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Pressureless sintering of *in-situ* toughened Yb α-SiAlON ceramics by adding seed crystals prepared by combustion synthesis

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Single-phase Yb α-SiAlON ceramics *in-situ* toughened by elongated grains were prepared by pressureless sintering, with the crystalline powder prepared by combustion synthesis used as seed crystals. The effects of seed addition on the densification, phase transformation, microstructure development, and mechanical properties of the samples were investigated in detail. From the experimental results, it was found that the added seed crystals could promote the phase transformation and facilitate the growth of elongated grains. By adding seed crystals the fracture toughness of the sintered α-SiAlON ceramics was considerably improved, with no obvious degradation in the bulk density and hardness at the same time.

1. Introduction

Among the various silicon nitride based ceramics, α-SiAlON has a relatively high hardness, superior wear resistance, and reduced grain-boundary phases, making it an ideal candidate for high temperature structural and tribological materials. However, the further application of α-SiAlON has been limited by its poor toughness associated with the equiaxed grain morphology [1, 2]. In recent years, various efforts for preparing tough α-SiAlON were successively made and a series of studies have shown that by controlling the nucleation and grain growth carefully, elongated α-SiAlON grains can also be acquired and new tough α-SiAlON ceramics can be developed [3–6]. Seed addition has proved to be an effective method for developing elongated α-SiAlON grains and aligned microstructure by controlling the nucleation process [7]. The preliminary job for seed addition is preparation of single-phase α-SiAlON seed crystals. Zenotchkine *et al.* [8] reported the synthesis of small α-SiAlON crystals by liquid-phase sintering under various processing conditions. At the same time, rod-like Ca and Y α-SiAlON seed crystals were also fabricated by combustion synthesis [5, 9]. The α-SiAlON crystalline powders prepared by combustion synthesis have a low contamination level and a high degree of conversion, and furthermore they are easy to be pulverized and dispersed because of little residual glassy phase and lower density than sintered ceramics. Due to these advantages, the α-SiAlON seed crystals prepared by combustion synthesis are more attractive for industry applications.

Up to now, however, few detailed studies on sintering of α-SiAlON ceramics by adding seed crystals prepared by combustion synthesis have been reported. It has not been fully studied yet whether the combustion-synthesized crystals are stable at elevated temperatures and as effective as the seed crystals prepared by liquid-phase sintering in producing elongated grains. With equal effectiveness, the combustion-synthesized seed crystals will show higher potential in fabricating *in-situ* self-reinforced α-SiAlON ceramics owing to the low cost and simple technique process. Compared with Ca α-SiAlON, α-SiAlONs stabilized by rare-earth (RE) metals have better mechanical properties at elevated temperatures because of relatively higher temperature for the formation of ternary oxides

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eutectic liquid phase. Among the various RE metal systems Yb system has proved to have the largest α-SiAlON phase area [10], which provides more feasibility in modifying the composition. Considering these advantages, Yb α-SiAlON is chosen here to be studied.

In this paper, single-phase Yb α-SiAlON powder consisting of both common isotropic grains and novel rod-like crystals was prepared by combustion synthesis. After acid-treatment and dispersion, the seed crystals were incorporated in the matrix to fabricate self-reinforced Yb α-SiAlON ceramics by pressureless sintering. All the precursor powders with various contents of seed crystals were sintered at 1500, 1600, 1700, and 1800°C, respectively, in order to investigate the effects of seed addition on the densification, phase transformation, microstructure development, and mechanical properties of the samples in detail.

2. Experimental

2.1. Composition

In the general formula of $Yb_{m/3}Si_{12-(m+n)}Al_{m+n}O_n N_{16-n}$ for Yb α-SiAlON, the composition of $m = 1.5$, $n = 1.2$ was investigated. This composition is approximately located at the center of single phase area of Yb α-SiAlON and thus it is thought to be rather stable.

2.2. Preparation of seed crystals by combustion synthesis

Starting powder mixture was prepared by using Yb_2O_3 (99.9%, General Research Institute for Nonferrous Metals, China), Si (99.0%, Fushun Al Factory, China), Al (99.5%, Gaizhou Al Co., China), α-Si_3N_4 (1.7 wt% O, Fangda High-Technology Ceramics Co., China), and SiO_2 (A. R., Beijing Chemical Co., China). The surface oxygen of α-Si_3N_4 particles was taken into account when calculating the chemical composition.

