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Microstructure and boundary phases of Lu–Al-doped silicon nitride by pressureless sintering

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ABSTRACT

Various silicon nitride materials were fabricated by pressureless sintering using lutetia and alumina as sintering additives. Densification behavior, microstructure, strength and formation of secondary crystalline phases were investigated. The combination of Lu_2O_3/Al_2O_3 sintering aids can promote the densification and evolution of a fine grain microstructure of Lu–Al-doped silicon nitride because of the low viscosity of the liquid. The J′ phase given by $Lu_4Si_{2-x}Al_xO_{7+x}N_{2-x}$ was considered to be secondary crystalline phase at the grain pockets. The composition with a Lu_2O_3/Al_2O_3 weight ratio 10/10 had highest strength of 690 ± 50 MPa.

1. Introduction

Silicon nitride (Si_3N_4) is an important engineering ceramics because of its superior mechanical properties. To improve operating temperature, highly heat resistant silicon nitride must be required. Degradation of silicon nitrides at high temperature have been considered in relation to softening of the glassy grain boundary phase and melting of secondary refractory phase. By choosing sintering additives and making refractory grain-boundary phase, high temperature strength can be improved [1,2]. Presently, the best additive for high temperature use is believed to be lutetia (Lu_2O_3) [3–8]. The hot-pressed Si_3N_4 with Lu_2O_3 additives exhibited an excellent high-temperature strength up to 1500 °C [9,10], however, the high liquid formation temperature is a major obstacle to sintering silicon nitride to full density, and suitable pressureless sintering condition has not been reported.

High temperature mechanical properties of silicon nitrides are strongly affected by softening of grain boundary glassy phase. Co-doping technique is one of the promising techniques to improve mechanical properties. Al_2O_3 as an ingredient of the sintering aid tend to compromise the high-temperature properties. It has a twofold effect: (i) the lowering of the eutectic temperature of the liquid (fast densification) and (ii) the formation of a SiAlON coating on the preexisting β-Si_3N_4 crystal facets [11–13]. In the present study, the relative merits of Si_3N_4 materials with the additive systems Lu_2O_3–Al_2O_3 were prepared by pressureless sintering. The effect of the sintering additives on the microstructure and the mechanical properties was investigated.

2. Experimental procedure

α-Si_3N_4 (over 95% α-phase content and 1.5 mass% oxygen content, Shanghai, China; mean particle size: 0.5 μm), Lu_2O_3 (99.9% purity, mean particle size: 0.5 μm) and Al_2O_3 (99.9% purity) powders were used. The weight fractions of $Lu_2O_3 + Al_2O_3$ added were 7.5/0, 7.5/2.5, 7.5/5, 7.5/7.5, 10/10, and 15 wt.%/15 wt.%/0 wt%, respectively.

The above starting powder mixtures were wet milled with high-purity Si_3N_4 balls in anhydrous alcohol for 24 h in a plastic bottle. After milling, the slurry was dried, sieved, and uniaxially pressed to form rectangular bars measuring 30 mm × 30 mm × 5 mm. The green bodies were sintered in a furnace (High multi-5000, Fijidempa Co. Ltd., Osaka, Japan) at 1800 °C for 2 h with a heating rate of 15 °C/min to 1200 °C and then 10 °C/min to 1800 °C under nitrogen-gas pressures of 0.6 MPa. The samples were covered with Si_3N_4–AlN–BN powder mixture to protect the samples from decomposition and deformation.

The bulk density of the sintered specimens was measured by the Archimedes displacement method. The theoretical density of the sintered specimens was calculated according to the rule of mixtures. Crystalline phases of the resultant samples were iden-

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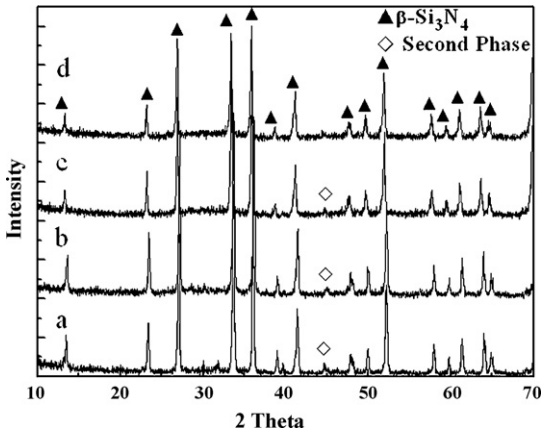

Fig. 1. X-ray diffraction patterns of Si_3N_4 ceramic with various amounts of the Lu_2O_3/Al_2O_3 additives: (a) 7.5 wt.%/5 wt.%, (b) 7.5 wt.%/7.5 wt.%, (c) 10 wt.%/10 wt.% and (d) 15 wt.%/15 wt.%.

tified by XRD (D/MAX-2400X, Rigaku Co., Tokyo, Japan) analysis. The specimens were machined into test bars for flexural strength measurement. The flexure strength was measured by three-point bending method with a 20 mm span at a cross-head speed of 0.5 mm/min at room temperature. Each final value was averaged over five measurements. Microstructure was characterized by TEM (JEM-3010) and the inter-granular phases were analyzed by using the selected-area electron diffraction (SAED). The TEM specimens were prepared by cutting and grinding the sintered specimen to a plate with a thickness of 20 μm, then dimpling and ion beam milling.

