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Formation of β-SiAlON micropalings consisting of nanorods during combustion synthesis

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Novel β-SiAlON micropalings consisting of nanorods have been prepared by combustion synthesis with proper additives. According to TEM images associated with SAD pattern, the preferred growth direction of the nanorods is proved to be [001]. An epitaxial nucleation and anisotropic growth mechanism is proposed to explain the formation of those micropalings. By this mechanism, new fine crystals are formed on the side faces of coarse crystals and each coarse prismatic β-SiAlON crystal is surrounded by parallel nanorods.

Keywords: Self-propagating high-temperature synthesis (SHS); Transmission electron microscopy (TEM); Anisotropic growth

Owing to their outstanding mechanical properties, superior thermal shock resistance, and good anticorrosion performance, SiAlON ceramics have been identified as one of the most promising structural materials [1–3]. Recently, transparent SiAlON ceramics and novel SiAlON powder have been reported [4–7], showing that in addition to traditional structural applications SiAlON can also be used for functional applications.

In the SiAlON family, β-SiAlON has been attracting much attention and many either papers have been published related to β-SiAlON powders or consolidated ceramics. With a hexagonal lattice structure, β-SiAlON crystals usually develop into elongated prisms, offering β-SiAlON ceramics relatively high-fracture toughness and enabling β-SiAlON particles to act as reinforcing agents in composite materials [8–10]. The anisotropic growth mechanisms of elongated prismatic β-SiAlON crystals have been widely investigated. In this research field, both experimental observations and theoretical models have been reported [11–15].

To fabricate β-SiAlON materials, several methods can be used such as reaction sintering, carbothermal reduction and combustion synthesis. With low energy consumption and short reaction period, combustion synthesis appears to be a facile technique to prepare β-SiAlON powders, especially for large-scale industrial production. In fact, preparation of β-SiAlON fibers by combustion synthesis has been reported [16,17], and α-SiAlON rod-like prismatic crystals and whiskers were also prepared by combustion synthesis [18,19].

With special physical and chemical properties, nanomaterials have been regarded as a very promising research field. As an important ceramic material, silicon nitride has been reported with various nanostructures, including nanorods, nanotubes, nanowires and microribbons with a nanoscale thickness [20–23]. However, few studies on SiAlON nanostructures have been reported, although α- and β-SiAlON have identical lattice structures to α- and β-Si_3N_4.

This paper describes novel β-SiAlON micropalings consisting of nanorods prepared by combustion synthesis with proper additives. The formation mechanism of these micropalings has been discussed and based on the experimental results an epitaxial nucleation and anisotropic growth model is proposed.

According to the general chemical formula of β-SiAlON described as $Si_{6-z}Al_zO_zN_{8-z}$, the composition

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of $Si_{4.5}Al_{1.5}O_{1.5}N_{6.5}$ ($z = 1.5$) was studied in this work. Elemental metallic powders of Si (purity > 99.0%, 300 mesh) and Al (purity > 99.0%, 300 mesh) were used as major reactants. Al_2O_3 was used as the oxygen source to fulfill the β-SiAlON composition. In order to moderate the agglomeration of metal melts and facilitate the nucleation of β-SiAlON, β-Si_3N_4 was also added as a diluent with the molar ratio of Si/β-Si_3N_4 = 6.0. At the same time, 2.0 wt.% $SrCO_3$ and 5.0 wt.% NH_4F were added, which proved to be effective in improving the growth of rod-like β-SiAlON crystals in our previous work.

Raw materials were mixed by ball milling for 24 h with ethanol as medium and the obtained slurry was then dried. Subsequently, the reactant powder mixture was contained in a porous graphite crucible and placed into a combustion chamber. The chamber was evacuated to a vacuum of 10^{-4} MPa and then filled with high-purity N_2 at a pressure of 2.0 MPa. The combustion reaction was induced by passing a direct current (~30 A) through a tungsten coil closely above the sample. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple and a computer system was used for data acquisition and processing.

Once triggered, the combustion reaction took place drastically and the reaction temperature reached as high as 1800 °C. During the short reaction period, the reactants were transformed into products, which were loose and could be easily pulverized into powders.

