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Microstructure and Mechanical Properties of SiC Whisker Reinforced ZrO_2 (2 mol% Y_2O_3) Based Composites

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Abstract: Microstructure, mechanical properties and toughening mechanisms of hot-pressed SiC whiskers (SiCw) reinforced ZrO_2 (2 mol% Y_2O_3) based composites were investigated by using TEM, SEM and XRD techniques and mechanical tests. It was shown that the Vickers hardness, elastic modulus, fracture toughness and flexural strength of ZrO_2(2Y) ceramics are obviously improved by the addition of SiCw. TEM observations showed that whiskers and the ZrO_2 matrix are bonded tightly and there is no obvious second phase formed on the SiCw/ZrO_2 interface. Both whisker toughening and transformation toughening are effective in ZrO_2 (2mol% Y_2O_3) ceramics so that a good combination of high strength and high fracture toughness can be obtained.

INTRODUCTION

The SiC whiskers have been successfully used at first by Becher and Wei[1] in 1984 to improve the fracture toughness of Al_2O_3 ceramics. Recently, increasing attention has been paid to whisker reinforced ceramics. Until now, Al_2O_3–SiCw composites have been studied extensively and consistent results were obtained.[1–6] However, only limited data can be found for ZrO_2–SiCw composites and the experimental results are seriously scattered. Claussen and co-workers[7,8] have shown that at room temperature the addition of SiCw can obviously improve the fracture toughness of ZrO_2 (3 mol% Y_2O_3) but reduces the flexural strength. Akimune *et al.*[9] have found that an addition of 20 vol% SiCw can improve simultaneously both fracture toughness and flexural strength of ZrO_2(3Y). It seems necessary to study further the strengthening and toughening effects of SiCw on ZrO_2 ceramics, especially for ceramics containing transformable ZrO_2 component so as to examine the combined effect of both SiC whisker reinforcement and t→m ZrO_2 transformation toughening.

EXPERIMENTAL

The raw materials for investigation were selected as ZrO_2 (2 mol% Y_2O_3) powders with a particle size of 0·65 μm (having 34% t–ZrO_2 and 66% m–ZrO_2) and TWS–400 type of β–SiC whiskers of 1–1·4μm in diameter and 20–30 μm in length. The powders and the whiskers are mixed to volume fractions of 0, 10, 20 and 30 vol% SiCw, and then inserted into plastic bottles together with ZrO_2 balls and non–aqueous ethanol alcohol. The mixtures were ground for 24 h and cold pressed at 200 MPa after drying. The cold pressed billets were then hot-pressed under nitrogen at 1600°C and 25 MPa for 1 h to 60 × 60 × 6mm billets.

The hot-pressed billets were cut into specimens 3 × 4 × 36 mm for three point bending tests for determining flexural strength (with a span of 30 mm and a crosshead speed of 0·5 mm/min) and specimens 2 × 4 × 20 mm of single edge notched beam (SENB) for fracture toughness with $S/W=4$, $a/W=0{\cdot}5$ (width of the notch 0·24–0·26 mm and a crosshead speed of 0·05 mm/min). Average values of the experimental data taken from six specimens were used for both flexural strength and fracture toughness tests for each composition and all these tests were performed on an Instron–1186 machine. The elastic moduli were obtained by measuring the strains in the three point bending tests and the hardness values were measured by using a Vickers hardness tester. The density of the specimens was determined by the Archimedes method. The Hitachi S–570 type of scanning electron microscope and CM–12 type of TEM were used for examining the microstructure and fracture morphology of the specimens. A D/max–rB type of X-ray diffractometer was used for the structural analysis of the ZrO_2 component in the ceramic composites.

RESULTS AND DISCUSSION

Microstructure

The relative density (measured density divided by calculated theoretical density) value of pure $ZrO_2(2Y)$ ceramics after hot pressing was 99·9%, and decreased to 98·2%, 98·3% and 97·8% after adding 10, 20 and 30 vol% SiCw, respectively. It is seen that the addition of SiCw slightly inhibits the densification of the $ZrO_2(2Y)$ matrix during hot pressing (sintering).

