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Fabrication and characterization of TiC-particle-reinforced $MoSi_2$ composites

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Abstract

TiC particle reinforced molybdenum-disilicide ($MoSi_2$) matrix composites have been fabricated by two step pH adjustment of aqueous slurry and hot press sintering processing. The effects of TiC on the microstructure and mechanical properties of $MoSi_2$ matrix were investigated systematically. Due to the well-dispersed containing up to 40 vol.% TiC_p, the composite showed finer structure and improved mechanical properties than unreinforced material; the average 3-point bending strength at room temperature increased from 268 MPa for monolithic $MoSi_2$ to 445 MPa for 40 vol.% TiC_p–$MoSi_2$. The fracture toughness at room temperature and load-bearing capability at elevated temperature also obviously was improved by the TiC particle reinforcement. This is in contrast to the result published in literatures in which a decrease in strength with the addition of TiC was reported.

Keywords: Composites; Mechanical properties; Microstructure-final; $MoSi_2$; TiC

1. Introduction

With the rapid development of aerospace technology, it is urgent to study the new material used in high temperature (>1200 °C) structural components. The intermetallic compound $MoSi_2$ has become an attractive candidate for structural application at temperatures up to 1600 °C because of its interesting combination of thermophysical and mechanical properties,[1,2] such as strength, ductility and oxidation resistance under service conditions. $MoSi_2$ is thermodynamically stable with a wide variety of potential ceramic reinforcements for composites, including SiC, Si_3N_4, ZrO_2, Al_2O_3, mullite, TiB_2, TiC etc. Its stability extends essentially to the full range of important structural ceramic materials. Because of its relatively high conductivity, $MoSi_2$ and $MoSi_2$-based materials can be electro-discharge machined. However, it exhibits ceramic-like brittleness at room temperature and metal-like plasticity at elevated temperatures. Hence, the improvements of fracture toughness and creep resistance are its major issues.

With the goal of improving mechanical properties, some $MoSi_2$ matrix composites contained SiC,[3–5] ZrO_2,[6,7] Al_2O_3[8]and carbon[9] reinforcements were fabricated and investigated. $MoSi_2$ reinforced with SiC whiskers was reported to have an increase of about 100% in flexural strength and an improvement of 54% in fracture toughness over the matrix.[10–12] This composite also possesses higher oxidation resistance than monolithic $MoSi_2$. However, the major problem in $SiC_w/MoSi_2$ composites is micro-cracking occurred in brittle matrix.[13] Compared to SiC, TiC is an interesting reinforcement because of its high melting point (above 3000 °C), strength, hardness, thermal stability and compatibility to $MoSi_2$.[2] Gibala et al.[14] reported that TiC flowed plastically above its ductile brittle transition temperature (DBTT) of about 600 °C, and its coefficient of thermal expansion is nearly the same as that of $MoSi_2$. Yang and Jeng[15,16] described the microstructure, mechanical properties and fracture behavior of 20 vol.% TiC-reinforced $MoSi_2$ composites. These results showed a decrease in strength and a slight improvement in the fracture toughness for composites compared to monolithic $MoSi_2$. They ascribed the low strength of these composites to the low volume fraction and/or the inhomogeneous distribution of TiC reinforcements.

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In this paper, the volume fraction of TiC particles in $MoSi_2$ matrix was increased up to 40%. The distribution of TiC particles was improved by an optimum processing method. The effect of TiC particle contents on the microstructure, mechanical properties and fracture behavior was investigated systematically.

