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Direct measurement of residual stresses and their effects on the microstructure and mechanical properties of heat-treated Si_3N_4 ceramics

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Abstract

For the first time, the residual stresses induced during crystallization of the amorphous grain boundary phase in heat-treated Si_3N_4 with Yb_2O_3 as a single additive have been directly measured by X-ray residual stress analyses. The magnitude of the room-temperature strength reduction is comparable to that of the corresponding residual stress. Most of the large residual stress is introduced by large volume changes during the phase transformation. Microscopically, the large residual stress essentially results in the formation of flaws including strain contrast and transgranular cracks in elongated β-Si_3N_4 grains. Consequently, the large residual stress is a controlling factor for the reduction of the room-temperature strength in the heat-treated material. However, the influence of residual stresses on mechanical properties would be less at higher temperatures.

Keywords: Residual stresses; Crystallization; Microstructure; Mechanical properties; Silicon nitride

1. Introduction

Silicon nitride (Si_3N_4) ceramics have been extensively studied [1,2] and are widely used as high-temperature structural components because of their superior thermomechanical properties [3–5]. However, Si_3N_4 is difficult to densify without sintering aids due to the highly covalent Si–N bonding [6,7]. Oxide additives such as MgO, Al_2O_3 and most of the rare earth oxides are usually used as sintering additives. After sintering, these additives remain as amorphous grain boundary phase which severely degrades the high-temperature mechanical properties of the Si_3N_4 ceramics [8–11].

Crystallization of the amorphous grain boundary phase by a post-sintering heat treatment has been employed to improve the high-temperature mechanical properties of Si_3N_4 [4,6,11–16]. Nevertheless, no satisfactory improvement in high-temperature strength has been achieved. Often, both room- and high-temperature strength decrease. The causes of these strength reductions are poorly understood, to some extent because of the quite complicated phase relationships between Si_3N_4 and the sintering additives which determine the composition and the properties of the grain boundary phase [11]. At the same time, many authors [8,13,14,17] thought that large residual stresses, which are induced in the material due to volume changes upon phase transformation and/or thermal expansion mismatch between the matrix Si_3N_4 grains and the crystallized grain boundary phase during the heat treatment, are an important contributing factor for these strength

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reductions. However, it is very surprising that no study, to our knowledge, has been devoted to making direct measurements of residual stress induced during crystallization of the grain boundary phase in Si_3N_4 ceramics.

Therefore, the main objective of the present study is to measure the residual stress values in heat-treated Si_3N_4 ceramics with an appropriate method and then use these residual stress values to examine the influence of the residual stress on the microstructure and mechanical properties of Si_3N_4. In addition, considering the effect of complicated phase relationships between Si_3N_4 and sintering additives on the strength, only a single additive was selected in the present study.

Although various quantitative techniques have been developed to analyse residual stresses, non-destructive methods play an extremely important role [18–20]. X-ray diffraction (XRD) is employed as an effective non-destructive evaluation method because it enables local measurements and real-time analysis of stress evolution [20]. X-ray residual stress analyses are based on the measurement of lattice strains by studying the variations in the interplanar spacing of the polycrystalline material from the shift of diffraction profiles by means of monochromatic X-rays. The lattice strains are then converted to stresses using the theory of elasticity [18–21]. Since this method is well established in the case of metallic materials, recently also systematic studies with respect to an appropriate choice of measuring parameters and to the development of suitable methods and the necessary data for residual stress evaluation for ceramic materials have been carried out [18]. Hence, X-ray residual stress analyses give access to the residual stress values for the crystalline β-Si_3N_4 phase, which is the matrix phase in ceramics based on Si_3N_4.

2. Experimental

2.1. Material preparation

Si_3N_4 powder (SN E-10, UBE Industries, Tokyo, Japan) was selected as a starting material. Yb_2O_3 (99.9%, Jiahua Adv. Mater. Resour. Co. Ltd, Jiangsu, China) was used as the single additive. The compositions with a 92:8 weight ratio of Si_3N_4:Yb_2O_3 were prepared by ball milling in ethanol for 24 h using silicon nitride milling balls (~5 mm diameter) as media, and then dried at 60 °C for 12 h. The compositions were subsequently hot-pressed in a graphite die of inner diameter 50 mm at 1800 °C with a mechanical pressure of 25 MPa in a steady-flow N_2 atmosphere for 1 h. These as-sintered silicon nitride samples are denoted ASSN. Samples 1350 SN, 1450 SN, 1550 SN, and 1700 SN were fabricated by a post-sintering heat treatment of the ASSN samples at 1350, 1450, 1550, and 1700 °C, respectively, in a steady-flow N_2 atmosphere for 12 h. The lowest heat-treatment temperature of 1350 °C used in the study was chosen for the following reasons: (i) Yb_2O_3 has the highest melting point among the rare earth oxides [5]; (ii) it has been shown previously [22–25] that Si_3N_4 material with added Yb_2O_3 and SiO_2 may produce liquid phase at ~1650 °C which is much higher than 1350 °C.

2.2. Flexural strength evaluation

Flexural strength tests were carried out at room temperature and at a higher temperature of 1200 °C in air. The heating rate was 10 °C/min, and after reaching the testing temperature of 1200 °C, the temperature was maintained for an additional 30 min prior to testing for thermal stability. According to the method employed by Park et al. [5], three-point flexure testing was conducted with an outer span of 30 mm on specimens with dimensions of 3 mm × 4 mm × 36 mm cut and machined from the samples. A testing instrument (Servopulser, EHF-EG50KNT-10L, Shimadzu Co. Ltd, Kyoto, Japan) was used with a crosshead speed of 0.5 mm/min. All the specimens were ground and tensile surfaces were polished with diamond pastes up to 0.5 μm with edges chamfered to eliminate machining flaws that could act as initiation sites for fracture origin.

2.3. X-ray residual stress analyses and microstructural characterization

For the X-ray residual stress analyses, an XRD instrument equipped with a position-sensitive proportional counter (Dmax-RB, Rigaku, Tokyo, Japan) was used. The {4 4 1} planes of the β-Si_3N_4 phase were measured using Cu Kα radiation with the instrument operating at 40 kV and 100 mA. The corresponding diffraction angle (2θ) was 117.007° and the ψ angle ranged from −45° to +45°. The evaluation of the residual stresses was performed according to the $\sin^2\psi$ method [20,26] using elastic constants $E = 310$ GPa and $\nu = 0.27$ [27–30]. In addition, the crystalline phase assemblies present in the Si_3N_4 samples were also identified using XRD.

In order to obtain microscopic information of the effect of residual stresses on Si_3N_4 grains, high-resolution transmission electron microscopy (HRTEM; JEM-2010F, JEOL, Tokyo, Japan, operating at 200 kV) was used. All specimens for HRTEM were prepared by mechanical thinning and subsequently by ion milling for electron transparency. A thin layer of carbon was then evaporated onto the HRTEM specimens to minimize electron beam charging.

The samples were polished down to a 0.5 μm finish with diamond slurries and chemically etched in melted NaOH at 350 °C for 1.5 min to expose grain boundaries to be observed using scanning electron microscopy (SEM; JSM-6301F). A thin layer of gold was evaporated onto all SEM specimens to minimize the effect of charging.

3. Results and discussion

SEM images show that large elongated β-Si_3N_4 grains were present in all samples. After the heat treatment,