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Mechanical Properties of Al_2O_3 + ZrO_2 + Nano-SiCp Ceramic Composites

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Abstract: The mechanical properties of Al_2O_3 matrix composites reinforced by ZrO_2(2 mol% Y_2O_3) and nanometre scale SiC dispersions have been investigated. It is shown that the Al_2O_3 matrix is simultaneously strengthened and toughened by both ZrO_2(2 mol% Y_2O_3) and nano-SiC particles. The maximum flexural strength and fracture toughness of the composites are 945 MPa and 7.3 MPam$^{1/2}$, respectively. The reinforcing effect of both t–m phase transformation of ZrO_2 (2 mol% Y_2O_3) and nano-SiC particles appears to be synergetic. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Nanometre scale SiC particles have recently been of great interest to materials scientists because of their ability to reinforce many brittle ceramics. Perhaps the most significant result has been reported by Niihara,[1] where a flexural strength of 1017 MPa was achieved in Al_2O_3 matrix composite containing 5 vol% nano-size SiC particles. In addition, the nano-SiCp/Al_2O_3 composite was found to have good resistance to thermal shock and high temperature strength degradation.[1] Transformation toughening of dispersed t-ZrO_2 particles in Al_2O_3 matrix has resulted in substantial increases in strength and toughness of Al_2O_3.[2] This kind of reinforcing effect is mainly attributed to the stress-induced martensitic phase transformation of the metastable t-ZrO_2 which absorbs energy and thus relieves the stress concentration in the tip region of the propagating crack.[3] However, the ZrO_2 reinforced composites show the strength degradation at higher temperature due to the decrement of driving force for phase transformation, while the addition of nano-SiC particles can only slightly increase the fracture toughness of Al_2O_3, from 3.25 MPam$^{1/2}$ to 4.70 MPam$^{1/2}$.[1]

Therefore, it is reasonable to combine the two above-mentioned strengthening and toughening routes to obtain high-strength and high-toughness Al_2O_3 matrix composites, which would have many potential applications as high-temperature structural materials. The purpose of the present study is to investigate the effects of the double reinforcing mechanism on the mechanical properties of Al_2O_3 + ZrO_2(2 mol% Y_2O_3) + nano-SiCp composites.

2 EXPERIMENTAL PROCEDURE

γ-Al_2O_3 with an average particle size of 50nm, ZrO_2(2 mol% Y_2O_3) with a particle size of 0.65μm (having 30% t-ZrO_2 and 70% m-ZrO_2), and β-SiC with an average particle size of 90nm, were selected as starting powders in this experiment. According to the compositions shown in Table 1, these powders were mixed by conventional ball-milling for 48 h in pure alcohol. The dried mixtures were green compacted at 100 MPa and then hot-pressed at 1650°C/25 MPa for 1 h into billets of 60mm × 60mm × 5mm.

The hot-pressed billets were cut into specimens 3 × 4 × 36mm for three-point bending test of flexural strength with a span of S = 30mm and a crosshead speed of 0.5mm/min, and specimens 2 × 4 × 20mm of single edge notched beam (SENB) for fracture toughness test with S/W = 4 (W is

Table 1. Compositions of the Al_2O_3 + ZrO_2 + nano-SiCp (AZS) ceramic composites

Content	AZS00	AZS05	AZS15	AZS25
Al_2O_3 (vol%)	80	75	65	55
ZrO_2 (vol%)	20	20	20	20
Nano-SiCp (vol%)	0	5	15	25

specimen width), $a/W = 0.5$ (a is notch length), width of notch 0.24–0.26mm, and a crosshead speed of 0.05mm/min. Testing was performed on an Instron 1186 machine. Average values were calculated from experimental data obtained from 6 specimens of each composition. The elastic modulus was obtained by measuring the slope of the stress–strain curve in the three-point bending test and the hardness values were determined via a Vicker's hardness tester using a load of 200N.

The density of the specimens was measured by the Archimedes method. The grain size was determined by the line intercept method after the polished surface was etched by hot HF acid. A Hitachi S-570 type of scanning electron microscope was used for examining the fracture morphology of the composites and a D/max-rB type X-ray diffractometer was used for the cystallographic analysis of the ZrO_2 component.