2. Experimental procedure

2.1. Materials and preparation process

$MoSi_2$ (3∼5 μm) and TiC (0.5 μm) were supplied by China Advanced Technology and Materials Co., Ltd., Refractory Metal and Ceramics Branch. With $MoSi_2$, spectrochemical analysis revealed Mo > 77%, Si ⩾ 21%, C ⩽ 0.2%, O ⩽ 1.0%, free Si ⩽ 0.7% and Fe ⩽ 0.2% (wt.%). X-ray diffraction (XRD) analysis confirmed the powder to be pure $MoSi_2$ with no other crystalline species detected. Composites containing 10, 20, 30, 40 vol.% TiC particles were wet-mixed with $MoSi_2$ with ethyl alcohol at a pH of 11 with agate balls for 24 h. Then the slurry pH was suddenly adjusted to 7, and the slurry became viscous. During two step operations of pH adjustment, a blender was applied to maintain the dispersed state. The stable slurry was dried rapidly, and allowed to pass a 100-mesh screen to obtain a raw mixture powder. The resulting powder mixtures were then cold pressed into a plate and hot-pressed in graphite dies and punches at 1700 °C for 1 h at a pressure of 30 MPa in argon. An additional monolithic $MoSi_2$ sample was fabricated under identical conditions. Densities of hot-pressed compacts ranged from 94 to 96% of theoretical density.

2.2. Microstructure and mechanical test

The specimens were cut by electro-discharge machining from hot-pressed compacts with the tensile surface perpendicular to the hot-pressing direction and then ground with a diamond wheel. Flexural strengths at room temperature and elevated temperature were determined by three-point bending test on 3×4×36 mm bars with a span of 30 mm, and the cross head speed was 0.5 mm/min at room temperature and 2.2 N/s at elevated temperature, respectively. The fracture toughness K_{IC} at room temperature was measured by three-point-bending on a single-edge–notched-beam specimen. The size of specimen was 6×4×30 mm with the notch parallel to the hot-pressing direction. The specimens were notched to a depth of 2.5 mm. K_{IC} was given by:[17]

$$K_{IC} = \frac{P_c S}{BW^{3/2}} f(c/W) \tag{1}$$

where, P_c is the load at fracture, S is the span length, B and W are the width and the height of the test specimen. c is the precrack depth and $f(c/W)$ is a function of c/W

$$f(c/W) = 2.9(c/W)^{1/2} - 4.6(c/W)^{3/2} + 21.8(c/W)^{5/2} - 37.6(c/W)^{7/2} + 38.7(c/W)^{9/2} \tag{2}$$

The densities of samples were measured with Archimedes method. At least five specimens were used for each mechanical test. Each result was average values from 5 samples under the same conditions.

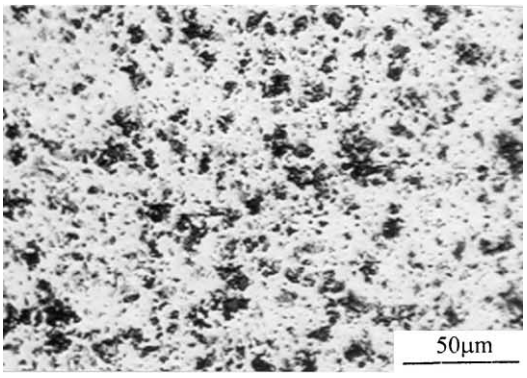
Phase identification was done by a D/mcx-RB X-ray diffractometer. The microstructures were observed by an Olympus BX50 optical/polarized light microscope and the grain size was measured by linear intercept method. The chemical composition of secondary phase in matrix was analyzed and the fracture surface was examined by a JSM-6301F scanning electron microscope. The Vickers hardness was measured on a HV-120 hardness tester with a load of 98 N.

3. Results and discussion

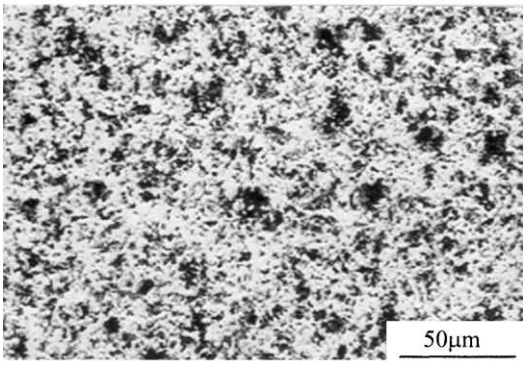
3.1. Microstructure

In order to make TiC particles homogeneously dispersed in $MoSi_2$ matrix, two step pH adjustment of mixed slurry was used. In the first step, the pH value of the slurry is adjusted to 11, at which TiC particles and $MoSi_2$ powders are dispersed homogeneously by electrostatic repulsion. In subsequent drying, a matrix enriched layer and a TiC particle layer are formed because the viscosity of the mixed slurry is low at high pH value and so the matrix powder precipitates faster than particles. In the second step, the slurry pH is rapidly changed from 11 to 7 so that the slurry becomes much viscous and the relative motion of $MoSi_2$ powders and TiC particles was prohibited. Thus, the delamination of the particles and powder is eliminated.

