Vol. 14 № 3 **Trans. Nonferrous Met. Soc. China** Jun. 2004

Article ID: 1003 - 6326(2004)03 - 0430 - 06

Mechanism of toughening and strengthening of Si_3N_4/SiC/ZrO_2 nanocomposites①

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Abstract: The Si_3N_4-based nanocomposites reinforced with micro ZrO_2 and nano SiC particles were prepared by polarity dispersant and vacuum-sintering technology. The mechanical properties and microstructures were tested. The results show that appropriate amount of micro ZrO_2 and nano SiC particles, not only enhance the microhardness, but also block the excessively growth of β-Si_3N_4 and β-Si_3N_4 grains, so they finally all grow up to uniformly pole-shaped grains. This process is similar to the strengthening and toughening mechanism of grain whiskers and makes a remarkable improvement on the toughness. Compared with Si_3N_4 ceramic, the toughness of Si_3N_4/SiC/ZrO_2 nanocomposites are increased from 6.2 MPa·$m^{1/2}$ to 11 MPa·$m^{1/2}$.

Key words: Si_3N_4; nanocomposites; toughening; strengthening
CLC number: TB 332 **Document code:** A

1 INTRODUCTION

In numerous ceramic materials, Si_3N_4 ceramic is called "omnipotent champion". It is not only a good construction material applied in high temperature, but also a new function material[1, 2]. With the development of nanocomposites, the application investigation of new type Si_3N_4 ceramic construction materials has entered a new age. It has vast applied perspective[3-9]. But the low toughness is the obstacle of the application of Si_3N_4 ceramic materials, so how to improve the toughness of Si_3N_4 ceramic materials is an urgent problem. The Si_3N_4/SiC nanocomposites can overcome the disadvantages of Si_3N_4 or SiC single phase ceramic materials, such as low toughness, grains growth-up easily in sintering process resulting in strength descent etc[10]. Adding nano-sized particles in composite ceramics can increase its mechanical properties geminately, and it shows that the mechanism of strengthening and toughening of nanocomposites is different from the microncomposite ceramics[11, 12]. Si_3N_4/SiC/ZrO_2 nanocomposites were prepared by polarity dispersant and vacuum-sintering technology in this paper. The aim of the present work is to investigate the microstructure, performance and the mechanism of strengthening and toughening of Si_3N_4/SiC/ZrO_2 nanocomposites. The study has great realistic significance for the application of nanocomposites.

2 EXPERIMENTAL

High-purity Si_3N_4 powders whose average granularity was 0.5 μm, were prepared by Si powders nitrogenation. And the content of α-Si_3N_4 was more than 92% (mass fraction, it was same hereafter). Nano-sized SiC powders, as a strengthening phase, was synthesized by means of laser method in the Institute of Metal Research, Chinese Academy of Sciences. Its purity was above 95%, and the average granularity was 30 nm. The average granularity of Y_2O_3 and ZrO_2 additive powders was 1.2, 1 μm, respectively. The components and properties of nanocomposites were listed in Table 1 (hereafter briefly called sample No. 1 and No. 2, respectively). The raw material powders were mixed in proper ratio with ethanol dispersed in ball-grinding-machine for 48 h, then pressed the dried mixture in mould and sintered in vacuum-heat-press-furnace. The sintered samples were d45 mm × 7 mm grey wafers. Specimens of 3 mm × 4 mm × 40 mm in dimension (according to GB6569-85) for flexural test were cut from the samples, and the span was 30 mm. Relative densities were tested by the draining water law of Archimedes. The phases of the raw powders and each specimen were identified with an X-ray diffractometer (XRD,

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① **Foundation item:** Project(60171043) supported by the National Natural Science Foundation of China; project(EC200101002) supported by Nanchang Institute of Aeronautical Technology
Received date: 2003 - 09 - 30; **Accepted date:** 2003 - 12 - 26

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D8 ADVANCE). The toughness experiments were tested with an HNA-10A Micro Sclerometer in a 29.4 N and loading time of 30 s. The samples were polished, then the toughness were calculated according to the Press-Mark-Law. Fractographs of specimens of flexural test eroded in melt NaOH were observed by scanning electron microscope(SEM, FEI Quanta200) and elements analyses were accomplished with INCA energy dispersive spectroscope(EDS).

