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Toughening Effect and Oxidation Behavior of MoSi2 -ZrO2 Composites

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Abstract

Toughening effect of ZrO_2-particles in $MoSi_2$-based materials is one of the important toughening mechanism. In this work, the influence of particle size and volume percentage of unstabilized ZrO_2-addition on toughening in $MoSi_2$-matrix composites was studied. The measured data revealed that the fine particle size, < 1 m, 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 $MOSi_2$-ZrO_2 composites in industry. Oxidation behavior of $MoSi_2$-ZrO_2 composites was also studied in the work. Clearly, the ZrO_2-addition made the oxidation resistance of the composites worse than that of monolithic $MoSi_2$, which means that a low ZrO_2-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 ºC have drawn special attention from materials scientists. The choice of materials is limited to the silicon-based structural materials. And, $MoSi_2$ is presently considered as one of the promising materials due to its high melting point (2030ºC) and excellent high temperature oxidation resistance. $MoSi_2$ 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 1350ºC [1].

Addition of alloying elements into $MoSi_2$ may lead to solid solution strengthening and improved toughness of $MoSi_2$. Clearly, the alloying effects depend on the solid solubility of the added alloying elements. The solid solubility of transition metal elements in $MoSi_2$ have been systematically studied [2-10] with these alloying process. So, the alloying additions have been found to have a limited toughening effect on $MoSi_2$. Further progress depends on the development of engineered composite materials. At the end of 1980´s, Mcdonnell Douglas Research Laboratories (MDRL) [11] reported that $MoSi_2$-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 ZrO_2-toughening effect may be employed to improve $MoSi_2$-based materials significantly. In 1992, Petrovic et al. [18] indicated that the presence of an unstabilized ZrO_2 particle phase in $MoSi_2$/ZrO_2 composites increased the room temperature indentation fracture toughness by a factor of 3 over that of monolithic $MoSi_2$. Observed composite toughness levels for partially stabilized and fully stabilized ZrO_2 were lower than those of unstabilized ZrO_2. In our earlier investigation [21], the toughness of $MoSi_2$/unstabilized ZrO_2 (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 table1, 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.

Table1. The starting powders of ZrO_2 used for preparing $MoSi_2$ – 20vol.% ZrO_2 composites

Commercial mark	SF-Extra	DK-1	SF-Premium	DK-2	DK-3
Average size (μm)	0.74	0.87	0.96	2.13	5.65

The powder mixtures were dispersed by milling in gasoline for 4 hours, and then dried at a temperature below 100ºC. 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.

Table2. Identities of the MoSi2 – 20vol.% ZrO_2 composites

Mark of sample	starting powder	sintering process
PLS – 1	KT-$MoSi_2$ + SF-Extra	Pressure-less sintered
PLS – 2	KT-$MoSi_2$ + DK-1	as above
PLS – 3	KT-$MoSi_2$ + SF-premium	as above
PLS – 4	KT-$MoSi_2$ + DK-2	as above
PLS – 5	KT-$MoSi_2$ + DK-3	as above
PLS – 6	KT-$MoSi_2$	as above

Table3. Identities compositions of KT-$MoSi_2$ + C208-ZrO_2 composites prepared by PLS + HIP processes

Mark of sample	Starting powder (vol. %)	Sintering process
HIP-1	90 vol. %KT-$MoSi_2$ + 10 vol. % C208	Hot Isostatic Press
HIP-2	85 vol. %KT-$MoSi_2$ + 15 vol. % C208	as above
HIP-3	80 vol. %KT-$MoSi_2$ + 20 vol. % C208	as above
HIP-4	75 vol. %KT-$MoSi_2$ + 25 vol. % C208	as above
HIP-5	70 vol. %KT-$MoSi_2$ + 30 vol. % C208	as above

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 HIPing without capsule under 200 MPa at 1600ºC for 4 hours to a near-full density. The sample identities were given in Table 3.

Hardness and Toughness Measurement

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 sample. 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 $MoSi_2$ and ZrO_2 using E_{MoSi_2} = 440 GPa [30] and E_{ZrO_2} = 210 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 $MoSi_2$-based alloys. Therefore, the influence of 20 vol. % ZrO_2-addition on oxidation resistance of the $MoSi_2$-matrix composite was also investigated in this study. A monolithic $MoSi_2$ 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 $MoSi_2$, m-ZrO_2 and t-ZrO_2 are 6.25, 5.56, and 6.05 g/cm^3, respectively. Due to a small amount of heavy Mo_5Si_3-phase always existed on the $MoSi_2$ matrix, the calculated relative densities in the tables should be only considered as references.

Table4. Sintered density, RT- hardness and Toughness of $MoSi_2$ – 20vol.%ZrO_2 composites by PLS process

Specimen	Sintered density (g/cm^3)	RT-Hardness (Hv, GPa)	RT-toughness (MPam$^{1/2}$)
PLS-1	6.07 (98%)	7.82 ± 0.41	5.79 ± 0.49
PLS-2	6.13 (99%)	7.80 ± 0.46	6.89 ± 0.47
PLS-3	6.08 (98%)	7.48 ±0.41	5.63 ± 0.41
PLS-4	6.02 (97%)	6.97 ± 0.27	4.61 ± 0.42
PLS-5	5.89 (95%)	6.01 ± 0.25	4.06 ± 0.21
PLS-6	6.07 (97%)	9.19 ± 0.16	3.09 ± 0.19