The SEM photographs of the microstructure of ZrO_2–SiCw composites (after thermal fluorhydric acid etching) are shown in Fig. 1. It is seen that the addition of SiCw can effectively inhibit the growth of the ZrO_2 grains and the first 10 vol% SiCw has a very strong refining effect. Further increment of the SiCw content has less refining effect. The distribution of whiskers on planes perpendicular to the hot-pressing axis was homogeneous so that the improved and slightly oriented mechanical properties may be achieved. TEM observations shown in Fig. 2 indicate that SiC whiskers and the ZrO_2 matrix are bonded tightly and there is no obvious second phase formed at the ZrO_2/SiCw interface. A few defects such as stacking faults or twins can be seen in the cores of SiC whiskers. This is different from the observations given by Sarin[10] and Claussen.[7] Particles of

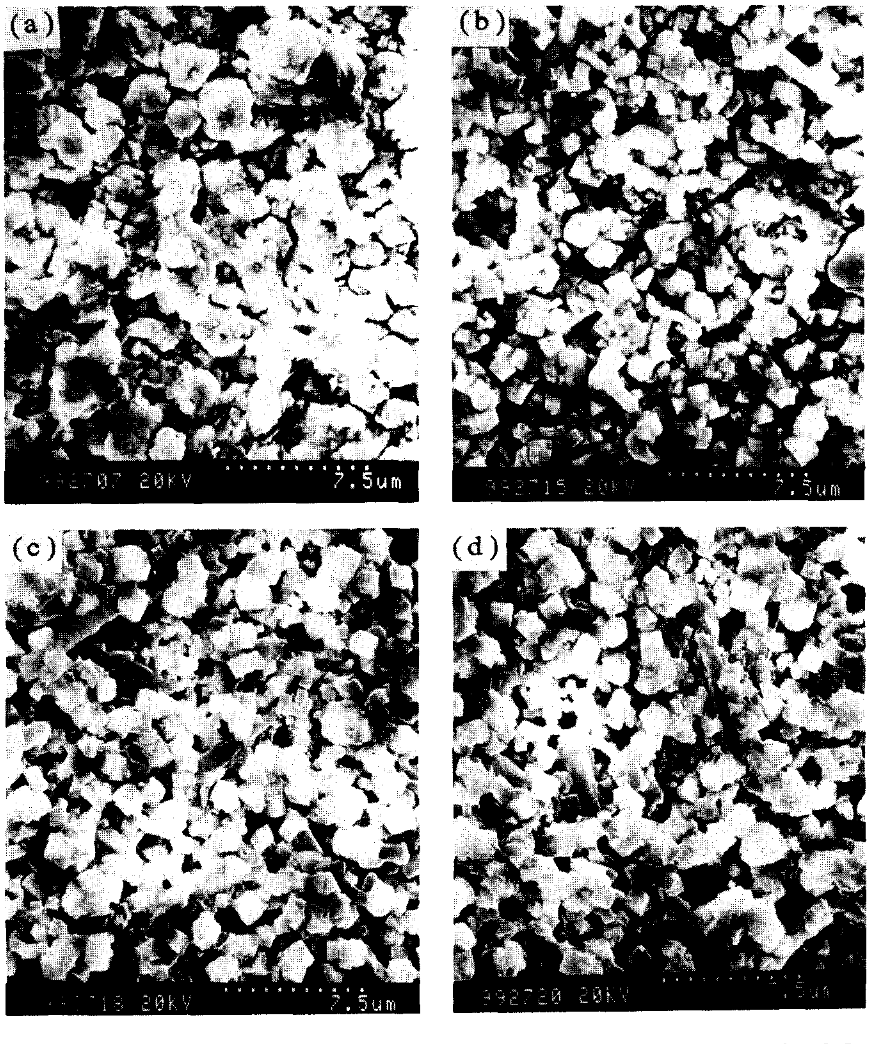

Fig. 1. SEM photographs of the microstructure of $ZrO_2(2Y)$–SiCw composites. (a) $ZrO_2(2Y)$, (b) $ZrO_2(2Y)$ + 10 vol% SiCw, (c) $ZrO_2(2Y)$ + 20 vol% SiCw, (d) $ZrO_2(2Y)$ + 30 vol% SiCw.