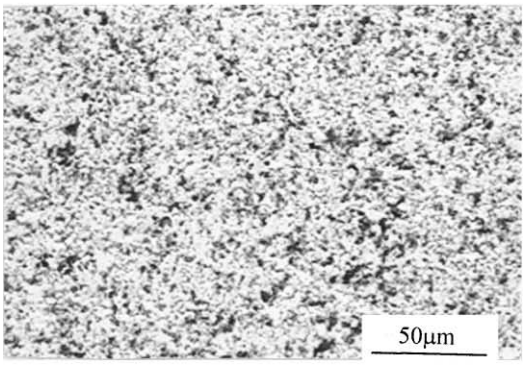
Typical micrographs of monolithic $MoSi_2$ and hot-pressed $TiC_p/MoSi_2$ composites with 20 and 40 vol.% TiC particles are shown in Fig. 1, respectively. As can be seen, the wet mixing processing accompanying pH adjustment produced reasonably uniform microstructure of $TiC_p/MoSi_2$. The magnified SEM micrographs of $MoSi_2$ and $TiC/MoSi_2$ composites with high resolution shown in Fig. 2 revealed that TiC particles were homogeneously distributed among $MoSi_2$ grains. The addition of the TiC particles clearly retarded grain growth of the $MoSi_2$ matrix during the consolidation process, leading to a finer microstructure, and the decrease of the amount of porosities was shown in Fig. 1. Therefore, the density of $TiC_p/MoSi_2$ composites is



(a) $MoSi_2$

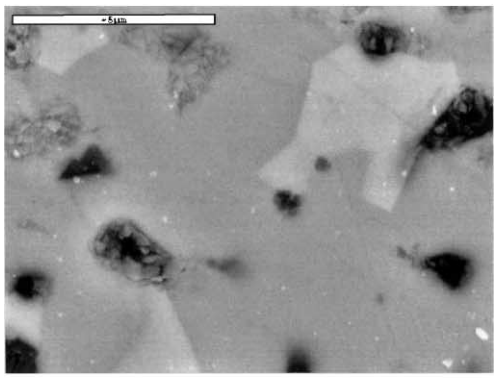


(b) 20vol%TiC_p-$MoSi_2$

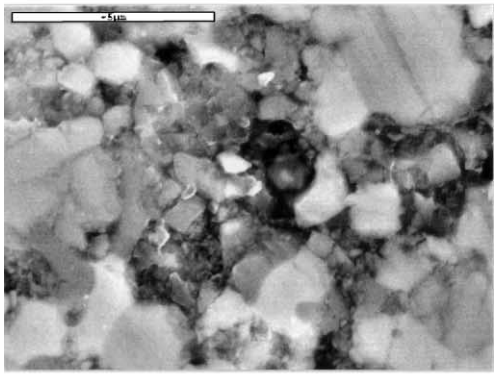


(c) 40vol%TiC_p-$MoSi_2$

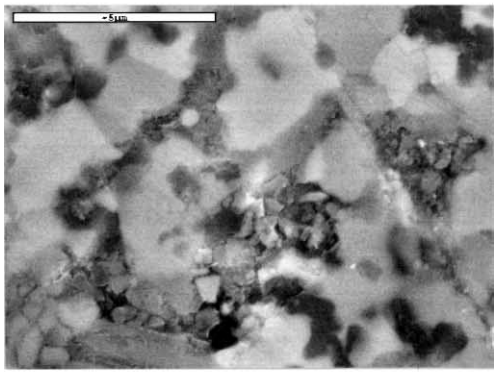
Fig. 1. As-polished microstructure of monolithic $MoSi_2$ and TiC_p–$MoSi_2$ matrix composites with different TiC_p content in polarized light.