3 RESULTS AND ANALYSIS

3.1 Grain size and relative density

The effect of nano-SiCp content on the grain size of Al_2O_3 and ZrO_2 matrices is shown in Fig. 1. It can be seen that the grain growth of Al_2O_3 and ZrO_2 matrix particles during hot-pressing is clearly retarded by the nano-SiCp because of a grain boundary pinning effect. Figure 1 also indicates that the addition of the first 5 vol% SiCp has a much higher refining effect on the grain size of the matrices than further additions of SiCp.

Figure 2 shows the relative density values of AZS series of composites. The result indicates that the addition of 5 vol% SiCp has little effect on the relative density of Al_2O_3 + 20 vol% ZrO_2 matrix, however, further additions of SiCp result in a slight decrease in the relative density. This phenomenon can be explained as follows. According to sintering theory, a reduction in grain growth rate should lead to an indirect enhancement of densification (densification rate $\propto 1/(\text{grain size})^n$, where $n = 3$ for lattice diffusion and $n = 4$ for grain boundary diffusion[4]), so the significant inhibition of grain growth by the presence of 5 vol% SiCp appears to have a beneficial effect on the densification of AZS05 composite. On the other hand, the addition of SiCp also has a deleterious effect on the densification of the composites due to the fact that the movement of pores along the grain boundaries may be limited by the presence of SiC particles on those boundaries during the final sintering stage. Therefore, with 15 and 25 vol% SiCp it seems that the deleterious effect overcomes the

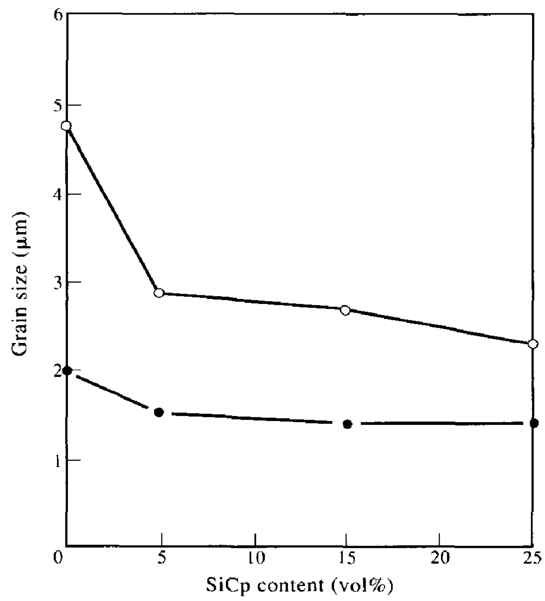

Fig. 1. Al_2O_3 (○) and ZrO_2 (●) grain sizes in the AZS series of composites as functions of nano-SiCp content.

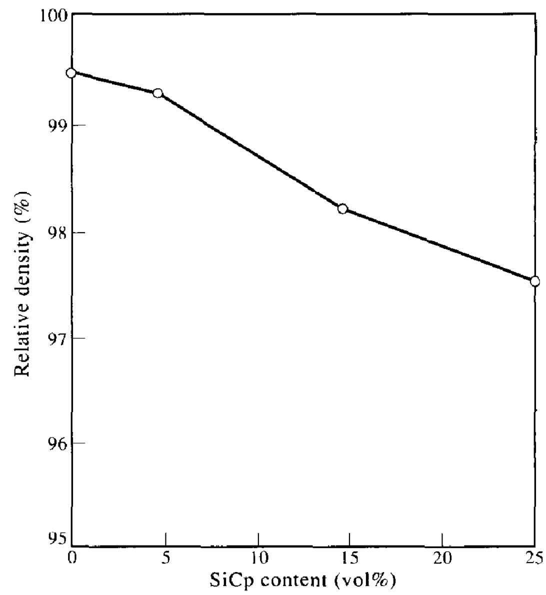

Fig. 2. Relative density of the AZS series of composites as a function of nano-SiCp content.

beneficial effect to result in an overall reduction in the relative density. However, it can be seen that a high density (≥98%) is obtained though it decreases by the addition of more than 5 vol% SiC particles.

3.2 Hardness and elastic modulus

For AZS composites, the Vicker's hardness and elastic modulus are improved with increasing nano-SiCp content, as shown in Fig. 3. With 25 vol% SiCp the hardness and elastic modulus increase from 15.9 GPa and 355 GPa for the Al_2O_3 + 20 vol% ZrO_2 to 18.4 GPa and 498 GPa, respectively. This comes undoubtedly from the direct contribution of high hardness and high elastic modulus of the SiC component.