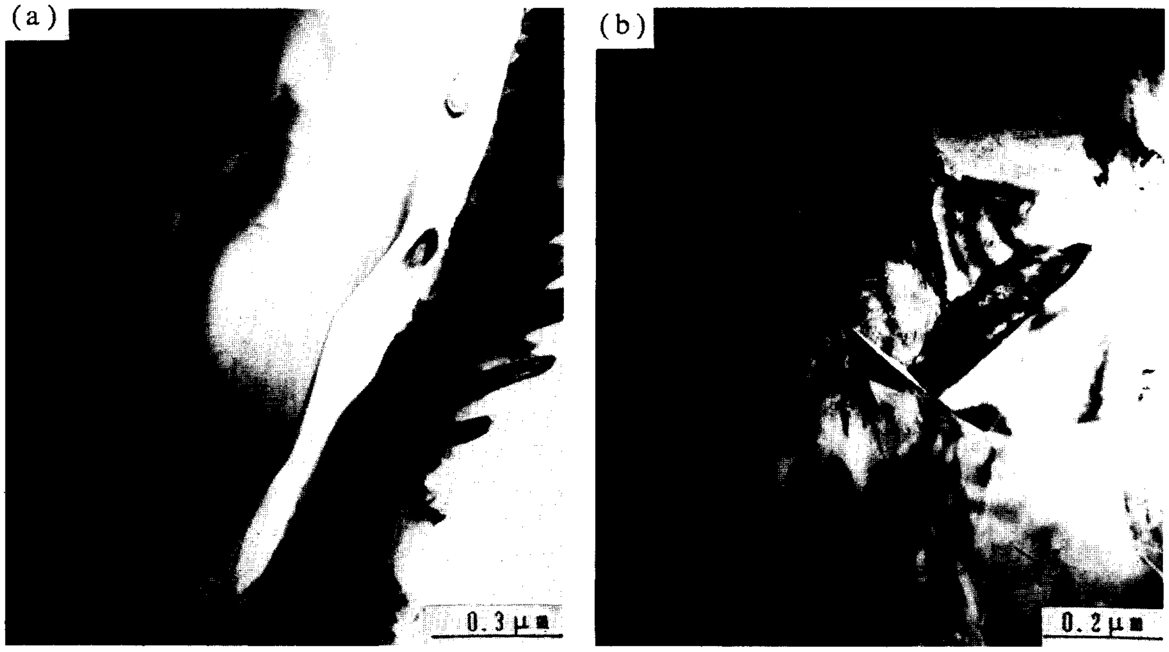

Fig. 2. TEM photographs of ZrO$_2$(2Y) + 30 vol% SiCw composite. (a) Interfaces of SiCw/ZrO$_2$(2Y) and m-phase structure in ZrO$_2$ particles near to the interfaces, (b) t + m dual phase structures and microcracks induced by t→m transformation in the ZrO$_2$ matrix.

the ZrO$_2$ matrix are composed of the tetragonal (t) phase and the monoclinic (m) phase as confirmed by the XRD results. The monoclinic phase structures can be found in the ZrO$_2$ particles near to the SiCw/ZrO$_2$ interfaces as shown in Fig. 2(a). Microcracks in the dual phase (t+m) structure of ZrO$_2$(2Y) ceramic matrix can be seen in Fig. 2(b), induced by the t→m transformation.