(a) $MoSi_2$



(b) 20vol%TiC_p/$MoSi_2$



(c) 40vol%TiC_p/$MoSi_2$

Fig. 2. Scanning electron micrographs of monolithic $MoSi_2$ and TiC_p–$MoSi_2$ matrix composites with different TiC_p content.

higher than that of monolithic $MoSi_2$. The average grain size of pure $MoSi_2$ was about 9.8 μm, while the grain size of the $MoSi_2$ matrix with 40 vol.% TiC was approximately 4.1 μm. The relative densities of 40 vol.% TiC–$MoSi_2$ composite and monolithic $MoSi_2$ were 95.6% and 94.0%, respectively.

3.2. Mechanical properties at room temperature

Fig. 3 shows three-point bending strength and fracture toughness as a function of TiC_p content at room temperature. The strength increases with increasing TiC_p volume content. The strengths for monolithic $MoSi_2$ and 40 vol.% TiC_p–$MoSi_2$ are 268 and 445 MPa, respectively. The 40 vol.% TiC_p–$MoSi_2$ composite displays about 66% increase. The fracture toughness of composites increased with increasing TiC content up to maximum of 4.9 MPa $m^{1/2}$ at 20 vol.% TiC_p, an increase of 53% over monolithic $MoSi_2$. Above 20 vol.% TiC_p content, the fracture toughness decreased a little. Examination of the fracture surface of the TiC/$MoSi_2$ composites using a scanning electron microscope

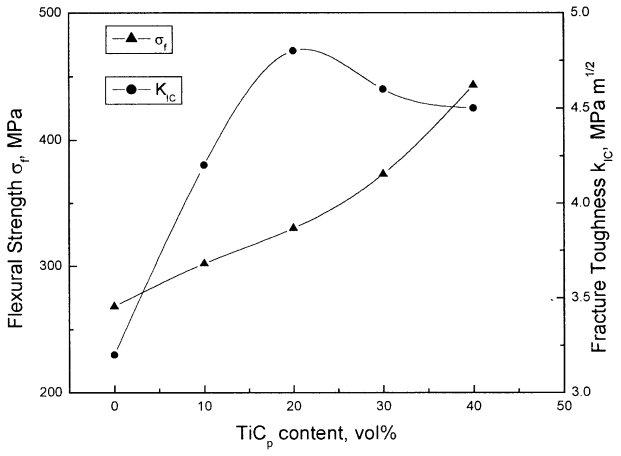


Fig. 3. Effect of TiC_p content on three-point bending strength and fracture toughness for TiC–$MoSi_2$ composites.

revealed a predominantly brittle fracture appearance, as shown in Fig. 4, but examining the surface macroscopically and many irregular planes can be seen. The microstructure of 40 vol.% TiC composite on the fracture surface was finer than that of 20 vol.% TiC composite. This was consistent with the grain refinement due to the addition of TiC particles. Vickers hardness values for the composites are plotted in Fig. 5. The hardness values increase with increasing TiC content.

The results above indicated significant improvement in the mechanical properties at room temperature for TiC/$MoSi_2$ composites compared to monolithic $MoSi_2$. This is in contrast to the result published in the literature[14–16] in which showed a decrease in strength with the addition of TiC. We ascribe the high mechanical properties of these composites to the uniform distribution of TiC reinforcements and increasing volume fraction of TiC. At present, detailed researches are being carried out on the interaction between the microstructure of the materials and the mechanical properties at the room temperature.

3.3. Mechanical properties at elevated temperature

$MoSi_2$, like most ceramics, exhibits brittle behavior at room temperature due to the lack of independent active slip systems, but becomes a ductile material above 1000 °C due to a stress-relieving slip mechanism [18]. At and above 1200 °C, the bend test specimens could be bent to a very substantial degree and could not fracture. However, the addition of TiC particles improved the matrix materials' load-bearing capability. This is apparent in Fig. 6, which shows bend bars of monolithic $MoSi_2$ with 3.20% residual strain and 20 vol.% TiC_p–$MoSi_2$ composite with 1.02% under 40 N loading respectively. In the case of TiC particles reinforced $MoSi_2$ composites the samples fractured under applied load and the bending strength of composites could be obtained.

