Formation mechanism of intragranular structure in nano-composites[①]

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Abstract: The effect of sintering process and ZrO_2 contents on formation of intragranular ZrO_2 in Al_2O_3 matrix was investigated with α-Al_2O_3 micro-powders and ZrO_2 nano-powders as original materials. It is found that the second-phase particles coalesce with the growth of matrix grains during sintering. The process conditions that benefit the growth of matrix grains benefit the formation of intragrains. The formation procedure of intragrains could be described as follows. At first, the particles are driven to agglomerate during densification of the matrix . Some particles move along with the migration of the matrix grain boundaries and tend to further gather, then become intergrains. Those gripped between the matrix grain boundaries become intragrains during the growth of matrix grains.

Key words: intragranular structure; grain growth; nanocomposites; formation mechanism

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1 INTRODUCTION

Ceramic matrix nano-composites made of the micro-matrix phases reinforced by the second nano-particles have been a new method of improving the mechanical properties of ceramic materials[1−5]. Because the nano-particles are dispersed among the matrix phases, abnormal growth of the nano-particles can be avoided during sintering so that quantities of nano-particles could be survived. Some nano-particles are named intergranular structures which are located at major phase grain boundaries, and the others, embed in the grain of major phases, are called "intragranular structures" or intragrains. Niihara et al[6] owe the improvement of mechanical properties of ceramic nano-composites to "intragranular structure".

The "intragranular structure" is the structure characteristic of nano-composites. Up to now, a few of studies dealt with the formation mechanism of intragrains. Niihara et al[6] thought that the nano-particles would be as nuclei of major phase crystallization. PAN et al[7] believed that intragrains would result from the matrix grains covering nano-particles in liquid sintering. While the mechanisms could explain neither the effects of sintering processes on formation of intragrains, nor the relationship between the intergrains and intragrains. In this paper, a new explanation for the formation mechanism of intragranular structure was put forward based on the experimental results of grain growth at different crystallization

stages in micro-nano Al_2O_3-ZrO_2 systems.

2 EXPERIMENTAL

The α-Al_2O_3 powders used as original materials had a mean particle diameter of 0.37 μm (made by Zibo Acid Manufactur Factory, China). The nano-sized ZrO_2 powders with diameter of 30−80 nm were made from hydrolyzing $8H_2O \cdot ZrOCl_2$[8]. Different volume fractions of Al_2O_3 and ZrO_2 mixed powders were prepared by aqueous suspension precipitation method[9]. The ceramics were prepared by hot pressing in High Multi-5000 sintering furnace (1 550−1 650 ℃, 1 h, 35 MPa, N_2 atmosphere). In order to study the influence of major phase grain growth on intragrains and the interaction of the two phases' growth, the materials were heat-treated at different temperatures and holding times in SX-12-16 electric resistance furnace. The specimen surfaces were polished and thermally etched in air at 1 400 ℃ for 1 h. Then the polished surfaces and the fractured surfaces were examined by S-2500 SEM. The grain size was determined using linear intercept technique. The fine microstructures were tested by H800 type TEM.