Mechanical properties

The Vickers hardness and elastic modulus values of ZrO$_2$(2Y)–SiCw composites are shown in Fig. 3. These two parameters are obviously increased by the addition of SiCw. A 30 vol% SiCw increases the hardness and elastic modulus from 11·66 GPa and 220 GPa for the ZrO$_2$(2Y) matrix to 15·29 GPa and 308 GPa, respectively. This is undoubtedly the direct contribution of the high hardness and high elastic modulus of SiCw to the composite material. The room temperature flexural strength and fracture toughness values of the composites are shown in Fig. 4. An addition of 10 vol% SiCw increases the flexural strength from 888 MPa for the matrix to a maximum value of 1404 MPa (Fig. 4(a)). The further increment of SiCw decreases it to 1354 MPa for 20 vol% SiCw and 1337 MPa for 30 vol% SiCw. This is quite different from that obtained by Claussen,[7,8] but is consistant with that of Akimune.[9] It is shown in Fig. 4(b) that the fracture toughness of the composites increases continuously with SiCw content and the first 10 vol% SiCw has a relatively higher toughening effect which increases the fracture toughness from 13·71 MPa m$^{1/2}$ for the matrix to 16·10 MPa m$^{1/2}$. Further increment of the SiCw content leads to much less toughening and the fracture toughness values are only 16·74 MPa m$^{1/2}$ for 20 vol% SiCw and 17·14 MPa m$^{1/2}$ for 30 vol% SiCw, respectively. The toughening effect of SiCw to the ZrO$_2$(2Y) matrix is consistent with that obtained by Claussen[7,8] and Akimune.[9]

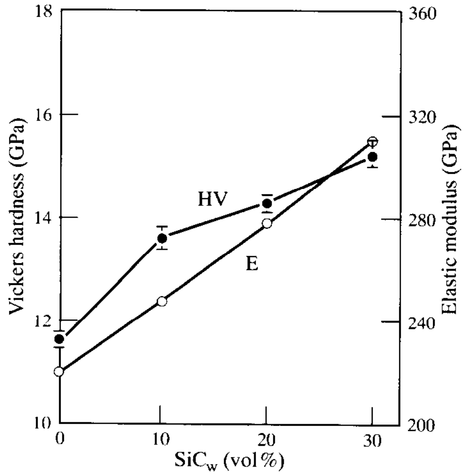

Fig. 3. Vickers hardness and elastic modulus values of ZrO$_2$–SiCw composites as a function of SiCw content.

Evidently, the strengthening and toughening effects of SiCw reinforcement are very obvious so that the strength and toughness of the composites are much higher than that of the ZrO$_2$(2 mol% Y$_2$O$_3$) matrix at room temperature.

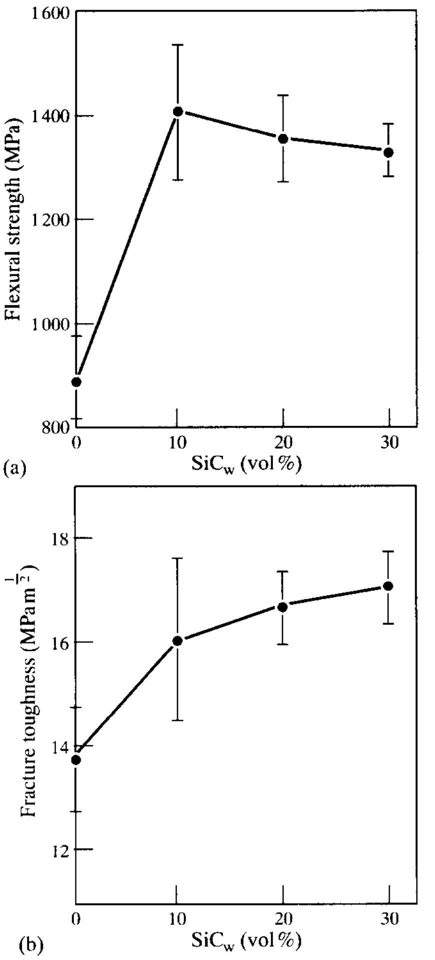

Fig. 4. (a) Flexural strength and (b) fracture toughness values of ZrO_2(2Y)–SiCw composites as a function of SiCw content.