Table5. Sintered density, RT-hardness and Toughness of five different ZrO_2- content composites prepared by PLS + HIP processes

Specimen	Sintered density (g/cm^3)	RT-Hardness (Hv, GPa)	RT-toughness (MPam$^{1/2}$)
HIP-1	6.31 (100%)	9.76 ± 0.20	4.50 ± 0.35
HIP-2	6.34 (100%)	9.64 ± 0.22	6.40 ± 0.35
HIP-3	6.17 (99.5%)	9.13 ± 0.25	5.65 ± 0.54
HIP-4	6.16 (99.5%)	8.96 ± 0.15	6.13 ± 0.41
HIP-5	6.16 (99.5%)	9.00 ± 0.20	5.79 ± 0.24

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 $MoSi_2$ 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 $ZrSiO_4$ and 30 wt% of tetragonal SiO_2. Obviously, this loose layer is un-protective, and most parts of it were spalled off from the substrate during cooling.

Discussion

In the work, $MoSi_2$-20vol.%ZrO_2 (USZ) composites using five different sizes of ZrO_2-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 ZrO_2-particles. It seems that the ZrO_2-addition worked as a sintering agent for a high sintered density of the composites due to the reaction between the thin layer of SiO_2-glassy phase on $MoSi_2$-particles and the added ZrO_2-particles [17, 21]. And, it could also help to understand that the composites with fine ZrO_2-particle addition showed higher sintered density and hardness due to a better dispersive distribution of ZrO_2-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 ZrO_2-particles (PLS-1, PLS-2 and PLS-3) was also higher than the composites contained the large ZrO_2-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 ZrO_2 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 ZrO_2-particle sizes of less than 1 μm have higher hardness values than the large ZrO_2-particle added composites. So far, it can be clearly concluded that the small ZrO_2-particles, less than 1 μm in size, are necessary to produce MoS_2-ZrO_2 (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 ZrO_2-particles in the composites on toughening effect, five composites with the volume percentages of ZrO_2, as 10, 15, 20, 25, and 30 vol.%, were prepared by PLS + HIP processes. The used ZrO_2 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 $MoSi_2$-matrix and ZrO_2-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 $MoSi_2$ and $MoSi_2$-matrix composites [25, 26]. In the present study, oxidation of the composite involved two reactions under 1400°C. Mo_5Si_3 and SiO_2 were formed at first, and then the resultant SiO_2 reacted with ZrO_2 in the matrix to form $ZrSiO_4$. The reactions can be described as following:

$$5MoSi_2 + 7O_2 \rightarrow Mo_5Si_3 + 7SiO_2 \qquad (1)$$

$$SiO_2 + ZrO_2 \rightarrow ZrSiO_4 \qquad (2)$$

When the reactions (1) and (2) take place simultaneously, a composite oxide layer of SiO_2+$ZrSiO_4$ will be formed. Since ZrO_2 and $ZrSiO_4$ are more stable thermodynamically with oxygen compared with Si/SiO_2. It will be difficult for them to establish a continuously protective scale [35]. If the scale contains mostly $ZrSiO_4$, 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 $ZrSiO_4/ZrO_2$ particles, on one hand, reserve the SiO_2 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 $MoSi_2$ (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 SiO_2 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 ZrO_2 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 $MOSi_2$ ZrO_2 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 $MoSi_2$-ZrO_2 composite compared to its monolithic counterpart is due to the formation of the porous oxide layer of $ZrSiO_4$+SiO_2 mixture and a retarded Si diffusion by the inner oxidation.

Figure captions

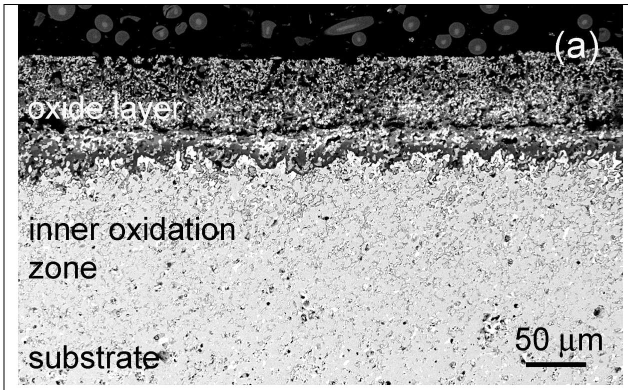

Fig.1 (a) shows the typical microstructures in the oxidized composite which is characterized by a thick oxide layer and an inner oxidation zone with thickness of 110 μm and 200 μm respectively.

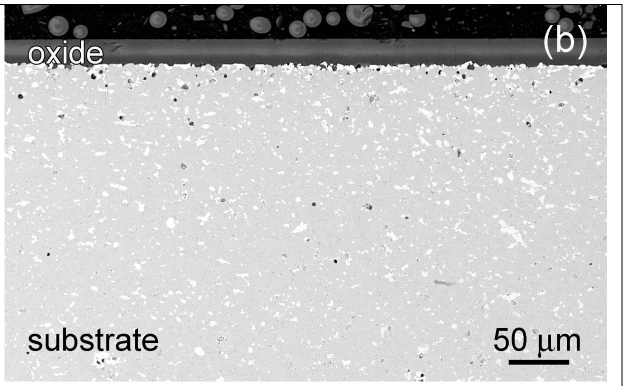

Fig.1 (b) the monolithic $MoSi_2$ exhibits an excellent oxidation resistance of silica scale with an average thickness 25 μm, which is under one fourth of that in the composite counterpart.

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