3 RESULTS

Fig. 1 shows the microstructure of Al_2O_3-5% $ZrO_{2(n)}$ composite heat-treated at different temperatures, which indicates that the formation of intra-
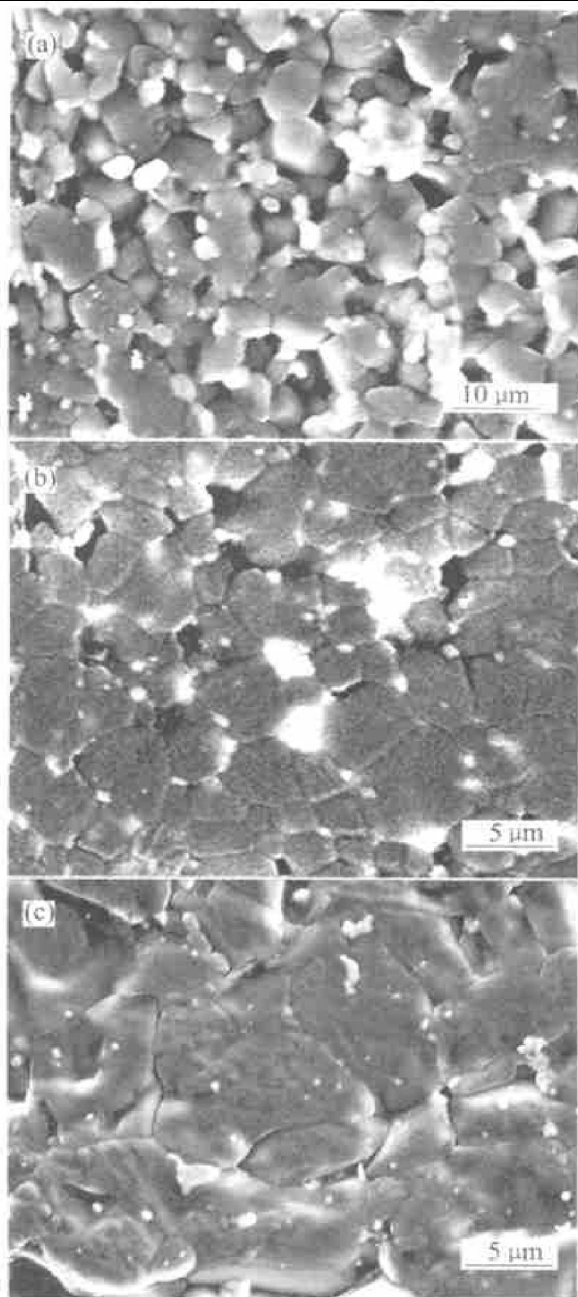
Fig. 1　SEM micrographs of Al_2O_3-5% $ZrO_{2(n)}$
heat treated at different temperatures
a) —No annealing; (b) —1 500 ℃, 1 h; (c) —1 650 ℃, 1 h

granular ZrO_2 has a direct relation to grain growth of Al_2O_3 matrix. Fig. 1(a) shows the morphology of ceramics sintered at 1 600 ℃ for 1 h with only relative density of 91%. Most ZrO_2 particles congregate among Al_2O_3 grains, but there are a few of intragranular ZrO_2 particles with very small size. Figs. 1(b) and (c) show the micrographs of the ceramics annealed for 1 h at 1 500 ℃ and 1 650 ℃ after sintering, respectively. The Al_2O_3 grains in Fig. 1 (b) are equiaxed with straight boundaries. The number of intragranular ZrO_2 is slightly more than that in Fig. 1 (a). Most ZrO_2 particles are located at Al_2O_3 triboundary junctions with bigger size than intragrains. Some ZrO_2 particles congregate to be irregular lumps

at the matrix grain boundaries. The abnormal growth of Al_2O_3 grains occur in Fig. 1(c) with grain size up to 10 μm, and the number of intragranular ZrO_2 increases obviously, even some micron ZrO_2 agglomerates are enwrapped by Al_2O_3 grains.

The effect of annealing at 1 500 ℃ on matrix grain growth is shown in Fig. 2 for composites containing 5%, 10% and 15% zirconia (marked as Z5, Z10 and Z15 respectively). The grain size increases with the increase of annealing time. The more ZrO_2 the composites contain, the more slowly the Al_2O_3 grains grow. But the grain growth becomes very slow when the annealing time exceeds 4 h.
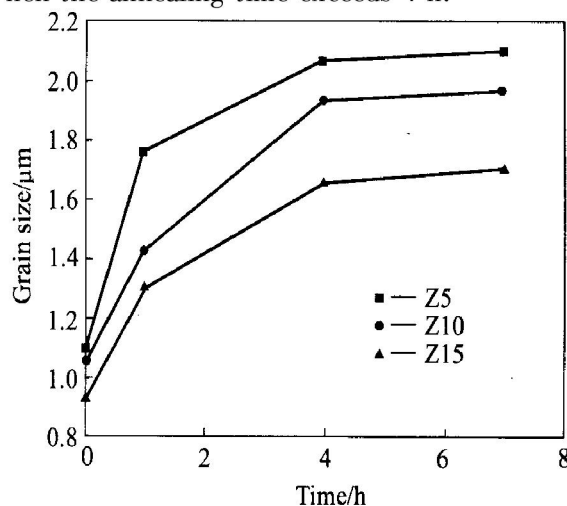

ig. 2　Changes in alumina grain size of samples Z5, Z10 and Z15 with heat-treatment time