3 RESULTS

3.1 XRD RESULTS

Fig. 1 shows the X-ray diffraction spectrums of the raw powders and sintered sample No. 1 and No. 2. The raw Si_3N_4 powders were made up by two phases α-Si_3N_4 and β-Si_3N_4, and the SiC powders were made up by monophase α-SiC. Only the Si_3N_4 diffraction peaks appeared in sample No. 1, and the diffraction peaks of nano-sized SiC powders and micro-sized ZrO_2 powders appeared in the diffraction spectrum of sample No. 2. Compared with the raw powders, the peak locations of α-Si_3N_4 in sample No. 1 and sample No. 2 shifted, or disappeared. The diffraction peaks of Y_2O_3 didn't appear in sample No. 1 and No. 2.

3.2 Mechanical properties of hot-pressing nanocomposites

Table 1 lists the mechanical properties of samples No. 1 and No. 2. The relative density increased from 98.12% to 99.20%. The microhardness of sample No. 2 increased by 45% compared to sample No. 1, and the bending strength of sample No. 2 increased by 32% compared to sample No. 1. The toughness(K_{IC}) of sample No. 2 attained to 11.0 MPa·$m^{1/2}$, which was two times of sample No. 1.

Table 1 Components and mechanical properties of nanocomposites

Sample No.	Si_3N_4/ %	SiC/ %	Y_2O_3/ %	ZrO_2/ %	t/ ℃	p/ MPa
1	97	0	3	0	1 750	30
2	77	15	3	5	1 750	30

Sample No.	T/ min	K_{IC}/ (MPa·$m^{1/2}$)	σ_{bb}/ MPa	Hardness/ MPa	Relative density/ %
1	60	6.2	513	1 334	98.12
2	60	11.0	676	1 963	99.20

3.3 Results of SEM and EDS

The secondary electron image of the fractured sample No. 1 is shown in Fig. 2(a). The grains of sample No. 1 at room temperature were equal axe and coarse shape α-Si_3N_4 grains, and only individual grains were shaped to coarse pole. The grains of sample No. 2 at room temperature shown in Fig. 2(b) and Fig. 2(c) were pole-shaped β-Si_3N_4 and uniformly distributed SiC and ZrO_2 grains. It also can be verified by Fig. 4.

