Materials Science and Engineering A 402 (2005) 242–249

www.elsevier.com/locate/msea

Low-temperature preparation of in situ toughened Yb α-SiAlON ceramics by spark plasma sintering (SPS) with addition of combustion synthesized seed crystals

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Received in revised form 7 April 2005; accepted 18 April 2005

Abstract

By applying SPS technique, new Yb α-SiAlON ceramics in situ toughened by rod-like grains were prepared at a relatively low temperature of 1600 °C, with combustion synthesized seed crystals added. The effects of sintering temperature, heating rate, and the addition of seed crystals on the densification process, phase transformation, microstructure development, and mechanical properties of the samples were discussed in detail. The experimental results showed that Yb α-SiAlON ceramics could be almost fully densified quickly by SPS, and the fast heating rate was helpful to reduce the amount of intermediate phases. Higher sintering temperature and appropriate holding time were beneficial to the promotion of phase transformation and grain growth. It was also demonstrated that the added seed crystals played an important role in enhancing the phase transformation and facilitating the growth of rod-like grains. Being toughened by the rod-like grains via the mechanisms such as grain pull-out and debonding, the fracture toughness of as-sintered Yb α-SiAlON ceramics with additive seed crystals was remarkably improved.

Keywords: Yb α-SiAlON; SPS; Combustion synthesis; Seed crystals; Fracture toughness

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1. Introduction

SiAlON ceramics have been identified as one of the most promising structural materials since they were discovered because of their superior mechanical properties and good thermal shock resistance, which are even more pronounced at elevated temperatures. Nowadays, SiAlON ceramics are used widely in high temperature industrial, automotive and aerospace appliances such as cutting tools, wire drawing, dies and blast nozzles [1–3].

There are two well-known polymorphs of SiAlON called α and β, corresponding to α- and β-Si_3N_4 in crystal structure, respectively. It is generally accepted that α-SiAlON usually occurs in equiaxed grains while β-SiAlON tends to develop into rod-like grains. As a consequence of these typical different morphologies, α-SiAlON exhibits lower fracture toughness in comparison to β-SiAlON. This poor toughness has considerably limited further application of α-SiAlON, in spite of its much higher hardness than that of β-SiAlON [4–6].

In recent years, a variety of efforts on toughening α-SiAlON ceramics have been made and some reports have shown that α-SiAlON can also develop into rod-like morphology by properly controlling the nucleation and grain growth processes [7–11]. This breakthrough indicates that new α-SiAlON ceramics with both high hardness and improved toughness simultaneously can be fabricated and

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doi:10.1016/j.msea.2005.04.031

the importance of α-SiAlON in engineering field is enhanced.

Generally, in order to obtain sufficient bulk density and required mechanical properties, a relatively high sintering temperature from 1800 to 1950 °C is necessary for fabrication of α-SiAlON ceramics. More recently, however, Shen et al. [11,12] reported in situ toughened α-SiAlON ceramics with an interlocking microstructure of rod-like grains prepared at 1750 °C by a novel sintering technique called spark plasma sintering (SPS). In the SPS process, the surface of materials powders can be purified by the released electrons, cations and anions and thus the sintering activity is improved [13]. In this way, by the SPS technique the sample can be densified at a lower temperature compared with that by the conventional sintering methods. At the same time, the densification process takes place very quickly in SPS and can be completed in a short time period. Due to these advantages, SPS has been considered as an efficient and quick sintering technique for fabricating a wide range of materials including various structural or functional ceramics.

To produce tough α-SiAlON ceramics reinforced by rod-like grains, seed addition has proved to be an effective method by simplifying the manipulation of nucleation [14]. Two techniques for synthesizing α-SiAlON seed crystals have been reported either by liquid-phase growth or by combustion synthesis [10,15–17]. The crystalline α-SiAlON powders prepared by combustion synthesis have a low contamination level and a high degree of conversion, and furthermore they can easily be pulverized and dispersed because of little residual glassy phase and lower bulk density than sintered ceramics. These advantages make the combustion synthesized α-SiAlON seed crystals more attractive and confer them a higher potential for industry applications [17].

This paper makes an attempt to prepare in situ toughened α-SiAlON ceramics by SPS at low temperatures (1500 and 1600 °C) with combustion synthesized seed crystals added. The effects of sintering temperature, heating rate, and the addition of seed crystals on the densification process, phase transformation, microstructure development, and mechanical properties of the sintered samples are discussed in detail.

Among α-SiAlONs modified by various cations, Yb α-SiAlON system is chosen here to be studied because of the following reasons. Compared with Li or Ca α-SiAlON, α-SiAlONs modified by rare-earth (RE) metals have better mechanical properties at elevated temperatures because of relatively higher temperature for the formation of ternary oxides eutectic melt. Among the RE α-SiAlON systems, Yb system has proved to have the largest α-SiAlON phase area [18], which provides more feasibility in modulating the composition. At the same time, it is generally accepted that Yb α-SiAlON is relatively difficult to develop into rod-like grains because of high driving force for phase transformation. In this case, it seems more significant and challenging to prepare tough Yb α-SiAlON ceramics with rod-like grains.

2. Experimental procedure

2.1. Composition

The overall composition investigated here is located in the single-phase area of Yb α-SiAlON, which can be represented by the general formula of $Yb_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$. In this study, the composition of $m = 1.2$, $n = 1.2$ was selected for both the seed crystals prepared by combustion synthesis and the sintered ceramics densified by SPS.

2.2. Fabrication of single-phase Yb α-SiAlON seed crystals by combustion synthesis

Starting powder mixtures were prepared by using Yb_2O_3 (99.9%, General Research Institute for Non-Ferrous Metals, China), Si (99.0%, Fushun Al Factory, China), Al (99.5%, Gaizhou Al Co., China), α-Si_3N_4 (94%, 1.7 wt.% O, Fangda High-Technology Ceramics Co., China) and SiO_2 (99.9%, Beijing Chemical Co., China). The surface oxygen content of α-Si_3N_4 was considered when calculating the composition.

The raw materials were mixed by agate balls in a Teflon jar for 24 h with absolute ethanol (Beijing Chemical Co., China) used as medium. The obtained slurry was dried in an oven at 70 °C for 8 h. Then the powder mixture was put into a porous graphite crucible, which was subsequently placed in a 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 reactant powder was ignited by passing an electric current through a tungsten coil. The reaction temperature was recorded by a W-Re3/W-Re25 thermocouple, which was directly inserted into the sample and connected with a computer system for data acquisition.

After the combustion reaction was over, the product was mechanically pulverized and then treated by the acid mixture of HNO_3 and HF in order to eliminate the residual glassy phase. The as-treated powder was further dispersed in alcohol for an appropriate time period by ultrasonic vibration (KQ-300DE, Kunshan Co., China) so as to reduce the agglomeration of the small seed crystals.

2.3. Preparation of dense Yb α-SiAlON ceramics by SPS

The matrix powder for SPS was prepared by using Yb_2O_3, α-Si_3N_4, AlN (1.8% O, self-fabricated by combustion synthesis) and Al_2O_3 (99.9%, Beijing Chemical Co., China) as raw materials, and additionally the seed crystals were added according to the proper weight percent.

The matrix powder together with added seed crystals was mixed by agate balls for 24 h and then dried and sieved. Each batch of 5.0 g powder was poured into a graphite die with the inner diameter of 20 mm and sintered in vacuum by the SPS system (SPS-1050, Japan). A mechanical pressure with the value of 25 MPa was applied during the sintering process. The sintering parameters including heating rate, sin-