3.3 Flexural strength and fracture toughness

Figure 4 shows the effect of nano-SiCp content on the flexural strength and fracture toughness of the AZS composites. It can be seen from Fig. 4(a) that the first addition of 5 vol% SiC particles has a very high strengthening effect and increases the flexural strength from 514 MPa to 847 MPa. The amount of 15 vol% SiCp gives a further improvement in flexural strength (to 945 MPa), but the strengthening tendency becomes lower. Further increment of the nano-SiCp content leads, on the other hand, to

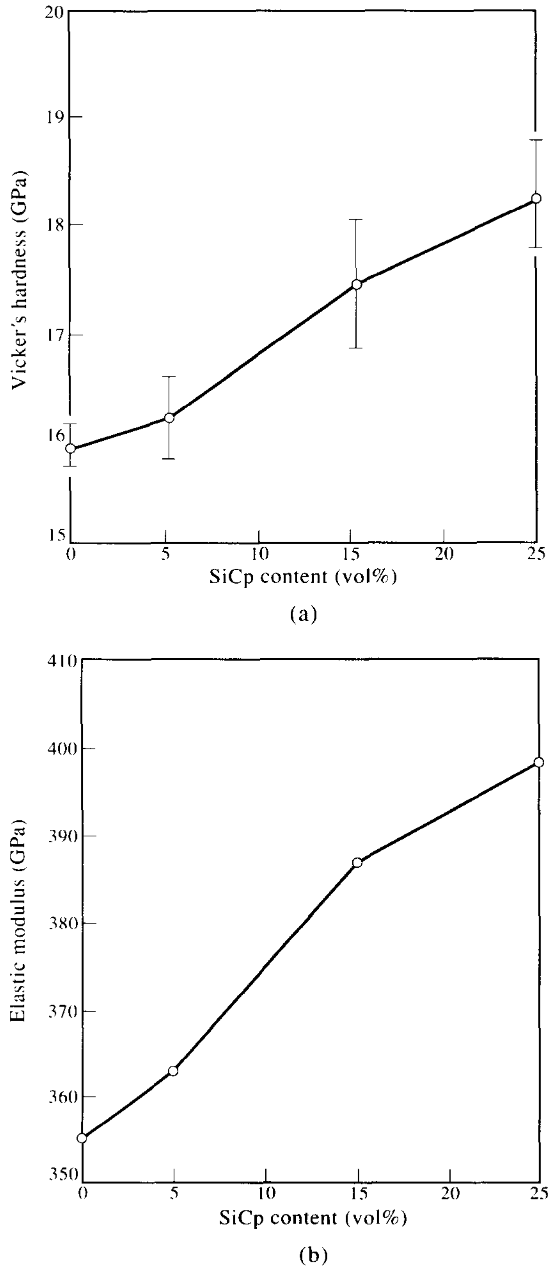

Fig. 3. (a) Vicker's hardness and (b) elastic modulus of the AZS series of composites as functions of nano-SiCp content.