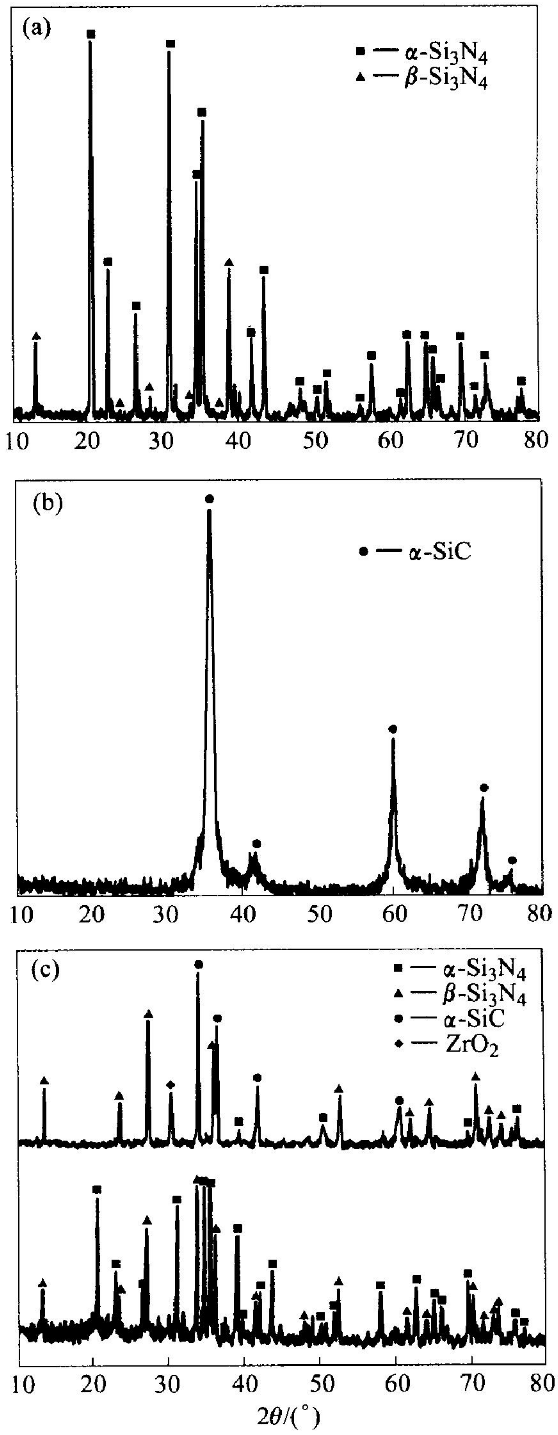

Fig. 1 X-ray diffraction spectrums of powders of Si_3N_4, nano SiC and Si_3N_4 ceramics after sintering
(a) —Si_3N_4; (b) —SiC;
(c) —Si_3N_4ceramics after sintering

The fractograph and EDS spectrums of Si_3N_4 grains of sample No. 1 are shown in Fig. 3, and Fig. 4 for sample No. 2. Pole-shaped grains have been verified as β-Si_3N_4, and the small grains distributed on the boundary of pole-shaped grains are SiC grains. The elements spectrums of Zr, O and Al shown in Figs. 4(b), (d) related to SiC and β-Si_3N_4 grains, illuminating that ZrO_2 and Al_2O_3 powders distribute in SiC and β-Si_3N_4 grains. The presence of element Al is due to debris from Al_2O_3 balls when the raw materials were ground.

Fig. 5 shows fractographs and EDS surface scanning images of No. 2. Element Si and Zr distribute uniformly, and this just illuminates that nano-sized SiC particles and micro-sized ZrO_2 particles disperses preferably.

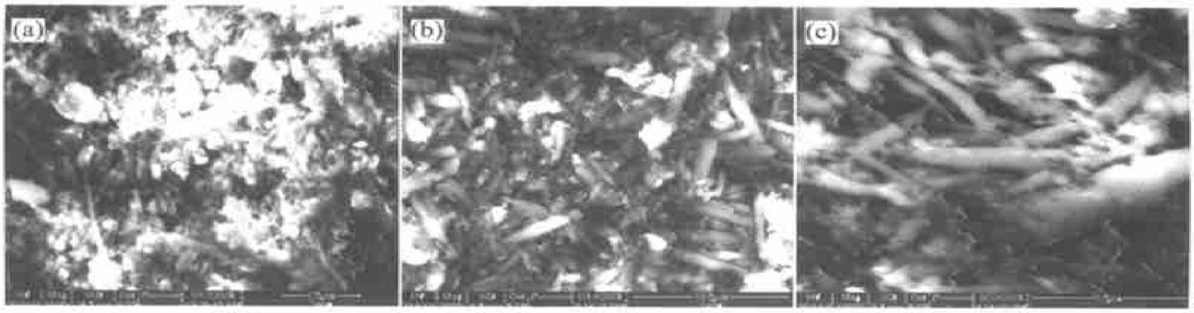

Fig. 2 Microstructures of Si_3N_4 nanocomposites
(a) —Sample No. 1; (b) —Sample No. 2, low magnification; (c) —Sample No. 2, high magnification