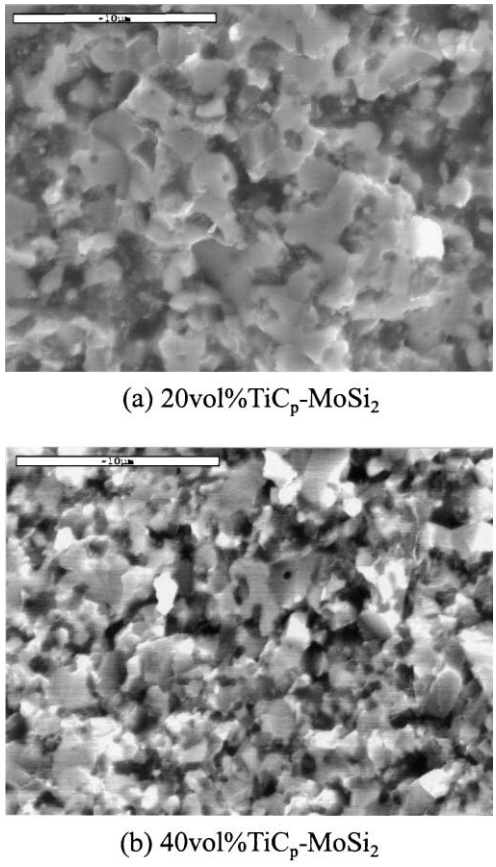


Fig. 4. Scanning electron micrographs of fracture of TiC_p–$MoSi_2$

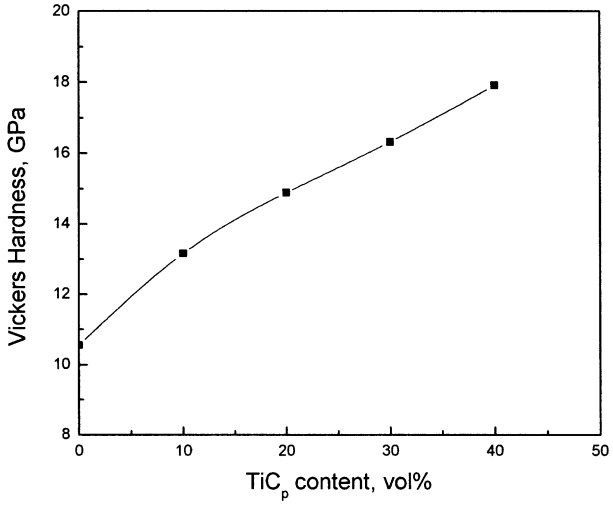


Fig. 5. Variation of Vickers hardness in TiC_p–$MoSi_2$ composites as a function of TiC content.

Fig. 7 gives the effect of TiC content on the three-point bending strength of composites at 1200 °C. The bending strength of composites obviously increases with increasing TiC contents. An explanation for the remarkable increase in strength is given below. The degree of strengthening resulting from second-phase particles depends on the distribution of particles in the ductile

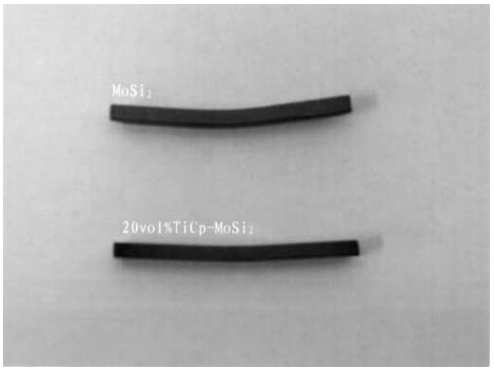


Fig. 6. Monolithic $MoSi_2$ and 20 vol.% TiC_p–$MoSi_2$ composite bend specimens after testing at 1200 °C.

