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Preparation of tough α-SiAlON ceramics by spark plasma sintering with β-Si_3N_4 as raw materials

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ABSTRACT

In-situ toughened Yb α-SiAlON ceramics were prepared by spark plasma sintering with β-Si_3N_4 as raw materials. Dense α-SiAlON sample with rod-like grains was prepared by sintering at 1600°C for 10 min, which showed a fracture toughness of 7.7 MPa·$m^{1/2}$. XRD analysis revealed a strong preferred orientation of rod-like grains in the α-SiAlON sample. It was proposed that, the higher toughness was caused by the reinforcing effect of rod-like grains, and the formation of rod-like crystals was favored by using β-Si_3N_4 as raw materials and applying a fast heating rate during sintering.

In the family of Si_3N_4–based ceramics, α-SiAlON has a high hardness, superior wear resistance, and reduced grain-boundary phases, making it an ideal candidate for high temperature and tribological applications[1]. A problem in the application of α-SiAlON is its poor toughness associated with the isotropic grain morphology. How to improve the toughness of α-SiAlON has been an important topic for a long time. Many efforts for preparing tough α-SiAlON have shown that, α-SiAlON can also develop into rod-like grains by careful manipulation of nucleation and grain growth kinetics, and thus new tough α-SiAlON ceramics can be fabricated[2,3].

For preparing α-SiAlON ceramics, α-Si_3N_4 is generally used as raw materials owing to its higher reactive activity than β-Si_3N_4. In reaction sintering, the α-Si_3N_4 particles provide nucleation sites for α-SiAlON by coherent nucleation[4], resulting in a large amount of α-SiAlON nuclei. These α-SiAlON nuclei will develop into isotropic grains because of impingement of neighboring grains. In order to reduce nucleation and provide sufficient space for grain growth, β-Si_3N_4 can be used instead of α-Si_3N_4 as raw materials, and rod-like α-SiAlON grains can be produced[2]. However, this requires a higher sintering temperature for complete densification due to the lower sintering activity of β-Si_3N_4 powders.

Spark plasma sintering (SPS) is a novel sintering technique, and by this technique ceramic powders can be densified quickly at lower temperatures compared with conventional sintering methods[3]. The purpose of this work is to prepare tough α-SiAlON ceramics by SPS at a relatively low temperature with β-Si_3N_4 as raw materials.

In the general formula of $Yb_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, the composition of m=1.5, n=1.2 was investigated. Starting powder mixtures were prepared from commercial Yb_2O_3, β-Si_3N_4, AlN, and Al_2O_3. The reactant powders were mixed by agate balls in a plastic jar for 24 h with absolute ethanol as medium. The obtained slurry was dried. Each batch of 5.0 g powder was put into a graphite die with the inner diameter of 20 mm and sintered in vacuum by SPS. During sintering, a heating rate of 100°C/min was used, and a mechanical pressure of 25 MPa was applied to improve densification.

The sintered samples were machined and polished with diamond paste. The bulk density was measured according to the Archimedes principle. The hardness was measured by the Vickers indentation method with a load of 98 N. The fracture toughness was evaluated according to the method reported by Anstis et al.[5], assuming a Young's modulus of 300 GPa. The phase composition was identified by X-ray diffraction (XRD) and the microstructure was observed by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS).

The phase assemblages and properties of as-sintered samples are summarized in TABLE 1. It is clear that, the holding time plays an important role. In the sample S-0 without holding, much β-Si_3N_4 remained, but in the sample S-10 with a holding time of 10 min, almost single-phase α-SiAlON was obtained except for trace of β-Si_3N_4. At the same time, the density of S-10 was much higher than that of S-0. In the reaction sintering of α-SiAlON, the densification and phase transformation take place via the dissolution-precipitation mechanism with the existence of a transient liquid[6]. In this case, proper holding time is necessary to complete densification and phase transformation.

TABLE 1 : Phase assemblages and properties of the samples prepared with different holding time

Sample	Holding time (min)	Phase assemblage	Density ($g·cm^{-3}$)	Hardness (GPa)	Fracture toughness ($MPa·m^{1/2}$)
S-0	0	α-SiAlON (s), β-Si_3N_4 (tr)	3.10	17.6	3.6
S-10	10	α-SiAlON(s), β-Si_3N_4 (s), $Al_2Yb_4O_9$ (m), AlN (w)	3.55	22.1	7.7

s: strong, m: middle strong, w: weak, tr: trace.