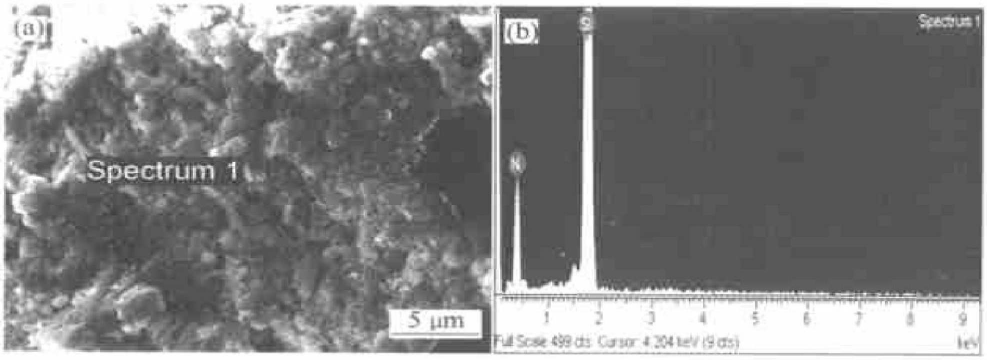

Fig. 3 Fractograph and EDS spectrum of sample No. 1
(a) —Fractograph of sample No. 1; (b) —EDS spectrum of Si_3N_4

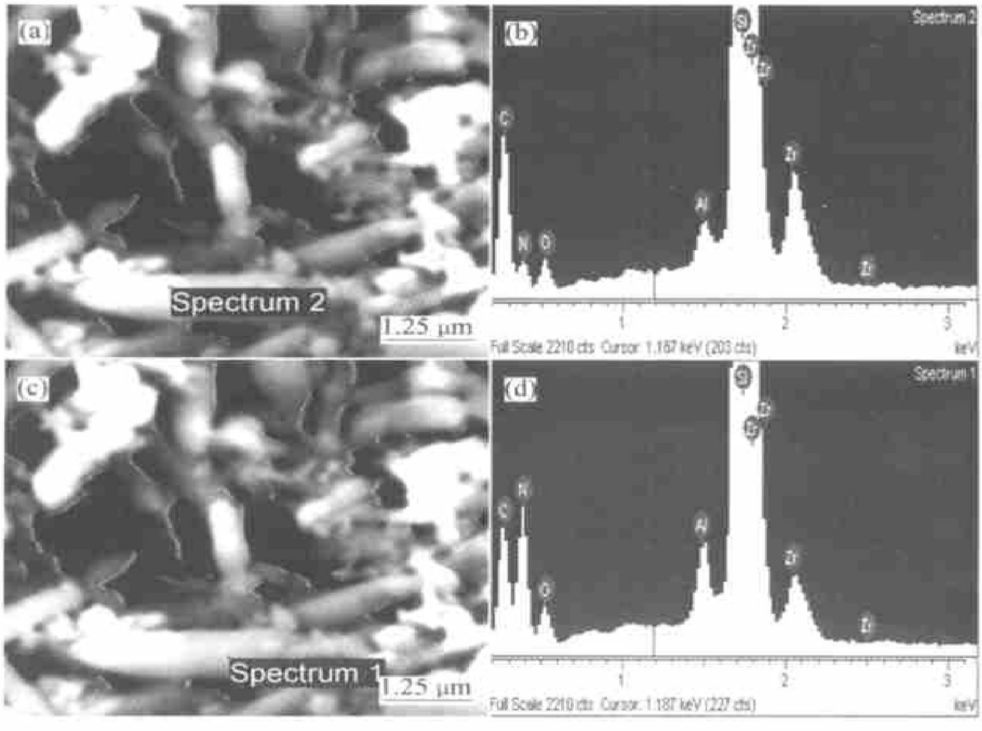

Fig. 4 Fractographs and EDS spectrums of sample No. 2
(a) —SiC grains; (b) —EDS spectrum of SiC; (c) —β-Si_3N_4 grains; (d) —EDS spectrum of Si_3N_4