The high temperature flexural strength data of the composites are shown in Fig. 5. At high temperatures the strengthening effect of SiCw is obvious and the strength of the composite is continuously increased with addition of SiCw. The addition of 30 vol% SiCw increases the flexural strength from 92 MPa for the ZrO_2 matrix to 455 MPa at 1000°C. This is because the residual stress induced by the thermal incompatibility at high temperatures is much lower than that at room temperature and the strengthening effect of the t→m transformation disappears at high temperatures.

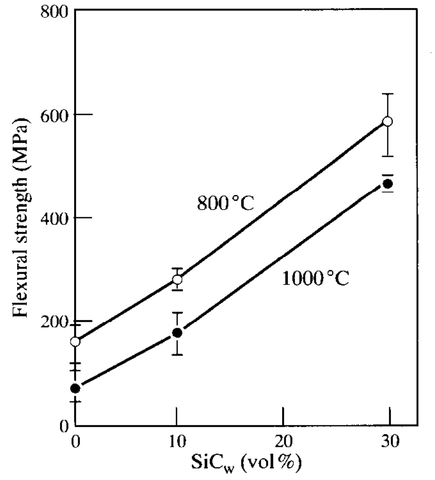

Fig. 5. Flexural strength values of ZrO_2(2Y)–SiCw composites as a function of SiCw content at high temperatures.

Strengthening and toughening mechanisms

The high flexural strength of ZrO_2(2Y)–SiCw composites can be explained as follows. Firstly, the strengthening effect of SiCw can be performed by the load transferring effect if the whiskers and the matrix are bonded tightly, since SiC whiskers have high elastic modulus and high strength and fit the condition $E_w > 2E_m$ (E_w is the elastic modulus of SiC whiskers, E_w=490 GPa, E_m is the elastic modulus of the matrix, E_m=220 GPa). Secondly, the SiC whiskers are distributed homogeneously in the matrix, the strengthening effect can be obtained by grain refinement of the matrix (as shown in Fig. 1), the inhibition of main crack propagation and in some cases the SiCw may directly join the rupture processes during the main crack propagation. On the other hand, the addition of SiCw also have harmful effects on the flexural strength of the composites due to high residual stresses caused by the thermal incompatibility between the SiC whiskers and the ZrO_2 matrix ($\alpha_{SiCw} = 4{\cdot}7 \times 10^{-6}$/K, $\alpha_{ZrO_2} = 10 \times 10^{-6}$/K). Phillips[12] has shown that the thermal incompatibility stresses increase with increasing SiCw content and Claussen *et al.*[7] have found that it is the thermal incompatibility stress that reduces substantially the flexural strength of the composites. Furthermore, the possibility of SiC whisker agglomeration becomes larger as the SiCw content increases and the critical defect size in the composites grows, resulting in the reduction of flexural strength.

With 10 vol% SiCw the thermal stresses in the matrix are lower and the possibility of agglomeration of whiskers is small so that the strengthening mechanism can play the main role. When the SiCw content is increased to 20 vol% and 30 vol%, the harmful effect of the thermal stresses and the possibility of whisker agglomeration becomes more intense so that the flexural strength should be decreased. ZrO_2(2Y) particles are partially stabilized and the t→m phase transformation can be induced by the external stress. Claussen and Petzow[13] have shown that the residual stresses induced by thermal incompatibility between whiskers and the matrix can be reduced by the t→m phase transformation so that the substantial reduction in flexural strength can be avoided and the strengthening effect may be achieved. These facts can explain the obviously improved flexural strength of ZrO_2(2Y)–SiCw composites.