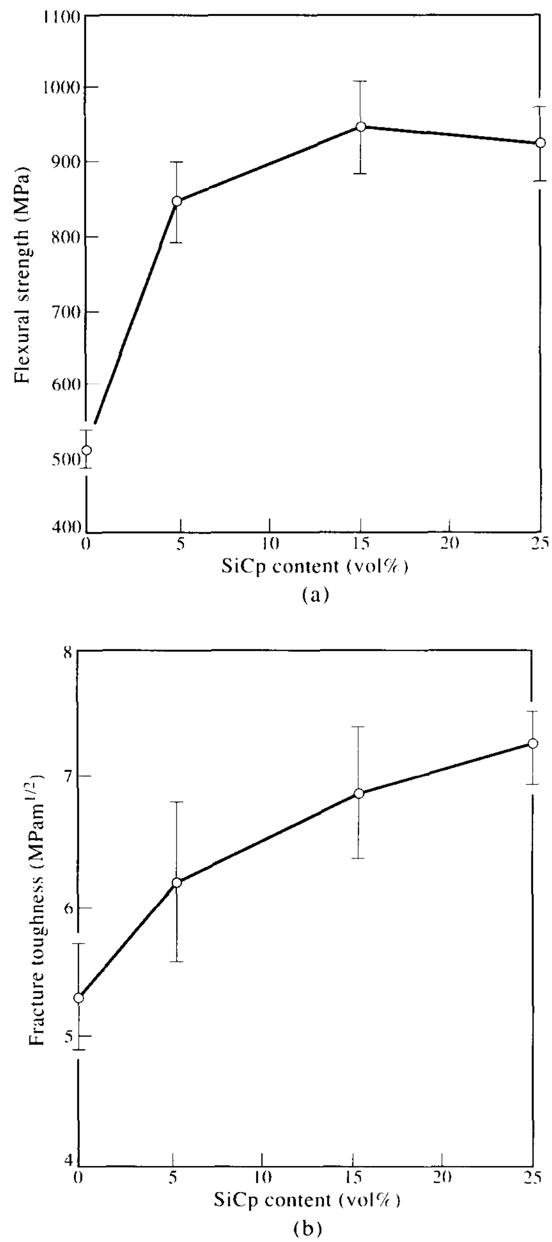

Fig. 4. (a) Flexural strength and (b) fracture toughness of the AZS series of composites as functions of nano-SiCp content.

a slight decrease in the strength (923 MPa at 25 vol% SiCp). The fracture toughness of the AZS series of composites increases monotonically with increasing nano-SiCp content. An addition of 25 vol% SiCp can increase the toughness from 5.3 $MPam^{1/2}$ for Al_2O_3 + 20 vol% ZrO_2(2 mol% Y_2O_3) to 7.3 $MPam^{1/2}$.

The change trend of the strength and toughness of the present AZS series is different from that obtained by Niihara and co-workers in Al_2O_3 + nano-SiCp (AS) series of composites.[1] They have reported that both the strength and fracture toughness of the AS series increase to their maximum values with only 5 vol% SiCp, and then remain at slightly-decreased values up to 32 vol% SiCp. That is to say, the strength and fracture toughness of AS composites do not increase further as SiCp content increases at fairly high volume fraction (greater than 5 vol%). However, the improving tendency of the strength and toughness with increasing nano-SiCp content remains unchanged at higher volume fraction of nano-SiCp for the AZS composites, as indicated in Fig. 4. Obviously, this different reinforcing effect of nano-SiCp additions on the AS and AZS series should be attributed to the presence of phase transformation toughening of ZrO_2 in the AZS composites. The detailed explanation for the interactions between the reinforcing effect of nano-SiCp and that of ZrO_2(2 mol% Y_2O_3) on the Al_2O_3 matrix will be given in Section 3.5.

3.4 Toughening and strengthening mechanisms of nano-SiCp

Scanning electron micrographs of the fracture surfaces of AZS composites (shown in Fig. 5) reveal that the addition of nano-SiCp changes the fracture mode of the Al_2O_3 matrix from a mixture of transgranular and intergranular to complete transgranular fracture. This change of fracture mode is perhaps caused by the high tensile hoop stress around the particles within the Al_2O_3 matrix grains, which is generated from the large thermal expansion mismatch between Al_2O_3 and SiCp.[1] Usually, such changes in fracture morphology can