3. Results and discussion

The XRD patterns of Lu–Al-doped Si_3N_4 ceramics are shown in Fig. 1. In Si_3N_4–Lu_2O_3–Al_2O_3 system, only the β-Si_3N_4 was detected, confirming a full transformation from α- to β-Si_3N_4. With increasing the addition of Al_2O_3, diffraction peak positions of the Si_3N_4–Lu_2O_3–Al_2O_3 composites were discernible shift, which suggested the formation of an epitaxial β-$Si_{6-z}Al_zO_zN_{8-z}$ layer between β-Si_3N_4 and the intergranular film through simultaneous substitution of some (Si–N) bonds by (Al–O) bonds. For the materials with the Lu_2O_3–Al_2O_3 additive, an additional secondary crystalline phase thought to be a grain-boundary phase was observed. Analysis of the Lu_2O_3-stabilized material revealed that this phase could be indexed as the J′ phase, an aluminum-containing solid solution based on the J phase ($Lu_4Si_2O_7N_2$), which could be formed in Lu_2O_3-doped Si_3N_4 ceramics. The general formula of the J′ phase is given by $Lu_4Si_{2-x}Al_xO_{7+x}N_{2-x}$ and is formed through solid solution of J phase and $Lu_4Al_2O_9$ which was stable in $1Lu_2O_3$:$1Al_2O_3$ system [14], which, in the other RE–Si–Al–O–N systems, have been shown to form a continuous solid solution [15]. Huang and Chen [16] have shown that J′ phase forms in other RE–Si–Al–O–N systems and that its stability increases with a decrease in ionic radius of the RE element. It had suggested that this phase probably existed for rare earth elements from dysprosium to ytterbium and that the degree of substitution, *x*, decreases with a decrease in ionic radius. The phase relationship in the Si_3N_4–SiO_2–Lu_2O_3 system has been shown to be very similar to those of the Si_3N_4–SiO_2–Yb_2O_3 system, which includes the formation of J phase [17], and, because the ionic radius of lutetium (0.85 Å) is very similar to that of ytterbium (0.87 Å) [18], it is not surprising that J' phase also may also exist in the Lu–Si–Al–O–N system.

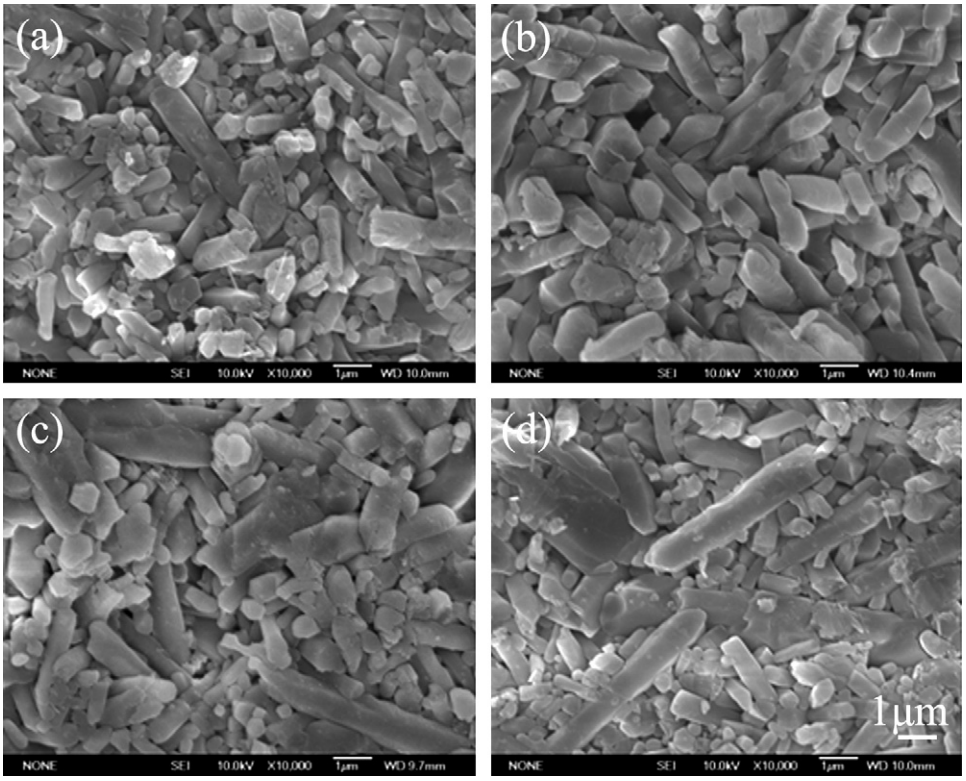

Fig. 2. SEM images of polished and NaOH-etched surfaces of Si_3N_4 ceramics with various amounts of the Lu_2O_3/Al_2O_3 additives: (a) 7.5 wt.%/5 wt.%, (b) 7.5 wt.%/7.5 wt.%, (c) 10 wt.%/10 wt.% and (d) 15 wt.%/15 wt.%.