Table 1. The relative amount (m(t + m)) of t→m ZrO_2 transformation during SENB fracturing in ZrO_2(2Y)–SiCw composites by XRD

Materials	Z(2Y)S0	Z(2Y)S1	Z(2Y)S2	Z(2Y)S3
Amount of SiCw content (vol%)	0	10	20	30
Relative amount of m-phase on polished surface (%)	27·00	13·80	12·20	12·20
Relative amount of m-phase on fractured surface (%)	58·60	44·40	41·55	39·00
Relative amount of t→m transformation during fracture (%)	31·60	30·60	29·36	26·80

The first toughening mechanism in the ZrO_2(2Y)–SiCw composites is transformation toughening. The t→m phase transformation of the ZrO_2 particles can be revealed by X-ray analysis of polished and fractured surfaces of the ZrO_2(2Y)–SiCw composites as shown in Table 1. The ZrO_2(2 mol% Y_2O_3) powders have 34% t-phase+66% m-phase before hot pressing. Hot pressing was performed at 1600°C, which lies in the single t-phase region according to the ZrO_2–Y_2O_3 phase diagram, and after cooling to room temperature part of the t-phase may transform to m-phase (but to an amount much less than 66%). With the addition of 10 vol% SiCw, the amount of m-phase on the polished surface decreases quickly. Then it decreases more slowly at higher SiCw contents. The amounts of m-phase on the polished surfaces of the Z(2Y)SI, Z(2Y)S2, Z(2Y)S3 composites are almost the same. This is because the addition of SiCw has twofold effects on the t→m phase transformation. With addition of SiCw having much higher elastic modulus than the ZrO_2(2 mol% Y_2O_3) matrix a large constraint is formed which inhibits the t→m phase transformation. On the other hand, the thermal incompatibility between the SiCw and the matrix causes large residual