The raw materials were mixed by agate balls in absolute alcohol for 24 h. The obtained slurry was dried at 70°C for 6 h. Subsequently, the powder mixture was put into a cylindric porous crucible with the inner diameter of 24 mm and the height of 60 mm, which was then placed in a special reaction chamber for combustion synthesis. The reaction chamber was evacuated to a vacuum of 10^{-4} MPa and then inflated with high-purity N_2 at a pressure value of 2 MPa. The sample was ignited by passing an electric current through a tungsten coil.

After the combustion synthesis was completed, the reaction product was mechanically pulverized and treated by the acid mixture of HNO_3 and HF in order to eliminate the minor residual liquid phase. Subsequently, the powder was ultrasonically dispersed for 30 min by using absolute alcohol as medium to reduce the agglomeration before being used as seed crystals.

2.3. Pressureless sintering of Yb α-SiAlON ceramics

The starting composition was achieved by using Yb_2O_3, α-Si_3N_4, AlN (1.4 wt% O, self-fabricated by SHS), and Al_2O_3 (A. R., Beijing Chemical Co., China) as raw materials. The combustion-synthesized seed crystals were incorporated in the matrix additionally with designated proportions. Raw materials were mixed by agate balls in a Teflon jar for 24 h with absolute alcohol as medium, then dried and sieved. Each share of 4.0 g powder was cold-pressed into a cylindrical compact with the diameter of 20 mm. In order to investigate the influence of mechanical pressure on the density and microstructure of the sintered samples, two pressure values of 20 MPa and 1.0 MPa were applied. The green compacts were finally sintered in a nitrogen atmosphere at 1500, 1600, 1700, and 1800°C, respectively. The heating rate was 20°C/min from room temperature to 1200 and 5°C/min from 1200°C to the apex. After dwelling for 2 h, the samples were cooled down naturally.

2.4. Characterization

The phase composition was determined by X-ray diffraction (XRD; Cu Kα, Rigaku, Japan) and the microstructure was observed by scanning electron microscopy (SEM; JSM-6460LV, JEOL, and S450, Hitachi, Japan). Energy dispersive spectroscopy (EDS; INCA, Oxford Instruments, UK) was also applied to perform the element analysis for a certain selected area.

The as-sintered dense samples were machined and polished with diamond paste. The bulk density was measured according to the Archimedes principle. Hardness and indentation fracture toughness at room temperature were obtained using a Vickers diamond indenter with a 98 N load and the fracture toughness was evaluated according to the method of Anstis *et al.* [11], assuming a value of 300 GPa for Young's modulus.

3. Results and discussion

3.1. Single-phase Yb α-SiAlON seed crystals prepared by combustion synthesis

As a low-cost productive technique, combustion synthesis has been used to fabricate a variety of ceramic powders. In this technique, once the combustion reaction is triggered by an ignition process, it will progress very quickly and a large amount of heat energy will be produced, resulting in a steep increase in temperature. The high reaction temperature and rapid heating rate are helpful to purify the final combustion product and provide the chance to modify the grain morphology. Fig. 1 shows the XRD pattern of the combustion product. It can be seen that single-phase α-SiAlON has been obtained, without any intermediate phases or residual Si. In addition, according to XRD results with some Si powder added as internal standard, the lattice parameters of the combustion-synthesized α-SiAlON powder have been determined (a =7.8289 Å, c = 5.7016 Å), which are roughly consistent with the results (a = 7.8303 Å, c = 5.7028 Å) calculated from the empirical Equations [12] for α-SiAlON ceramics with the composition of m = 1.5, n = 1.2. This consistence

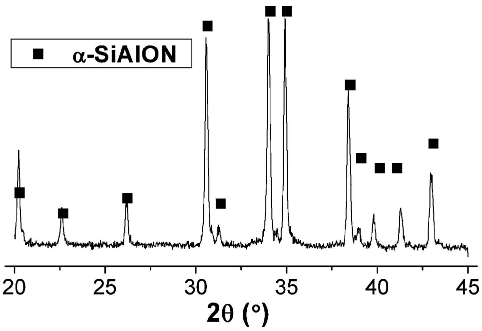

Figure 1 XRD result of the combustion product.