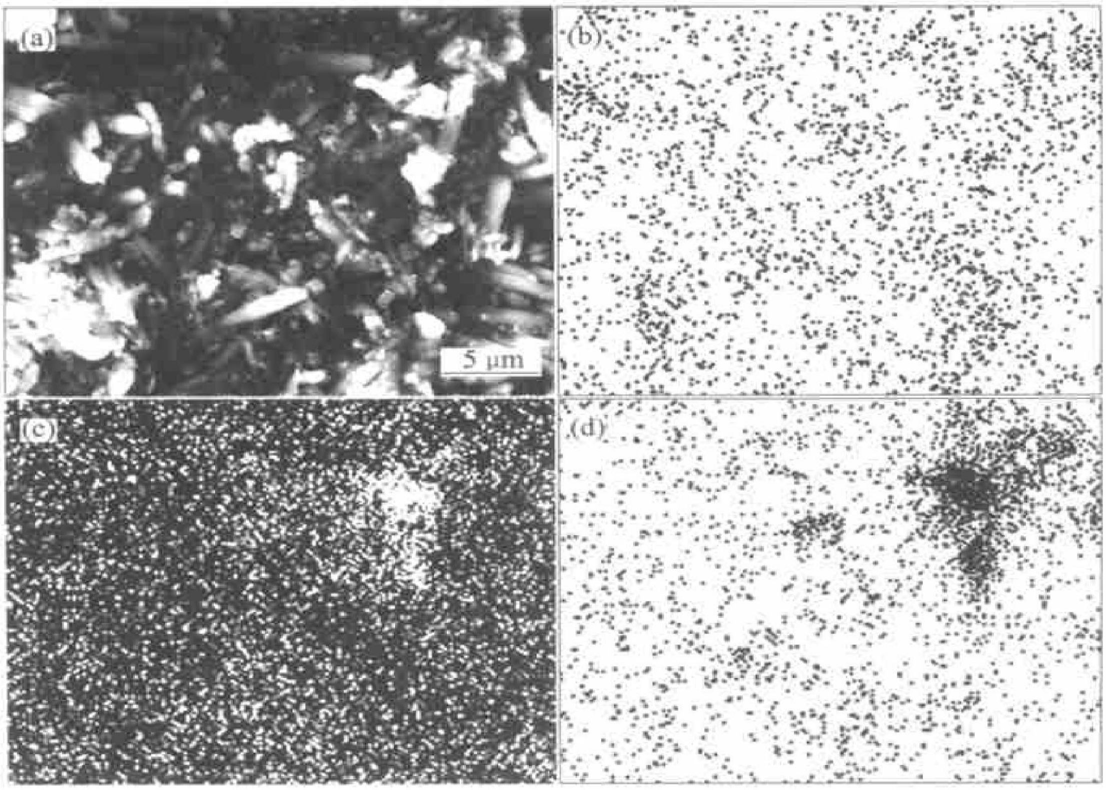

Fig. 5 Fractograph and EDS surface scanning images for elements distribution of sample No. 2
(a) —Microstructure; (b) —C element; (C) —Si element; (d) —Zr element

4 DISCUSSION

4.1 Phase transformation in sintering process

Compared with the XRD spectrums of raw powders, the peak locations of α-Si_3N_4 in samples No. 1 and No. 2 shifted, or disappeared. The diffraction peaks of Y_2O_3 didn't appear in samples No. 1 and No. 2. The phase change from α-Si_3N_4 to β-Si_3N_4 is happened in sintering of Si_3N_4 ceramic. The main reason is that the phase change from α-Si_3N_4 to β-Si_3N_4 is reconstructed and this type of phase transformation commonly happens when the α-Si_3N_4 grains touch liquid phase[13]. Liquid phase is created when reactions happen between the Y_2O_3 additive and other additives. Liquid phase dissolves instability α-Si_3N_4, then separate out β-Si_3N_4 which has low solubility and rather stability. The X-ray diffraction spectrum of sample No. 1 shows that the intension of diffraction peaks of α-Si_3N_4 is much larger than that of β-Si_3N_4. But the X-ray diffraction spectrum of sample No. 2 is opposite, and the intension of diffraction peaks of β-Si_3N is much larger than that of α-Si_3N_4. It was just 15% nano-sized particle SiC that with much large interface energy boosted the phase transformation and restrained the abominably growth of β-Si_3N_4 grains, which makes β-Si_3N_4 grains finally all grow up to uniform columnar grains and become the main phase of $Si_3N_4/SiC/ZrO_2$ nanocomposites[14].