The phase assemblage was identified by XRD (D/max-RB, Rigaku, Japan) using Cu Kα radiation with a scanning rate of 2°/min. Lattice parameters of β-SiAlON were calculated according to the XRD results with extra-added Si as the internal standard. The microstructure of β-SiAlON product was examined by SEM (JSM-6460LV, JEOL, Japan). TEM (JEM-2011, JEOL, Japan) was applied to perform further observations and acquire the selected area diffraction (SAD) patterns and high-resolution TEM (HRTEM) images of β-SiAlON nanorods. Energy dispersive spectroscopy (EDS) was also used to analyze the chemical compositions of the β-SiAlON nanorods.

The XRD pattern of the as-synthesized product is shown in Figure 1. It is clear that single-phase β-SiAlON was prepared by the combustion synthesis. From the added Si as internal standard, the lattice parameters of β-SiAlON were determined to be: $a = 0.7650$ nm, $c = 0.2942$ nm. These values are close to those ($a = 0.7648$ nm, $c = 0.2945$ nm when $z = 1.5$) calculated from the reported empirical equations [24]. According to the empirical equations and the experimentally-derived lattice parameters, the chemical composition of β-SiAlON synthesized here is estimated to be $1.4 < z < 1.6$, which is basically consistent with the starting nominal composition ($z = 1.5$).

Figure 2 shows SEM images of the β-SiAlON product. It was found that most β-SiAlON crystals developed into hexagonal prisms. The prismatic crystals had smooth basal faces with regular hexagonal outlines, as clearly shown in Figure 2(b). Moreover, based on the side faces of these relatively coarse prismatic crystals, many fine nanorods are formed. The thickness of most nanorods was in the range from 50 to 150 nm except for a few smaller (<30 nm) and larger (>200 nm) ones. The fine nanorods grew preferentially in the direction parallel to the side faces of those coarse prismatic crystals and finally micropalings formed. In each micropaling all the nanorods were aligned around a coarse hexagonal prismatic crystal with their longitude directions identical with that of the coarse crystal.

Figure 3 shows a typical EDS spectrum of β-SiAlON nanorods, showing the presence of Si, Al, O, and N elements. EDS analysis was also performed for several other nanorods and the EDS results gave the average molar ratio of Al/Si = 0.29 and thus $z = 1.35$. Considering the EDS results are semi-quantitative, the average composition of β-SiAlON nanorods is thought to be close to that of the coarse prismatic crystals ($1.4 < z < 1.6$), although the two compositions are not identical.

The TEM image associated with the SAD pattern of a β-SiAlON rod-like crystal is shown in Figure 4(a) and (b). From the SAD pattern, it was found that the longitudinal direction of this rod-like crystal was parallel to

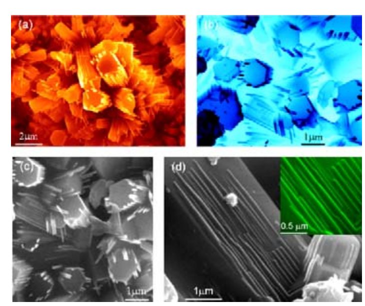

Figure 2. SEM images of β-SiAlON micropalings consisting of nanorods.

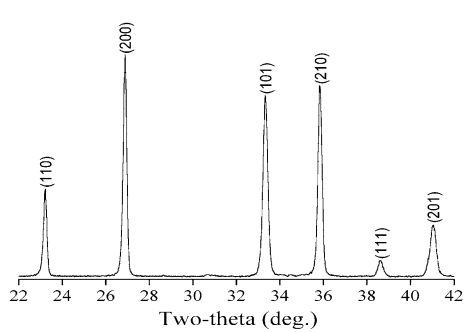

Figure 1. XRD pattern of as-synthesized β-SiAlON.

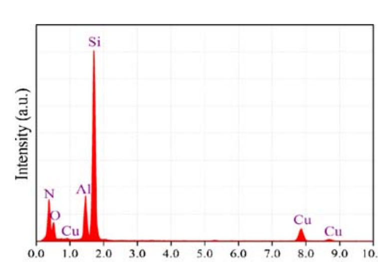

Figure 3. EDS spectrum of a β-SiAlON nanorod.