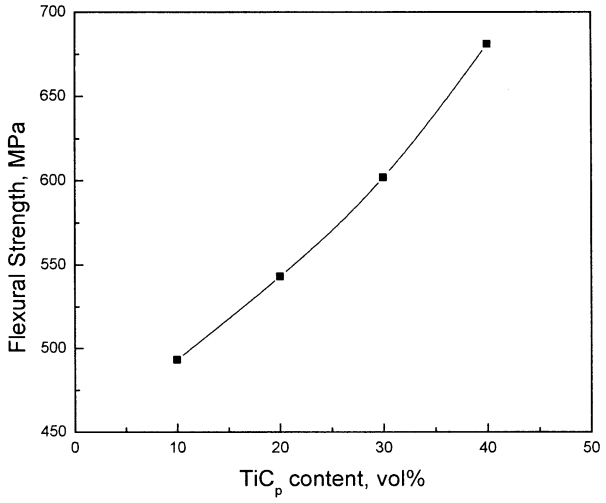


Fig. 7. The three-point bending strength of TiC_p–$MoSi_2$ composites at 1200 °C.

matrix. For homogeneous dispersion of reinforcements in matrix, increase of reinforcement volume fraction will shorten the average distance between the reinforcing particles, or the mean free path. For a constant volume fraction of reinforcement, a decrease in reinforcement size also will decrease the average distance between the reinforcing particles, or the mean free path. Therefore, the finer the particles and the more homogeneous the distribution of the particles, the higher the strength. A fine particle acts as a barrier to dislocations by requiring the dislocation cut to pass through it, thus requiring a large amount of stress, or a particle can resist the dislocation path altogether, forcing the dislocation to bypass the particle. Though most particles dispersion models are based on spherical particles, rods and plates strengthen about twice as much as spherical particles, at the same volume fraction. Whiskers can be thought of as small rods, which satisfy the geometry for a more optical strengthening. If TiC particles were instead by TiC whiskers, the effect of strengthen will be better.

Fig. 8 shows the fracture surface of 40 vol.% TiC_p–$MoSi_2$ composites at 1200 °C. Many TiC particles were found and the whole surface was rough. Further study on the strengthening mechanism of TiC particle-reinforced $MoSi_2$ matrix is being carried out.

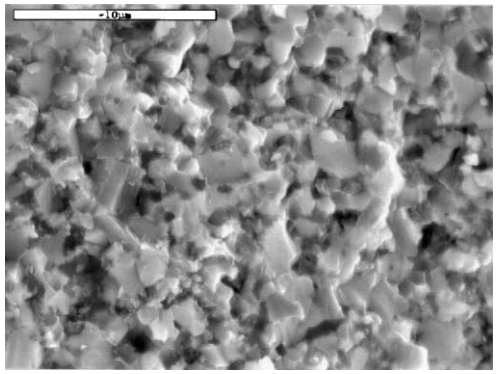


Fig. 8. Scanning electron micrographs of fracture surface of 40 vol.% TiC_p–$MoSi_2$.

4. Conclusion

1. The composite which TiC particle dispersed in $MoSi_2$ matrix homogeneously was obtained by a slurry processing in which a two-step PH adjustment was utilized. The grain size of composites decreased and the densities of composites increased with increasing TiC particle content, respectively.

2. TiC particles reinforced $MoSi_2$ matrix composites obviously improved strength and fracture toughness at room temperature. The flexural strength of 40 vol.% TiC_p–$MoSi_2$ composite increased 63% and the fracture toughness of 20 vol.% TiC_p–$MoSi_2$ composite increased 53%, compared to monolithic $MoSi_2$. TiC_p/$MoSi_2$ composite had a higher Vickers hardness than that of monolithic $MoSi_2$.

3. Both the TiC_p/$MoSi_2$ composites and the monolithic $MoSi_2$ deform plastically at 1200 °C. The bending resistance of the composites is much higher than that of the matrix material. The bending strength of composites increases with increasing TiC_p volume fraction.

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