4.2 Toughening mechanism of nanocomposites

The increase of microhardness of sample No. 2 compared to sample No. 1 illuminated that the dispersed nano-sized SiC particle and micro ZrO_2 can distinctly increase the hardness of $Si_3N_4/SiC/ZrO_2$ nanocomposites. The reasons why the rigidity of sample No. 2 was increased due to the following factors: first, the density of sample No. 2 is increased compared to sample No. 1; second, the grain of sample No. 2 is smaller than that of No. 1; third, the quantity of glassy soft phase of sample No. 2 is less than that of No. 1, and it boosted the transformation from α-Si_3N_4 to β-Si_3N_4. Liquid phase changed to soft phase and distributed on the boundary of sample No. 1 in cooling process after sintering, therefore the slipping of dislocations easily came into the soft phase resulting in lower hardness of Si_3N_4 ceramic than that of $Si_3N_4/SiC/ZrO_2$ nanocomposites. Another reason that the hardness of $Si_3N_4/SiC/ZrO_2$ nanocomposites was higher than that of Si_3N_4 ceramic resulted from residual stress. Because the hot expansion coefficient of Si_3N_4 is different from that of SiC ($\alpha_{Si_3N_4} = 2.75 \times 10^{-6}/K$, $\alpha_{SiC} = 4 \times 10^{-6}/K$), the expansion of two phases mismatched in sintering process and the residual stress was produced which existed in the matrix phase and the second phase particles. When the pressure was loaded, partial pressure was counteracted by residual stress, in other words, the efficiency stress was reduced. In this way, the hardness of Si_3N_4/SiC/ZrO_2 nanocomposites was increased. The reason why strengthening and toughening of Si_3N_4/SiC/ZrO_2 nanocomposites increased distinctly compared with the Si_3N_4 ceramic related to the changing of microstructures and stress field.

4.2.1 Influence of dispered nano SiC and micro ZrO_2 on matrix grain

From the SEM fractographs of sample No. 2 shown in Figs. 2(b) and (c), the matrix grains of Si_3N_4/SiC/ZrO_2 nanocomposites are distinctly fine, and the ratio of length to diameter is large. Long and thin columnar β-Si_3N_4 grains are the main phases. The quantity of glassy soft phase is reduced. Fig. 2 (b) and Fig. 2(c) show that nanometer SiC and micrometer ZrO_2 grains distribute mainly on the boundary of matrix grains, making the matrix grains be fine and boosting the formation of the matrix grains which have large ratio of length to diameter. The nanometer SiC and ZrO_2 grains also blocked the excessive growth of β-Si_3N_4 and restrained the coarse of β-Si_3N_4 grains, hence improved the microstructures of Si_3N_4/SiC/ZrO_2 nanocomposites with uniform columnar grains and large ratio of 3 of length to diameter at the same time. β-Si_3N_4 grains are bridged and interconnected as a network and also can be pulled out as shown in Figs. 2(b) and (c), which is similar to the strengthening and toughening mechanism of grain whiskers. The formation of columnar β-Si_3N_4 grains is the main reason which increases the toughness of sample No. 2. The spectrum of elements of Si_3N_4 of sample No. 2 in Fig. 4 shows that there is Si and C in it, which reveals that nano SiC always distributes on the boundary of matrix grains and restrains the coarse of β-Si_3N_4 grains. According to the theory of Hall-Petch, the strength and toughness increase with decreasing dimension of matrix grains.

4.2.2 Influence of residual stress

From above-mentioned analysis, the nano SiC particles distribute primarily on the boundary of matrix grains. Because the hot expansion coefficient of SiC is different from that of Si_3N_4, the expansion and elastic modulus of two phases mismatched in sintering process and the residual stress was produced among the matrix phase and the second phase particles. The matrix was strengthened and toughened by strong rubbing of thin long columnar β-Si_3N_4 grains and consumpting energy[13]. The quantity of local stress in unit spheroid particle can be expressed by Salsing formula[15]:

$$\sigma_r = -2\sigma_\theta = (\alpha_m - \alpha_p)\,\Delta T / [(1-\upsilon_m)/2E_m + (1-2\upsilon_p)/E_p]$$