Compared with conventional sintering techniques, the sintering temperature involved here (1600°C) is relatively low, especially considering that β-Si_3N_4 powder with poor sintering activity was used. This can be attributed to the sintering mechanism of SPS. In SPS process, the temperature at the necks of particles is usually higher than that inside the particles, because the electrical current density flowing through the necks is higher. In this way, liquid phase will appear first at the neck and improve the neck growth, finally leading to fast densification.

Figure 1 shows the SEM images of as-sintered samples. The sample S-0 is not fully dense with many cavities, and the sample S-10 is almost fully densified. Such microstructures are consistent with the measured densities of the samples. In S-10, rod-like grains are observed

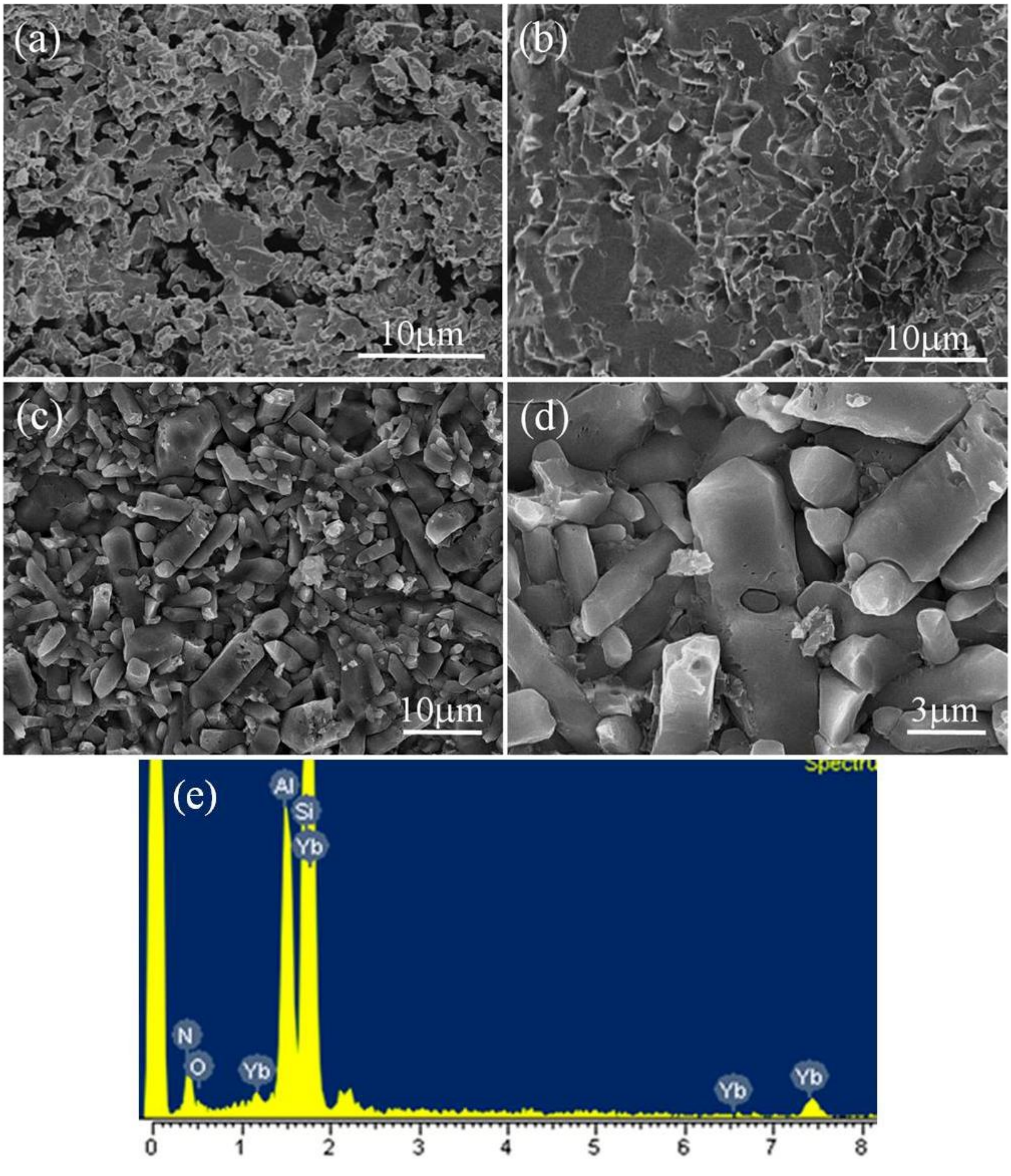

Figure 1 : SEM images and EDS results of as-sintered samples: (a) S-0, fracture surface; (b) S-10, fracture surface; (c) and (d) S-10, polished and then etched surface; (e) EDS spectrum of a rod-like Yb α-SiAlON crystal.

with a diameter of several microns and a length >10 μm. EDS analysis confirms that the rod-like grains are Yb α-SiAlON.

