead to a direct oxidation at the interface between oxide layer and MoSi2 substrate, and finally resulted in a linear oxidation rate. As a result, a severe inner oxidation (1) and the reaction (2) occur in the reactive zone in the sub-interface region due to a high oxygen activity. The resultant ZrSiO4/ZrO2 particles, on one hand, reserve the SiO2 in the reactive zone. On another hand, the inner oxidation also consumes the Si atoms diffused from the inner bulk to the scale interface. Therefore, the transferring of Si towards scale/substrate interface is significantly hindered, even though the Si diffusing from the bulk is in a similar level to that in the monolithic MoSi2 (estimated from the thickness of the depleted zone). A continuous and adhesive layer can be formed on the oxide/substrate interface only when the content of SiO2 in the scale is high enough. Therefore, a certain addition of alloying elements to form a protective oxide layer is needed to improve oxidation resistance for this type of composites.

Conclusions
1. The unstabilized ZrO2 particles of less than 1 μm improved sintered density, RT-hardness and RT toughness of the composites, compared with the bigger particles.
2. The composites containing 15 – 25 vol. % fine USZ-particles showed a better toughening effect, compared to the composites having less or more particles.
3. The PLS process could be a practical and economical method in industry for producing MOSi2 ZrO2 composites with high sintered density. External pressure during sintering process assisted in obtaining a higher hardness, but only slightly improved sintered density and toughness.
4. A deteriorated oxidation resistance of MoSi2-ZrO2 composite compared to its monolithic counterpart is due to the formation of the porous oxide layer of ZrSiO4+SiO2 mixture and a retarded Si diffusion by the inner oxidation.

Figure captions

![Fig.1 (a) shows the typical microstructures in the oxidized composite which is characterized by a thick oxide layer and an inner oxidation zone with thickness of 110 μm and 200 μm respectively.](image)

![Fig.1 (b) the monolithic MoSi2 exhibits an excellent oxidation resistance of silica scale with an average thickness 25 μm, which is under one fourth of that in the composite counterpart.](image)

References