研 究

Fabrication of Composite in the System ZrO_2 (2Y)/ WSi_2 Part I—Microstructures and Mechanical Properties of the Composites in the WSi_2 Rich Region—

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SYNOPSIS

Dense sintered composites of ZrO_2 (2 mol% Y_2O_3) and WSi_2 have been fabricated by hot isostatic pressing for 2 h at 1500°C under 196 MPa. They contain a small amount of W_5Si_3 ; during sintering, WSi_2 decomposes into W_5Si_3 and amorphous Si. The ZrO_2 particles in the composites consist of only *t*- ZrO_2 . Microstructures and mechanical properties are examined, in connection with ZrO_2 content. The fracture toughness and bending strength of the composite with 40 mol% ZrO_2 addition are 7.1 $\text{MPa}\cdot\text{m}^{1/2}$ and 1010 MPa, respectively.

KEY WORDS

zirconia, tungsten disilicide

1 Introduction

The intermetallic compound tungsten disilicide, WSi_2 , is a potential matrix material for high temperature structural composites under oxidizing conditions. This material with a body-centered-tetragonal C_{11b} structure has a melting point of 2164°C and exhibits excellent high temperature oxidation resistance¹⁾. The main difficulty of this material, however, as well as in the case of almost all intermetallics, is an inherent lack of toughness. It can not be therefore employed by itself as a structural material. This material needs to be reinforced in order to improve the mechanical properties. Transformation toughening has been shown to be a very important toughening mechanism in ZrO_2 -based materials²⁻⁴⁾. A very attractive reinforcing species for

WSi_2 is ZrO_2 , due to its potential for toughening and strengthening, and the fact that its thermal expansion coefficient is a reasonably good match to that of WSi_2 ^{1,5)}. However, because of the difficulty for obtaining of dense composites by normal sintering or hot pressing, no data for their mechanical properties have been reported. In the present study, hot isostatic pressing was adopted to prepare ZrO_2 (2Y)- WSi_2 composites. As a result, the room-temperature toughness of the composites was ≈ 2.7 times that of pure WSi_2 . The present paper deals with the mechanical properties of the composites with different mole fractions of ZrO_2 .

2 Experimental Procedure

Powders of ZrO_2 containing 2 mol% Y_2O_3 (Sumitomo Osaka Cement

Co. Ltd.) and WSi_2 (Japan New Metals Co. Ltd.) were used as starting materials. The former was of high purity and had an average particle size of $0.023\ \mu\text{m}$. The latter was screened to -400 nominal opening size prior to mixing with the ZrO_2 powders. Appropriate amounts of both powders with various compositions, shown in Table 1, were mixed for 20 h by wet-ball-milling with zirconia balls and ethanol in a polyethylene pot and then dried at 80°C under reduced pressure.

Densification was performed by hot isostatic pressing (HIPing) under argon gas as the pressure-transmitting medium. Before HIPing, the mixed powders without calcining were pressed into pellets at 196 MPa and then cold isostatically at 392 MPa. The green compacts, covered with boron nitride powders, were sealed in a Pyrex-glass tube under vacuum. HIPing conditions were as follows: heating rate of $400^\circ\text{C}/\text{h}$; increasing pressure rate of ≈ 180

MPa/h above 800°C ; and sintering for 2 h at 1500°C under 196 MPa. Bulk densities, after lapping with a diamond powder, were measured by the Archimedes method. Phases for polished surfaces were identified by X-ray diffraction (XRD) analysis using Ni-filtered $\text{CuK}\alpha$ radiation. Scanning electron microscopy (SEM) was utilized for microstructural observations. Test samples ($3\times 3\times 20\ \text{mm}$) for mechanical measurements were cut from the composites with a diamond saw; then were lapped with a diamond powder (nominal size 1 to $2\ \mu\text{m}$). Fracture toughness (K_{IC}) measurements were made by the microindentation technique^{6,7)} with a 100-N load. Three-point bending strength was measured with a 16-mm span and a crosshead speed of 0.5 mm/min.

3 Results and Discussion

XRD analysis showed that the as-received ZrO_2 was the mixed phase of tetragonal (*t*) ZrO_2 and monoclinic (*m*) ZrO_2 , and WSi_2 was a

Table 1 Chemical composition of starting powders and characterization of $\text{WSi}_2/\text{ZrO}_2(2\text{Y})$ composites fabricated by hot isostatic pressing for 2 h at 1500°C and 196 MPa