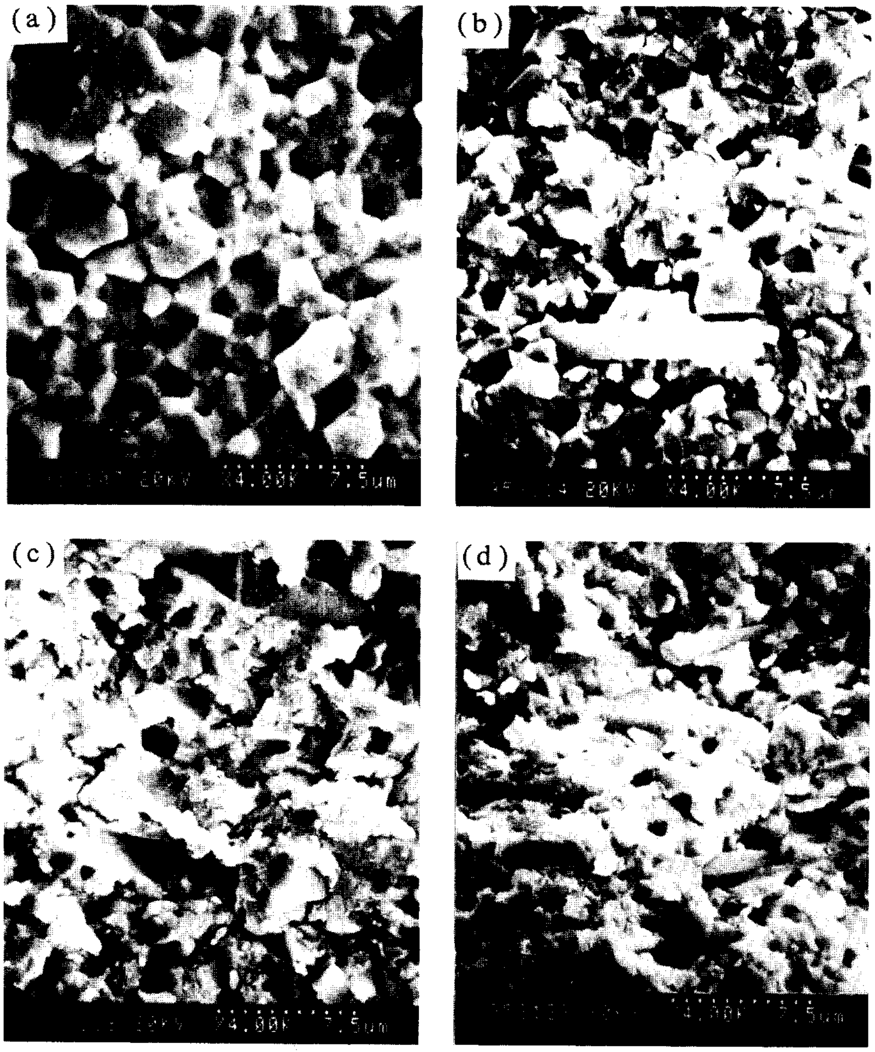

Fig. 6. SEM fractographs of ZrO_2(2Y)–SiCw composites. (a) ZrO_2(2Y), (b) ZrO_2(2Y) + 10 vol% SiCw, (c) ZrO_2(2Y) + 20 vol% SiCw, (d) ZrO_2(2Y) + 30 vol% SiCw.

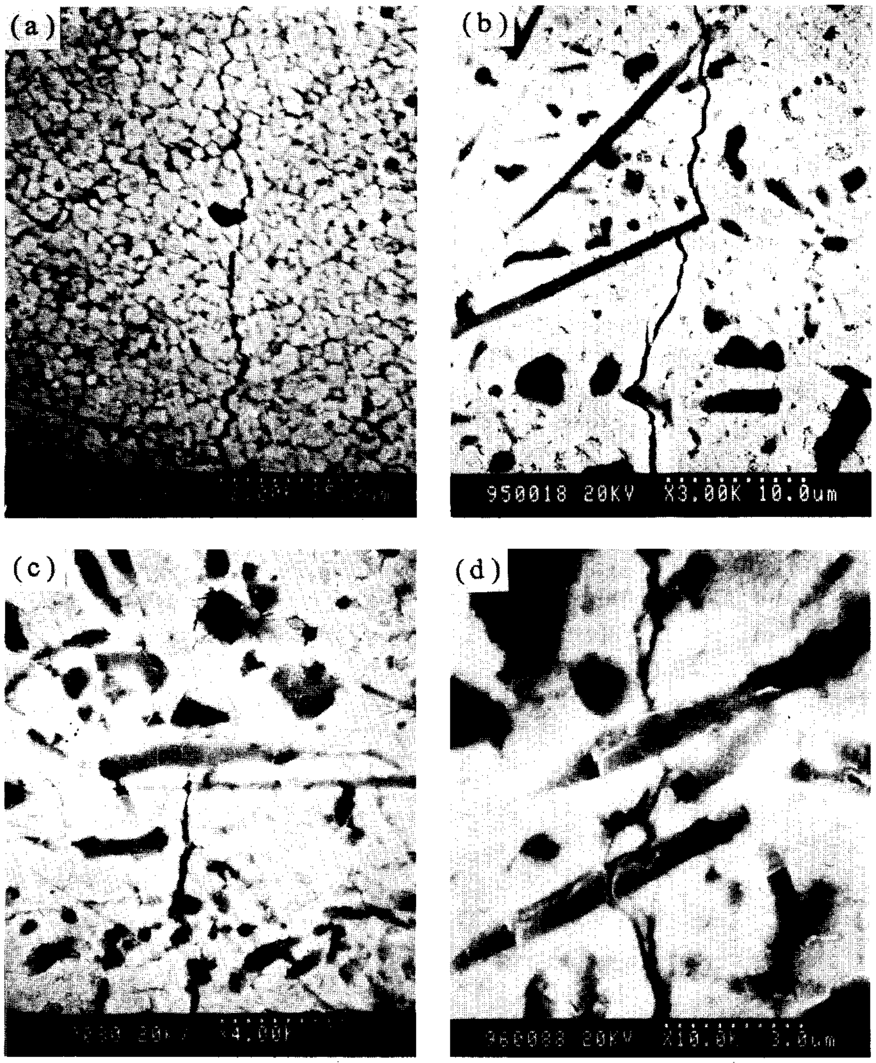

Fig. 7. SEM photographs of indentation crack propagation paths in ZrO_2(2Y)–SiCw composites. (a) ZrO_2(2Y), (b) ZrO_2(2Y) + 10 vol% SiCw, (c) ZrO_2(2Y) + 20 vol% SiCw, (d) ZrO_2(2Y) + 30 vol% SiCw.