where σ_r, σ_θ —the radial and tangent stress, respectively; m, p —the matrix grain and the second phase grain respectively; E —elastic modulus; υ —poisson ratio; α —thermal expansion coefficient; $\Delta T = t - 30$; t —temperature. If $\Delta T = 1\,993$ K, $E_m = 304$ GPa, $E_p = 414$ GPa, $\upsilon_m = 0.24$, $\upsilon_p = 0.14$, then $\sigma_r = -830$ MPa, $\sigma_\theta = 415$ MPa. That is, the radial stress in the nano SiC grains was 830 MPa, the tangent compress stress was 415 MPa and the radial pulling stress was 830 MPa in the matrix grains surrounding the nano SiC grains. When cracks propagated towards the grain, they deviated from the grain first, then returned to the m/p interface, making the crackle expanding path increase, thus the toughness was increased[11]. On the other hand, tiger clamp influence on the nano SiC grains distributed on the boundary of matrix grains was produced by the radial compressing stress. When cracks propagated across nano SiC grains, the cracks along the main grain boundary will be pinned, then the cracks were deflected and propagated into grains under a larger stress, resulting in traverse-grain fracture, thus the toughness was increased. Owing to the residual stress in the matrix of sample No. 2, external stress will be counteracted by the residual stress first when the sample was pulled, then effective pulling stress could affect on the sample. In addition, if residual stress is large enough, the subgrain boundary of Si_3N_4 grains will appear. Owing to the existing of nano SiC grains, deformation and a great deal of dislocation clusters appear while β-Si_3N_4 grains grow up. Thus the strength and toughness of Si_3N_4/SiC/ZrO_2 nanocomposites are increased.

4.2.3 Toughening mechanism of martensite phase transformation of ZrO_2

There are three paramorphs for ZrO_2 monolithic (m), cube(c), tetragonal(t), and their relation of transformation is as follows:

$$\text{m-}ZrO_2 \underset{1170\ ℃}{\overset{1070\ ℃}{\rightleftharpoons}} \text{t-}ZrO_2 \xrightarrow{2370\ ℃} \text{c-}ZrO_2$$

The retarding temperature of transformation from monolithic phase to tetragonal phase is 100 ℃. About 3%−4% volume expanding produced in transformation from tetragonal phase to monolithic phase[13]. This kind of transformation belongs to martensite phase transformation, and it results in toughening of matrix. There are two toughening mechanisms of ZrO_2: one is stress inducing phase transformation and the other is phase transformation inducing tiny crack. When Si_3N_4/SiC/ZrO_2 nanocomposites cool from 1 750 ℃, martensite phase transformation will take place in partial ZrO_2 grains (diameter excess a critical value), and its volume will expand, which results in some tiny cracks. Martensite phase transformation won't take place in the ZrO_2 grains whose diameter is less than a critical value because of the restriction of matrix. As soon as external force stress on this grains, the restriction of matrix is released, martensite phase transformation occurs and produces some tiny cracks. In addition, the volume expansion oppresses the main cracks and counteracts partial tip stress of cracks.

5 CONCLUSIONS

The phase transformation from α-Si_3N_4 to β-Si_3N_4 can be accelerated by adding micrometer ZrO_2 and nanometer SiC powders in Si_3N_4 ceramic. The nanometer SiC and ZrO_2 grains also block the excessive growth of β-Si_3N_4 and restrain the coarsening of β-Si_3N_4 grains, hence improve the microstructures of Si_3N_4/SiC/ZrO_2 nanocomposites with uniform columnar grains. β-Si_3N_4 grains are bridged and interconnect a network and also can be pulled out, similar to the strengthening and toughening mechanism of grain whiskers. Phase transformation from tetragonal phase to monolithic phase induces tiny crack, stress inducing phase transformation and the expansion and the mismatch of the elastic modulus of two phases produces residual stress, which results in the strengthening and toughening of Si_3N_4/SiC/ZrO_2 nanocomposites.

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(Edited by HUANG Jin-song)