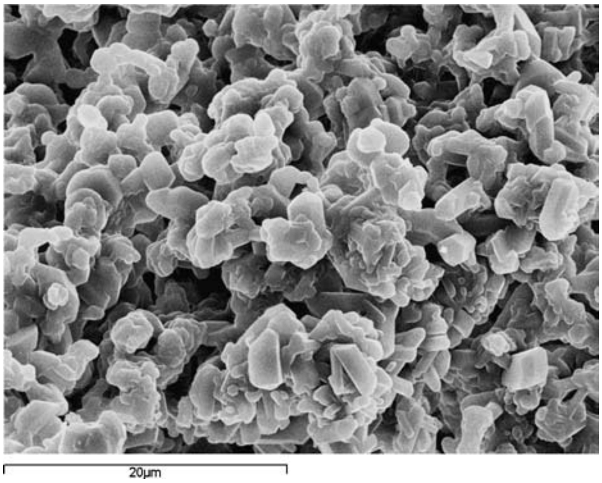

Figure 2 Typical microstructure of the combustion product.

indicates that the composition of seed crystals basically matches that of sintered bulk ceramics in this study. The typical microstructure of the combustion product is shown in Fig. 2, where small crystalline grains with the size of several micrometers are visible. Residual glassy phase is also found, by which most grains are connected with each other. In order to eliminate the glassy phase and reduce the agglomeration, the combustion product was mechanically pulverized and treated by the acid mixture of HNO_3 and HF. After the acid treatment, the product was further ultrasonically dispersed for 30 min by using absolute alcohol as medium and then could be used as seed crystals.

3.2. Effects of seed addition on the pressureless sintering of Yb α-SiAlON ceramics

3.2.1. Densification

Fig. 3 shows the effect of seed addition on the relative density of the samples sintered at 1800°C for 2 h. When the content of seed crystals was less than 15 wt%, seed addition did not lead to remarkable decrease in density, and the relative density was beyond 90% for the samples from the green compacts cold-pressed at 20 MPa. However, when the content of seed crystals was further increased up to 20 wt%, the sample density was obviously debased. The effect of seed addition on sample density may be attributed to different solubility of added seed crystals and silicon nitride particles in the dissolution-reprecipitation mechanism, by which the densification of α-SiAlON ceramics can be completed. In this mechanism, with the advantages in thermodynamic stability and grain size, the seed crystals are more stable and difficult to dissolve into the co-existing liquid phase compared with the silicon nitride particles in raw materials. The lower solubility of seed crystals will delay the densification process and decrease sample density more or less. When the content of seed crystals was relatively low, the deteriorative effect was minor and sample density was not remarkably decreased. When more seed crystals were added, however, this deterioration became more important and sample density was debased obviously.

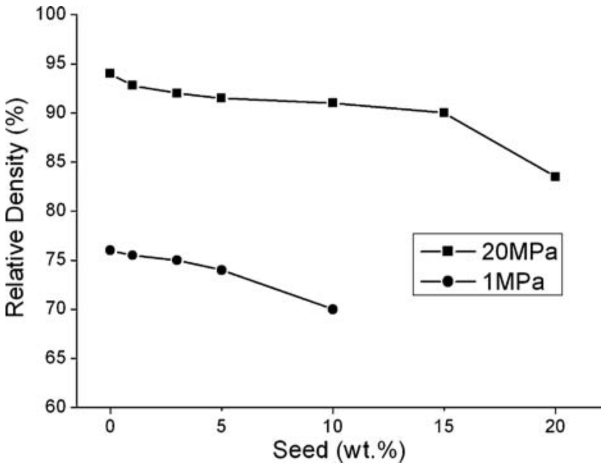

Figure 3 Effect of seed addition on the relative density of samples sintered at 1800°C for 2 h.

From Fig. 3, it can also be seen that the mechanical pressure values had a prominent effect on the sample density. Whether the seed crystals were added or not, the relative densities of the sintered ceramics derived from the compacts pressed under 1.0 MPa were lower than 80%. This is easy to understand, for the density of pressureless sintered samples usually depends on the original density of the cold-pressed green compacts to a great extent.