stresses and enhances the t→m phase transformation (as shown in Fig. 2(a)). It is seen from Table 1 that the inhibiting effect plays the main role at the first 10 vol% SiCw and the two effects cancel each other out at higher SiCw contents. The direct evidence of this conclusion is shown in Fig. 1 — the first 10 vol% SiCw has a very high refining effect on the ZrO_2 particle size and further increment of the SiCw content leads to much less refining. Although the amounts of m–phase on the polished surfaces are quite different with the addition of SiCw, the addition of SiCw has little effect on the amount of t→m phase transformation during fracturing. The amount of the transformation decreases slowly from 32% for pure ZrO_2 to 27% for the composite with 30 vol% SiCw. The microcracks (shown in Fig. 2), induced by the volume expansion effect due to the t→m phase transformation during cooling from the sintering or hot pressing temperature, also have a toughening effect. Therefore, both the microcrack toughening due to the prior t→m phase transformation during cooling and the toughening due to dynamic t→m phase transformation during fracturing have an obvious improvement on the fracture toughness values of the ZrO_2–SiCw composites.

The second toughening mechanism in the ZrO_2(2Y)–SiCw composites is the whisker reinforcement which can be clearly demonstrated by the SEM photographs of the fractured surfaces of specimens for testing fracture toughness (as shown in Fig. 6) and the crack propagation paths at the corners of indents during hardness tests (as shown in Fig. 7). It can be found from Fig. 6 that the fracture mode of pure ZrO_2 is a mixture of intergranular and transgranular modes, where the intergranular fracture is preferential and its fractured surface is rough. This can also be clearly observed in Fig. 7(a), and may be considered as the evidence that the crack deflection, probably induced by the t→m phase transformation, is a toughening mechanism in the ZrO_2 matrix. The roughness of the fractured surfaces is increased and the fracture mode of the ZrO_2 matrix is changed to preferentially transgranular by the addition of SiCw (as shown in Figs 6 (b)–(d)). The addition of SiCw also significantly refines the grain size of the ZrO_2 particles and the microvoids and the residual sides of whiskers are left due to the pull-out of whiskers. These factors can increase the energy absorbed during fracture. The crack deflection, SiCw rupture and SiCw pull-out and bridging are clearly observed in the indentation crack propagation paths, as shown in Figs 7(b)–(d). Therefore both transformation toughening and SiCw toughening are effective in the ZrO_2–SiCw ceramics.

CONCLUSIONS

1. The addition of SiCw significantly refines the grain size of the ZrO_2 matrix. SiCw and ZrO_2 matrix are bonded tightly and no obvious second phases or intermediate layers can be observed under TEM.
2. The addition of the SiCw obviously improves the mechanical properties of the ZrO_2 ceramics. The hardness, elastic modulus and fracture toughness values of ZrO_2(2Y)–SiCw composites are continuously increased with increasing SiCw content, but the flexural strength achieves its highest value at 10 vol% SiCw.
3. The main mechanisms of strengthening and toughening of ZrO_2(2Y)–SiCw composites are whisker bridging and pull-out and crack deflection, as well as t→m phase transformation. The toughening effects of both SiCw reinforcement and t→m phase transformation have obvious additivity.
4. The addition of SiCw inhibits the t→m phase transformation during cooling from the hot pressing temperature but has little effect on the relative amount of t→m phase transformation induced by the external stress during fracturing.

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