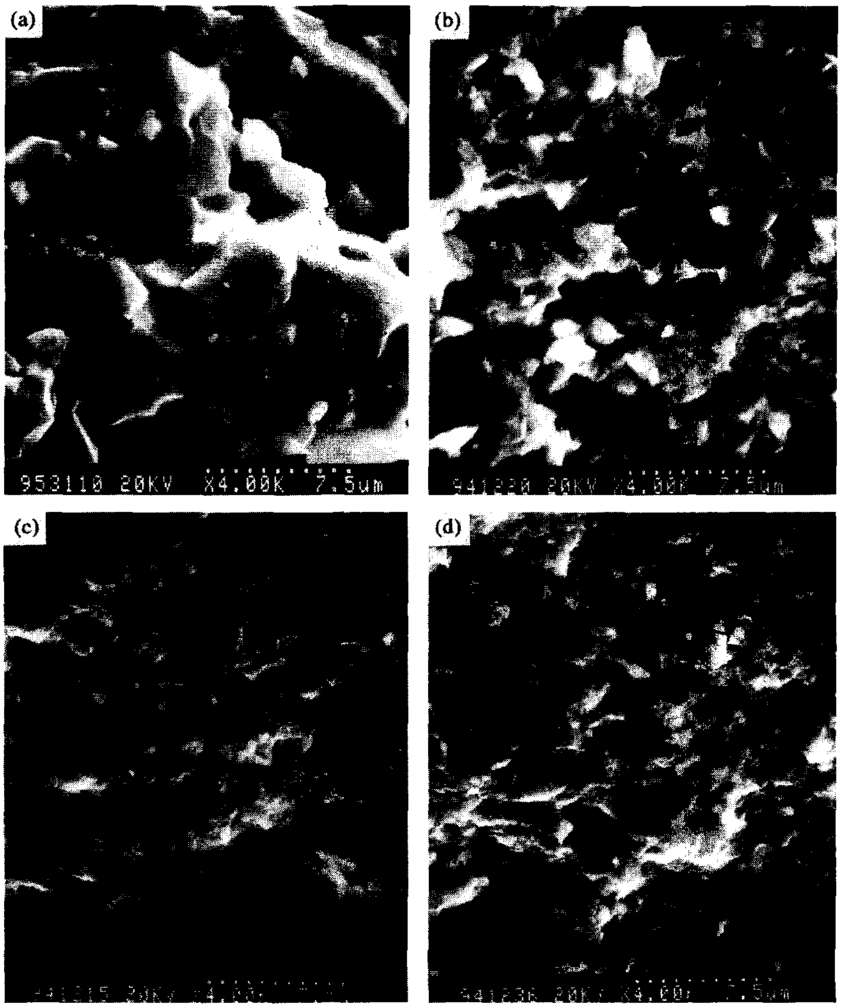

Fig. 5. Scanning electron micrographs showing the fracture surface morphologies of the AZS series of composites. (a) AZS00, (b) AZS05, (c) AZS15, (d) AZS25.

lead to a significant improvement in toughness due to the fact that much more energy will be consumed in transgranular fracture. In addition, the nano-size hard SiC particles within Al_2O_3 grains can pin the crack tip, which also has some toughening effect.

However, the notable strength improvement of Al_2O_3 + ZrO_2 + SiCp composites can not be explained from only the increment of toughness. There are some other strengthening mechanisms. Firstly, the nano-size SiC dispersions restrain the grain growth of the matrix (see Fig. 1) and decrease the possibility of abnormal grain growth, which can lead to a remarkable decrease in the critical flaw size of the matrix. Secondly, according to Niihara's report,[1] the nano-SiCp can pin and pile-up the dislocations which are generated during hot-pressing, and thus strengthen the matrix. Nevertheless, the addition of nano-SiCp also has a harmful effect on the strength of the composites via the average residual tensile stress which exists in the matrix and is caused by the thermal incompatibility between SiCp and the Al_2O_3 + 20 vol% ZrO_2 matrix ($\alpha_{SiCp} \approx 4.7 \times 10^{-6}/°C$, $\alpha_{Al2O3} \approx 8.5 \times 10^{-6}/°C$, $\alpha_{ZrO2} \approx 10.0 \times 10^{-6}/°C$), for the tensile stressed matrix is the favoured site for crack nucleation. When the SiCp content increases, the deleterious effect of this tensile stress will become more intense. Furthermore, with increasing SiCp content, the possibility of agglomeration of SiC particles becomes greater. These two harmful effects of SiCp additions may explain the decrease in the strength of AZS25 (see Fig. 4(a)).