3.2.2. Phase transformation

In order to investigate the phase transformation during the pressrueless sintering, the cold-pressed compacts were sintered at different temperatures from 1500 to 1800°C at an interval of 100°C. Table I lists the phase compositions of the samples sintered at different temperatures. At 1500°C, a small amount of α-SiAlON was formed, and the main phases were α-Si_3N_4 and YAG. At 1600°C, α-SiAlON became the predominant phase, with some residual α-Si_3N_4 and intermediate phases also existing. When the sintering temperature was elevated to 1700°C, single-phase α-SiAlON was prepared, indicating that the phase transformation was completed.

TABLE I Phase compositions of the as-sintered samples without seed addition

Sintering temperature (°C)	Phase composition				
	α-SiAlON	α-Si_3N_4	β-SiAlON	AlN	YAG
1500	m	s	w	m	s
1600	s	m	w	w	w
1700	s				
1800	s				

Note. s = strong, m = mediate, w = weak.
All the samples involved here were cold-pressed at 20 MPa.

In the samples sintered at 1500 and 1600°C with some intermediate phases, the accurate content of α-SiAlON was difficult to determine. So, ignoring the intermediate phases we only considered the relative contents of α-SiAlON and α-Si_3N_4 in sintered samples. In the XRD patterns, the average diffraction intensity (I) of (210) and (102) peaks was simply used to calculate the phase contents of α-SiAlON (α') and α-Si_3N_4 (α). TR $= I_{\alpha'}/(I_{\alpha'} + I_{\alpha})$ was introduced to describe the percent of α-SiAlON in the mixture of α-SiAlON and α-Si_3N_4, which was also used to roughly evaluate the phase transformation degree from α-Si_3N_4 to α-SiAlON.

Fig. 4 shows the TR values of the samples sintered at 1500 and 1600°C with different contents of seed crystals. It is obvious that the phase transformation ratio was determined by sintering temperature at first. For all the sintered samples, TR values at 1600°C were clearly higher than those at 1500°C. On the other hand, seed addition also affected the phase transformation process of the samples. It can be seen that the TR values gradually increase with rising of seed content at both temperatures. For example, at 1500°C only 1 wt% seed crystals enhanced the TR values approximately twice from 16 to 31%.

The positive effect of seed addition on the phase transformation should be attributed to the following two reasons. At first, compared with the α-Si_3N_4 particles in raw materials the added seed crystals have larger size and higher stability in thermodynamics. Therefore, during the sintering process the seed crystals have more opportunity to surviving the dissolution and thus can serve as effective nucleation sites. Additionally, the seed crystals have very similar lattice parameters with those of new forming α-SiAlON, which guarantees smaller misfit on interface and lower energy barrier for nucleation [13]. In this way, the nucleation process can take place more easily and the phase transformation can be enhanced.

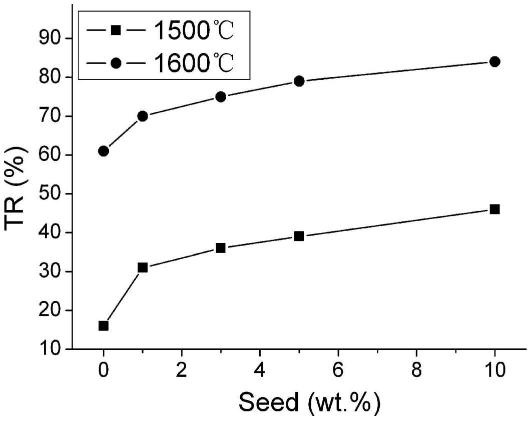

Figure 4 Calculated TR values of the samples cold-pressed at 20 MPa and sintered at 1500 and 1600°C with different seed contents.