Starting powder	Composition (mol%)		Bulk density (g/cm^3)	Relative density (%)	Grain size (μm)	
	WSi_2	$\text{ZrO}_2(2\text{Y})$			WSi_2	$\text{ZrO}_2(2\text{Y})$
A	100	/ 0	9.12	98.6	4.0	—
B	90	/ 10	8.88	98.7	3.5	0.3
C	80	/ 20	8.67	99.3	2.6	0.3
D	70	/ 30	8.40	99.4	2.1	0.3
E	60	/ 40	8.12	99.4	1.7	0.3

single phase. The sintered composites consisted of $t\text{-ZrO}_2$ and WSi_2 containing a small amount of W_5Si_3 ⁸⁾. There was no detectable $m\text{-ZrO}_2$. The presence of W_5Si_3 suggests that WSi_2 decomposed into W_5Si_3 and amorphous Si during HIPing. No reactions between ZrO_2 and WSi_2 (W_5Si_3) were observed. Note that the ZrO_2 particles in the composites were only $t\text{-ZrO}_2$. This indicates that the ZrO_2 particles under a critical size, which is needed to prevent the phase transformation from tetragonal to monoclinic symmetry during cooling, remained as metastable $t\text{-ZrO}_2$. The transformation of $t\text{-}$ to $m\text{-ZrO}_2$ depends on the critical size which is closely related to Young's modulus of the matrix⁹⁾. Young's moduli of WSi_2 and $\text{ZrO}_2(2\text{Y})$ are 468¹⁾ and 207¹⁰⁾ GPa, respectively. In view of the fact that the value of the former, as the matrix, is >2 times higher than that of the latter, it can be assumed that the $t\text{-ZrO}_2$ particles were retained in the composites.

Table 1 shows the bulk and relative densities of the composites. In the calculation of relative densities, there was no consideration for the presence of small amounts of W_5Si_3 (14.54 g/cm³)⁵⁾ and amorphous Si (2.33 g/cm³)¹¹⁾. The theoretical densities of $t\text{-ZrO}_2(2\text{Y})$ and WSi_2 were assumed to be 6.085¹²⁾ and 9.25⁵⁾ g/cm³, respectively. Sintered pure WSi_2 was 98.6% of theoretical. The composite densities increased from 98.7 to 99.4% of the theoretical densities with increased ZrO_2 content.

Photo. 1 Scanning electron micrographs for secondary electron image of (a) pure WSi_2 , (b) 80mol% WSi_2 /20mol% $\text{ZrO}_2(2\text{Y})$ and (c) 60mol% WSi_2 /40mol% $\text{ZrO}_2(2\text{Y})$ composites.

Thus, well-densified composites could be prepared in the present study.

Photograph 1 shows SEM micrographs of fracture surfaces. Spherical black grains in the photograph of pure WSi_2 , shown in Photo. 1(a), are probably amorphous Si. Grain sizes were measured directly by SEM. As shown in Table 1, the average grain size of ZrO_2 was $0.3 \mu\text{m}$ regardless of the starting composition. On the other hand, the grain size of WSi_2 depended on the composition; it decreased from 4 to $1.4 \mu\text{m}$ with increased ZrO_2 content. The nature of the dispersion could not be clearly resolved by the above observation. However, the backscattered electron image on the polished and thermally etched surface showed the dispersion to be homogeneous (Photo. 2).

Figure 1 shows the fracture toughness of the composites as a function of ZrO_2 addition. Pure WSi_2 gave a K_{IC} value of ≈ 2.7

Photo. 2 Scanning electron micrograph for backscattered electron image of 80mol% WSi_2 /20mol% $\text{ZrO}_2(2\text{Y})$ composite.

Fig. 1 Fracture toughness and bending strength of composites as a function of ZrO_2 addition.

$\text{MPa}\cdot\text{m}^{1/2}$. The K_{IC} values of the composites increased linearly with increased ZrO_2 content. The composite containing 40 mol% ZrO_2 was ≈ 2.7 times tougher than pure WSi_2 . This is a significant toughening effect. Several possible mechanisms have been proposed to explain the toughness of various ZrO_2 ceramic materials, but two of them are important: one is toughening by microcracking¹³⁾ and the other is toughening by stress-induced transformation only if $t\text{-ZrO}_2$ is present¹⁴⁾. Microcrack toughening is the major phenomena when the ZrO_2 particles are monoclinic. Accordingly, it must be concluded that the mechanism responsible for the

improved fracture toughness was stress-induced transformation. The effect of mole fraction of ZrO_2 on the bending strength is shown in Fig. 1. The average bending strength without ZrO_2 addition was 456 MPa.

It increased to the maximum of 1010 MPa with 40 mol% ZrO_2 addition. The increase of bending strength was almost proportional to the increase of K_{IC} . It appeared, therefore, that the $t\text{-ZrO}_2$ particles increased the bending strength which proportionally enhanced the toughness. From the above mentioned results, it was proved that the well-sintered $\text{ZrO}_2(2\text{Y})$ particle- WSi_2 matrix composites with small grains had excellent mechanical properties.

4 Conclusions

ZrO_2 has been proved to be a very attractive reinforcement material for WSi_2 . Dense sintered $\text{ZrO}_2(2\text{Y})/\text{WSi}_2$ composites with small grains have been fabricated by hot isostatic pressing for 2 h at 1500°C and 196 MPa. All of the ZrO_2 particles in the composites remain as metastable $t\text{-ZrO}_2$. The composite with 40 mol% ZrO_2 addition gives 7.1 $\text{MPa}\cdot\text{m}^{1/2}$ and 1010 MPa for fracture toughness and bending strength, respectively. These results suggest the possibility for the application of ZrO_2 particle- WSi_2

matrix composites.

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