4　DISCUSSION

4.1　Analysis on previous theories of formation of intragrains

It has been reported extensively that the second reinforced phase particles are embedded in the matrix phase grains in ceramic matrix nano-composites, but the study on intragrains formation mechanism has not been paid attention to[10-14]. Niihara[2] indicated that the formation of intragranular structure is the result of growth of major phases based on the "intragrain nuclei" in Si_3N_4-$SiC_{(n)}$ systems, which could be proved by HRTEM photograghs that some interfaces between Si_3N_4 and SiC possess oriented relations. But the conclusion could not explain why there are many intragrains in some ceramic systems without coherent relation between major phase and the secondary phase such as Al_2O_3-$SiC_{(n)}$ and Si_3N_4-$TiC_{(n)}$ systems[15]. Even if in Si_3N_4-$SiC_{(n)}$ system, some amorphous phases around intragrains were observed in microphoto of HRTEM[7]. The facts indicate that it is a more universal phenomenon that the interfaces between the major phases and the intragranular nano-particles

needn't be of coherent crystal relations.

According to definite orientation between intragranular SiC grains and the major phases β- Si_3N_4 in Si_3N_4-$SiC_{(n)}$ systems by HRTEM, PAN et al[7] put forward a different formation mechanism of intragrains in which SiC nano-particles in liquid boundary could be wrapped into Si_3N_4 grains with primary phase growth. In order to examine how the liquid sintering influence the formation of intragranular structure in Al_2O_3-ZrO_2 composites, 0.5% MgO was added in composition so that the liquid boundary was formed during sintering, and the micrograph of the composite is illustrated in Fig. 3. It is not found that the number of intragrains increases greatly. On the other hand, the mass transfer would be easier through liquid grain boundaries, so ZrO_2 nano-particles would grow more quickly and some fine ZrO_2 particles could be melted into the liquid boundary phase to form eutectic structure with low melting point rather than intragrains, therefore the structure was unfavorable for forming a lot of intragranular structures in the system.
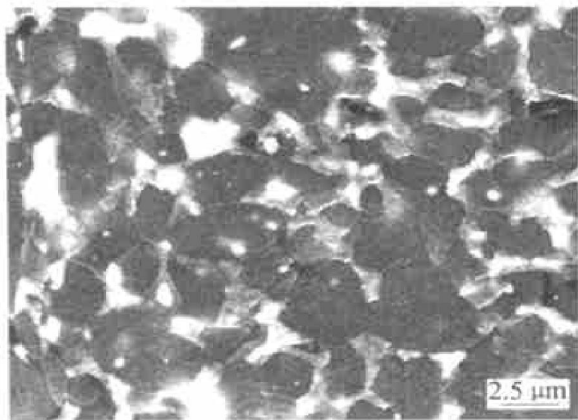

Fig. 3   SEM micrograph of liquid sintering sample

4. 2   Understanding of formation of intragranular structure

4. 2. 1   Formation process of intragranular structure

The authors think that the formation mechanism of intragrains would be based on the understanding of formation process of intragrains. With analyzing the formation of intragranular structure in ZTA ceramics at different sintering stages, the formation process of intragranular structure could be described as the following three periods.

1) At the beginning of densification, because of the volume contraction, the two phase particles close up to each other, so that a number of secondary nano-particles around the major-phase grains were combined into clusters including several even hundreds of particles, and the average size of ZrO_2 particles increased rapidly. The larger the volume fraction of the secondary phase and the smaller the particle size, the

more and bigger their agglomerates would be. A few of single nano-particles or small agglomerates nipped by the two adjoining Al_2O_3 grains will firstly become intragrains with major phase growth subsequently, while the gathered particles on boundaries will bring stronger pinning effect to the matrix growth. At the end of the stage, most grains touched each other. Al_2O_3 grains became spherical for reducing surface energy, and some pores still linked each other, as shown in Fig. 1(a).

2) Normal grain growth stage. With the ZrO_2 particle conglomeration in tri-grain junctions, their pinning effect on Al_2O_3 grain boundaries become stronger, so that the growth speed of Al_2O_3 grains decreased. In this period, the pores in the material became dwindled and their number decreased. Some ZrO_2 particles located at the Al_2O_3 boundary junction became irregular shape because the space of their growth would be determined by the shape of the matrix tri-grain junctions. Some ZrO_2 particles were nipped by two Al_2O_3 grains and couldn't move further, then they were enwrapped by Al_2O_3 with grain boundary migration. The ZrO_2 particle size was coarser obviously at this period than that at the first period. While most Al_2O_3 grain boundaries were short and straight to meet the need of decreasing grain-boundary curvature, as shown in Fig. 1(b).