3.2.3. Microstructure development

Fig. 5 shows the microstructure of the samples sintered at 1800°C for 2 h. In the samples without seed addition, the anisotropic grain growth was not obvious and only a small amount of elongated grains with lower aspect ratios were found, with most grains existing as an isotropic morphology. However, in the samples with 5 wt% seed crystals, the anisotropic grain growth is remarkably noticed and lots of coarse elongated grains are visible. These well-developed elongated grains have the width of several micrometers and the length beyond 10 μm. The EDS result shown in Fig. 5c confirmed that these elongated grains were Yb α-SiAlON crystals. In this way, it can be said that the anisotropic growth of elongated grains was enhanced by seeding.

In the reaction sintering of α-SiAlON ceramics, α-Si_3N_4 is usually used as one of the raw materials and thus a large amount of nuclei will be formed during the phase transformation. During the subsequent grain growth stage, these numerous nuclei will impinge on each other and have no adequate space to develop into elongated morphology [14]. Consequently, most grains occur in a granular shape. Compared with α-Si_3N_4, the seed crystals have two advantages in thermodynamic stability and particle size. These advantages offer the seed crystals higher stability in the co-existing liquid phase. So the seed crystals are more effective in providing nucleation sites. Additionally, as described above, the seed crystals can provide easier nucleation sites because of smaller misfit on interface and lower energy barrier. Owing to these two reasons, the nucleation process should be mainly determined by the added seed crystals.

During the sintering reaction, the α-Si_3N_4 particles in raw materials dissolve firstly into the co-existing liquid phase making it supersaturated. The species are transported onto the surface of the as-existed seed crystals, where they reprecipitate and α-SiAlON crystals grow up by this means. Since the content of seed crystals is relatively low, there are enough space and sufficient material supply for the as-formed grains to development into coarse elongated crystals.

Although seed addition appears helpful to the growth of elongated grains, it should be pointed out that the content of added seed crystals must be appropriate and too much seed addition is not favorable. High seed content will result in overabundant nuclei and is not beneficial to produce coarse elongated grains. In Fig. 5, the average