3.5 Interactions between nano-SiCp and the ZrO_2 (2 mol% Y_2O_3) component

The toughening effect of the ZrO_2(2 mol% Y_2O_3) component due to its t–m phase transformation can be revealed by crystallographic analysis. The results of the XRD analysis of polished and fractured surfaces of the AZS composites are shown in Table 2. It can be seen that in AZS00, the Al_2O_3 matrix with a high elastic modulus has such strong constraint to ZrO_2(2 mol% Y_2O_3) that a high fraction of t-phase (82.8% of the total ZrO_2) remains after cooling down from the hot-pressing temperature. The addition of 5 vol% SiCp, because of the refinement of ZrO_2 particles and the higher elastic modulus of SiCp, enhances this constraint, so the amount of t-phase increases slightly for AZS05. But further additions of SiCp, due to the larger thermal tensile stresses caused by the thermal incompatibility between SiC and ZrO_2, promote the t–m transformation during cooling down from the fabrication temperature. Consequently, the amount of t-phase on the polished surfaces of AZS15 and AZS25 decreases. It can also be found from Table 2 that the amount of t-phase in ZrO_2(2 mol% Y_2O_3) on fractured surfaces decreases in a more obvious manner with the increment of SiCp content, so that the amount of dynamic t–m transformation during fracture increases notably with the nano-SiCp content. One hypothesis regarding the rise in the amount of the dynamic transformation involves the toughening effect of nano-SiCp on the matrix. This is because the dynamic transformation zone size $h = B(K_{IC}^M/\sigma_c^T)^2$,[5] where K_{IC}^M is the fracture toughness of the matrix, σ_c^T is the critical stress for the t–m transformation and B is a material-independent constant which characterizes the stress state.[5] Consequently, the improvement of the K_{IC}^M value (here Al_2O_3 + nano-SiCp may be regarded as the matrix) will lead to a rise in the transformation zone size, and thus the amount of dynamic t–m transformation increases. In addition, the residual tensile stresses acting on ZrO_2 particles, caused by the thermal incompatibility between SiC and ZrO_2, also have a beneficial effect on the dynamic transformation. As we know, for an Al_2O_3 + ZrO_2 composite containing mostly t-phase ZrO_2 particles, the primary source of toughening is the stress-induced dynamic t–m transformation of these particles, with only a minor toughness increment due to microcracking around thermally formed m-ZrO_2 particles.[6] Therefore, it can be concluded that the addition of nano-SiCp improves the contribution of t–m phase transformation of

Table 2. Amount of t-phase in ZrO_2(2 mol% Y_2O_3) on polished and fractured surfaces of AZS composites

	AZS00	AZS05	AZS15	AZS25
Amount of t-phase on polished surface (%)	82.8	84.7	76.3	72.6
Amount of t-phase on fratured surface (%)	75.4	72.6	59.5	53.9
Amount of t–m transformation during fracture (%)	7.4	12.1	16.8	18.7

ZrO_2(2 mol% Y_2O_3) to the toughening of AZS composites.

As mentioned in Section 3.3, the presence of the t–m transformation in AZS composites has a remarkable influence on the toughening and strengthening effect of nano-scale SiC particles. The explanation for this is suggested as follows. In Al_2O_3 + nano-SiCp composites, the large thermal expansion mismatch between SiCp and Al_2O_3 can create regions of tension between the nano-SiC particles. A crack path which follows these regions of tension would give rise to a decrease in fracture toughness.[7] Perhaps this is why there is no further increase in the fracture toughness of AS composites at higher SiCp content (greater than 5 vol%). In AZS composites, however, the compressive stress resulting from the dilational component of the transformation strain can partially offset the tension, thereby reducing the harmful effect caused by those regions of tension, and thus the fracture toughness of the AZS composites can still increase with larger amounts of nano-SiCp. This compressive stress, which can create a better stress state in the tensile stressed matrix and then restrain the nucleation of cracks, also has a promotive influence on the strengthening effect of nano-SiCp. Therefore, the ascending tendency of flexural strength with the increment of SiCp amount remains unchanged at a higher SiCp content for the AZS composites than for the AS composites.

From the above discussions, it can be concluded that the good strength and toughness of AZS composites result from the combined contribution of the t–m transformation toughening of ZrO_2 and the reinforcing effect of nano-SiCp. Furthermore, the effects of both nano-SiCp and ZrO_2(2 mol% Y_2O_3) on improving the mechanical properties appear to be synergetic.

4 CONCLUSIONS

The following conclusions can be drawn from the work described above:

1. The flexural strength and fracture toughness of the Al_2O_3 matrix are significantly improved by introducing nano-SiCp and ZrO_2(2 mol% Y_2O_3) together, the maximum flexural strength and fracture toughness of the composites are 945 MPa and 7.3 MPam$^{1/2}$, respectively.
2. The reinforcing effects of nano-SiCp derive mainly from refinement of matrix grains, inducement of transgranular fracture of Al_2O_3 and crack pinning. The toughening effect caused by ZrO_2(2 mol% Y_2O_3) particles comes mostly from the dynamic t–m phase transformation of these particles.
3. Both ZrO_2 and nano-SiCp play their reinforcing roles at the same time, and there is obvious synergy with respect to these reinforcing effects.

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