In SPS process, a mechanical pressure was applied, which caused a preferred orientation of rod-like α-SiAlON grains. A quantitative analysis of XRD data for the sample S-10 is shown in TABLE 2. In comparison with the reference data (PDF 41-0360), larger I_{hkl}/I_{201} values are observed in S-10 for the planes parallel or close to [001] direction, and smaller I_{hkl}/I_{201} values for the planes with large angles to [001] direction. Because the length direction of rod-like grains is likely normal to the mechanical pressure, the observed preferred orientation agrees with the reported result indicating that [001] is the fast growth direction of rod-like α-SiAlON crystals[7].

TABLE 2 : Quantitative analysis of XRD data for the sample S-10 compared with reference

{hkl}	φ (°)	Reference		S-10	
		I_{hkl}	I_{hkl}/I_{201}	I_{hkl}	I_{hkl}/I_{201}
{201}	31	100	1	62	1
{102}	67	85	0.85	51	0.82
{210}	0	99	0.99	100	1.61
{211}	24	54	0.54	82	1.32

φ means the angle between {hkl} plane and [001] direction. The XRD data for a–Si_3N_4 powder (PDF 41-0360) are used here as a reference.

In SPS process with a high heating rate, the reaction system has no adequate time to reach equilibrium, and thus a non-equilibrium state occurs. The composition of the liquid phase much deviates from the equilibrium with that of the as-existed grains. Accordingly, a strong chemical driving force for the liquid and the grains to equilibrate is created. This driving force remarkably accelerates the kinetics of the dissolution and mass transportation, leading to a fast anisotropic grain growth[8]. On the other hand, the nucleation is limited when β-Si_3N_4 is used, which provides sufficient space and material supply for fast growth of rod-like grains. In the SEM images of S-10, small particles wrapped in coarse rod-like grains are noticed, as shown in Figure 1 (d). This morphology is probably caused by the fast growth of coarse rod -like α-SiAlON grains, where some un-dissolved β-Si_3N_4 particles at the growing front can be trapped.

The sample S-10 showed a fracture toughness of 7.7 MPa·$m^{1/2}$ (Table 1), which is relatively high for α-SiAlON. This higher toughness should be attributed to in-situ toughening effect of the rod-like grains. It has been found that rod-like grains can prolong the path of crack propagation and increase energy absorption by the mechanisms such as crack deflection, grain pull-out, and debonding[9].

In summary, in-situ toughened Yb α-SiAlON ceramics can be fabricated by SPS at a relatively low temperature of 1600°C with β-Si_3N_4 as raw materials. A strong preferred orientation of rod-like grains occurs in the α-SiAlON ceramics, resulting in a higher fracture toughness of 7.7 MPa·$m^{1/2}$. It is proposed that, both the fast heating rate in SPS and β-Si_3N_4 raw materials favor the anisotropic growth of α-SiAlON and thus the formation of rod-like grains.

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REFERENCES

[1] T.Ekstrom, M.Nygren; J.Am.Ceram.Soc., **75**, 259 **(1992)**.

[2] I.W.Chen, A.Rosenflanz; Nature, **389**, 701 **(1997)**.

[3] Z.J.Shen, Z.Zhao, H.Peng, M.Nygren; Nature, **417**, 266 **(2002)**.

[4] S.L.Hwang, I.W.Chen; J.Am.Ceram.Soc., **77**, 1711 **(1994)**.

[5] G.R.Anstis, P.Chantikul, B.R.Lawn, D.B.Marshall; J.Am.Ceram.Soc., **64**, 533 **(1981)**.

[6] M.Menon, I.W.Chen; J.Am.Ceram.Soc., **78**, 553 **(1995)**.

[7] G.H.Liu, K.X.Chen, H.P.Zhou, J.M.F.Ferreira; J.Mater.Res., **19**, 3408 **(2004)**.

[8] Z.J.Shen, M.Nygren; Key Eng.Mater., **247**, 79 **(2003)**.

[9] 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, M.E.Brito; J.Am.Ceram.Soc., **81**, 2821 **(1998)**.