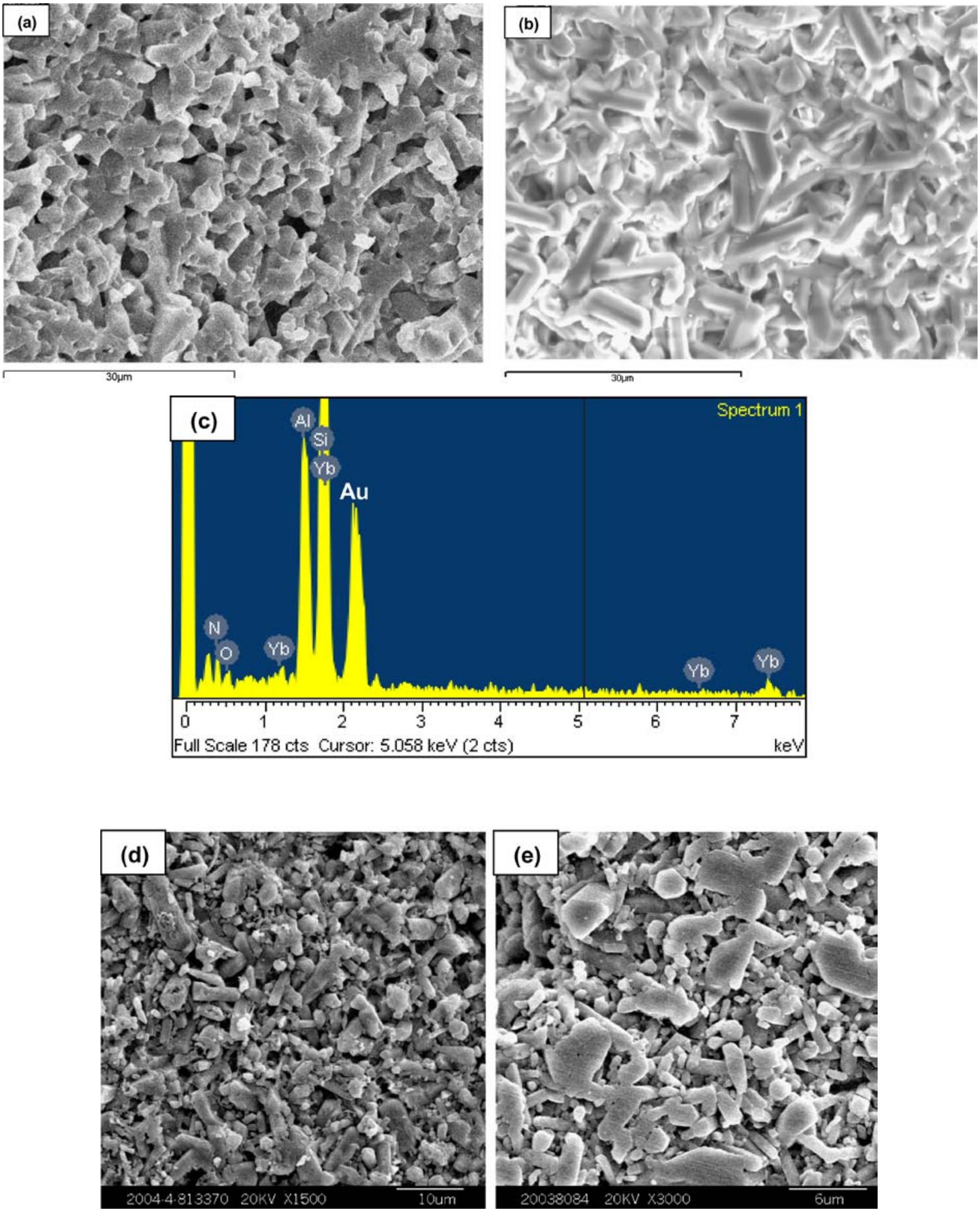

Figure 5 Microstructure of the samples sintered at 1800°C for 2 h with different cold-pressing conditions and seed contents: (a) 1 MPa, no seed, fracture surface; (b) 1 MPa, 5 wt% seed, fracture surface; (c) EDS result for an elongated grain in (b); (d) 20 MPa, 5 wt% seed, etched surface; (e) 20 MPa, 10 wt% seed, etched surface.

size of elongated grains in (e) with 10 wt% seed crystals is smaller than that in (d) with 5 wt% seed crystals.

From Fig. 5b and d, it can also be noticed that the morphology of elongated α-SiAlON crystals is better in the sample derived from the green compact cold-pressed at 1 MPa than at 20 MPa. In loose samples the elongated grains can develop more perfectly into prismatic rod-like crystals with regular faceted planes, while in dense samples the elongated grains can not develop so perfectly. This result may be attributed to the growing space and limitation by neighboring grains during the growth of elongated grains [8]. In loose compacts the grains have adequate space and less impingement with others. In this way, they can grow more freely and their final morphology

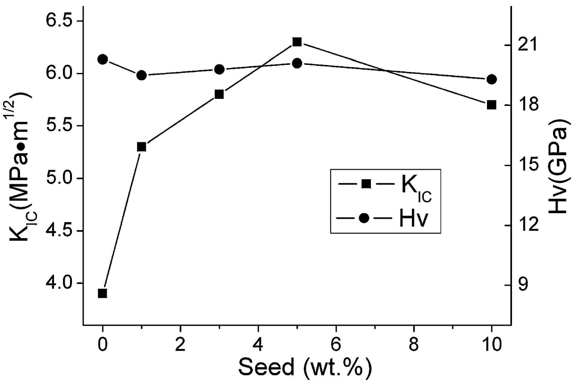

Figure 6 Effect of seed addition on the mechanical properties of samples cold-pressed at 20 MPa and sintered at 1800°C for 2 h.

is more close to the ideal crystal shape with straight edge and smooth faces. On the contrary, in dense samples, the growth of grains is limited by their neighboring ones and they can only develop towards the empty interspace. Consequently, these grains can not reach an ideal shape and exhibit an irregular morphology.