3) Abnormal growth. As the conditions meet the need of crystallization, for instance high temperature, the migration rate of the Al_2O_3 grain boundary will increase rapidly and the grains grow greatly. Many ZrO_2 particles among the matrix are enwrapped into Al_2O_3 grains, even some irregular agglomerated ZrO_2 become intragranular grains. The big pores and ZrO_2 agglomerations are effective to pinning the major grain boundaries. The stage is the most effective to get intragrains, as shown in Fig. 1(c).

4. 2. 2   Formation mechanism of intragranular structure

ZrO_2 nano-particles tend to gather through moving along Al_2O_3 boundaries. A necessary condition of intragrain formation would be that the secondary phase particles were clamped by major grains so that the particles couldn't move, then they were enwrapped into major grains in the following grain boundary migration of major phase. The process is shown in Fig. 4. Fig. 5 shows the TEM micrograph of Al_2O_3-ZrO_2 composites. It is shown in the central part of the picture that two white Al_2O_3 grains enwrap the black ZrO_2 grain. The common boundary of two Al_2O_3 grains on the right of the intragranular ZrO_2 has disappeared, but the boundary on the left of it is clear, which means that the ZrO_2 particle would
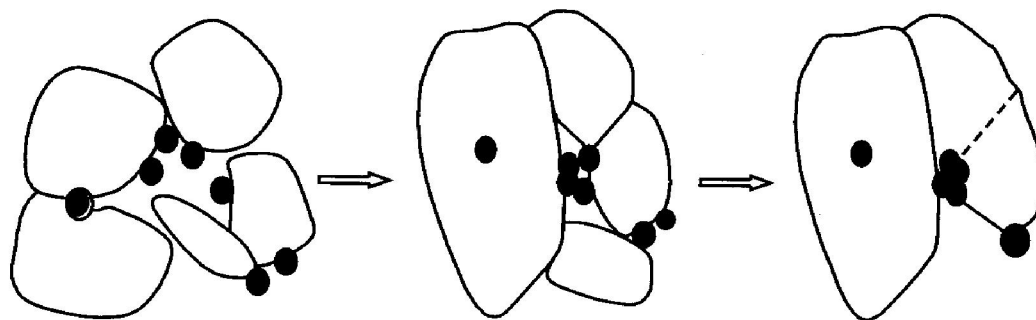
Fig. 4   Illustration of formation of intragranular structure

Fig. 5   TEM micrograph of micro-nano
Al_2O_3-ZrO_2 composites

be forming intragranular one in Al_2O_3 grains. The lattice coherence of two phases is not important because the formation of intragranular structure lies mainly on the major phase growth, and the combination of intragrain with primary phase would be either bond connection or coverage. While those ZrO_2 particles that are not clamped by Al_2O_3 grains conglomerate to be bigger intergranular grains.

The number of intragrains is affected by the number of "two Al_2O_3 grains nip one ZrO_2 particle" structure and major phase crystallization. However, the major phase growth is restricted by the secondary phase particles located at the matrix grain boundaris. The factors that benefit the primary phase growth are beneficial to forming the intragrains. The matrix growth makes the secondary phase particles congregate and grow, which brings the stronger pinning effect in restraining grain boundary's migration. Under the conditions, it's very difficult for the big agglomerates to enter the major grains. So we conclude that "two Al_2O_3 grains nip one ZrO_2 particle" structure would result in intragranular structure, which means that some conditions would be favorable to forming intragrains, such as adequate content of secondary phase, well dispersed and uniformly mixed composite powders, high density of blank and high sintering

temperature.

5   CONCLUSIONS

1) The formation of intragranular ZrO_2 is closely related to the grain growth of major phase, and any conditions that benefit the major phase grain growth also benefit the formation of intragrains.

2) The formation of intragrains can be viewed that two neighboring major grains clamp the secondary phase particle and make it immobile, so that the particle becomes intragrain with the following grain boundary migration of major phase. Those secondary phase particles that are not clamped could move and conglomerate to be bigger intergrains, which restrict both the growth of matrix grains and formation of intragranular grains.

3) Some advantageous conditions for forming intragrains are put forward as follows: adequate content of secondary phase, well dispersed and uniformly mixed composite powders, high density of blank and high sintering temperature.

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