3.2.4. Mechanical properties

Fig. 6 shows the effect of seed addition on the mechanical properties of the samples sintered at 1800°C for 2 h. It can be seen that with the content of seed crystals increased, the hardness does not change remarkably, but the fracture toughness varies obviously, increasing at first and decreasing subsequently. With 5 wt% seed crystals added, the maximum fracture toughness of 6.3 MPa · $m^{1/2}$ can be achieved, which is improved by more than 60% compared with the value without seed addition (3.9 MPa · $m^{1/2}$). The peak in fracture toughness with 5 wt% seed addition may be explained as follows. When the seed content is too low (1 or 3 wt%), there are not adequate elongated grains in sintered ceramics and the interaction among these grains is not considerable, and thus the toughening effect of elongated grains is not satisfying. With increasing of seed content (5 wt%), more elongated grains are produced and interaction effects become important, forming an interlocking structure (Fig. 5), which is favorable to improve the fracture toughness. When the seed content is further increased (10 wt%), too much nuclei will be provided and the average size of elongated grains will be decreased, as discussed above. This reduction of grain size is probably the reason leading to the falling of fracture toughness, as shown in Fig. 6.

It is generally proved that elongated grains can improve the fracture toughness of ceramics by prolonging the track of crack propagation and enhancing the energy absorption via the mechanisms such as crack deflection, branching, grain pull-out and debonding [15]. The experimental results here have confirmed the *in-situ* toughening effect of elongated grains and showed that novel Yb α-SiAlON ceramics with high hardness and improved toughness simultaneously can be fabricated by pressureless sintering adding the seed crystals prepared by combustion synthesis.

4. Conclusions

1. Single-phase Yb α-SiAlON ceramics were prepared by pressureless sintering with the seed crystals prepared by combustion synthesis. Appropriate seed addition did not debase the bulk density of samples remarkably.

2. In the pressureless sintering, the phase transformation was completed at 1700°C. The added seed crystals promoted the phase transformation by providing more effective nucleation sites resulted from their higher stability and lower nucleation energy barrier.

3. Seed addition simplified the manipulation of nucleation and in this way, well-developed elongated Yb α-SiAlON grains were obtained in the sintered samples. In contrast, most grains exhibited a granular morphology without seed crystals.

4. By adding seed crystals properly, advanced Yb α-SiAlON ceramics possessing both high hardness and improved toughness simultaneously were prepared. This has confirmed the feasibility of fabricating *in-situ* toughened α-SiAlON by adding combustion synthesized seed crystals and thus provided a low-cost way to manufacture new tough α-SiAlON ceramics.

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References

1. S. HAMPSHIRE, H. K. PARK, D. P. THOMPSON and K. H. JACK, *Nature* **274** (1978) 880.
2. H. MANDAL, *J. Eur. Ceram. Soc.* **19** (1999) 2349.
3. Y. B. CHENG and D. P. THOMPSON, *ibid.* **14** (1994) 343.
4. I. W. CHEN and A. ROSENFLANZ, *Nature* **389** (1997) 701.
5. K. X. CHEN, H. B. JIN, M. OLIVEIRA, H. P. ZHOU and J. M. F. FERREIRA, *J. Mater. Res.* **16** (2001) 1928.
6. Z. J. SHEN, Z. ZHAO, H. PENG and M. NYGREN, *Nature* **417** (2002) 266.
7. M. ZENOTCHKINE, R. SHUBA and I. W. CHEN, *J. Am. Ceram. Soc.* **86** (2003) 1168.
8. *Idem.*, *ibid.* **87** (2004) 1040.
9. R. L. FU, K. X. CHEN, X. XU and J. M. F. FERREIRA, *Mater. Lett.* **58** (2004) 1956.
10. A. ROSENFLANZ and I. W. CHEN, *J. Am. Ceram. Soc.* **82** (1999) 1025.
11. G. R. ANSTIS, P. CHANTIKUL, B. R. LAWN and D. B. MARSHALL, *ibid.* **64** (1981) 533.
12. W. Y. SUN, T. Y. TIEN and T. S. YEN, *ibid.* **74** (1991) 2547.
13. S. L. HWANG and I. W. CHEN, *ibid.* **77** (1994) 1711.
14. I. W. CHEN, R. A. SHUBA and M. Y. ZENOTCHKINE, *Key Eng. Mater.* **237** (2003) 65.
15. P. F. BECHER, E. Y. SUN, K. P. PLUCKNETT, K. B. ALEXANDER, C. H. HSUEH, H. T. LIN, S. B. WATERS, C. G. WESTMORELAND, E. S. KANG, K. HIRAO and M. E. BRITO, *J. Am. Ceram. Soc.* **81** (1998) 2821.

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