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New route to improve the fracture toughness and flexural strength of Si_3N_4 ceramics by adding $FeSi_2$

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ABSTRACT

Silicon nitride (Si_3N_4) ceramics were pressureless sintered with 0.2 wt% $FeSi_2$ at 1780 °C for 2 h in nitrogen with Al_2O_3 and Y_2O_3 as sintering aids and found to have high toughness and strength. During the sintering process, β-Si_3N_4 crystal seeds and Fe_5Si_3 reinforcing particles were in situ generated by $FeSi_2$. Abnormal growth of Si_3N_4 grains was promoted by β-Si_3N_4 crystal seeds. High thermal expansion coefficient of Fe_5Si_3 particles induced residual stresses in the ceramics matrix, which deflected the crack. Ultimately, the fracture toughness and flexural strength of Si_3N_4 ceramics reached 9.8 ± 0.5 MPa·$m^{1/2}$ and 1086 ± 48 MPa respectively.

Si_3N_4 ceramics have excellent strength, high hardness, and good resistance to erosion, which place them among the prime candidates in high-temperature industrial, automotive and aerospace application [1]. However, Si_3N_4 ceramics materials still break catastrophically, and the fracture behavior is considered to be the major obstacle for wider use as a structural material. During past decades, much effort had been made to improve their strength and toughness, which included the adjustment of Si_3N_4 grain morphology [2–4] and introduction of reinforcing phases [5–7].

It's well known that the rod-like β-Si_3N_4 grains could bridge the cracks, similar to the whisker-reinforced ceramics, and the fracture toughness of Si_3N_4 ceramics increases with the diameter of the larger elongated grains [8], while large grains also bring big flaws which decrease the flexural strength [2]. However, Si_3N_4 ceramics with a distinct bimodal distribution of grain diameters were found to have high fracture resistance and flexural strength [3]. It is often achieved by adding rod-like seeds to careful control of the size and amount of well-dispersed large elongated β-Si_3N_4 grains in a fine-grained matrix [3,9–13]. Further study indicated that the rod-like seeds selectively grew to develop a bimodal microstructure after densification during sintering process [14,15], while size distribution and morphology of seeds made a significant impact on the microstructure and mechanical properties of Si_3N_4 ceramics [16–18]. For example, model experiments have shown that seeds with broad size distribution induced unfavorably large particles [18]. However, the preparation of rod-like β-Si_3N_4 seeds with uniform size, moderate aspect ratio and few agglomeration is a complex process, and the addition of impurity is always inevitable [19,20]. The seeds may also be damaged in ball milling or mixing process.

Another way to enhance the mechanical properties of Si_3N_4 ceramics is the introduction of reinforcing phases including fibers [5,6] and particles [7]. Compared with fiber-reinforced composites, particle-reinforced composite has stable performance, simple process and high density. In most particle-reinforced composite, the reinforcing mechanism of particles is inducing residual stress by different coefficient of thermal expansion (CTE) with the matrix [21]. The compressive residual stress closures cracks and delays cracks propagation, and the tensile residual stress deflects cracks and delays fracture. Peterson et al. [22] found that the presence of tensile residual stress at the grain boundary caused by different CTE between Si_3N_4 grain and grain boundary phase enhanced cracks' deflection and grain bridging, and the fracture toughness of Si_3N_4 ceramics almost increased linearly from 4–4.5 to 5–6 MPa·$m^{1/2}$ with the CTE of grain boundary phase. Therefore, introduction of particles with higher CTE will further toughen Si_3N_4 ceramics. Iron silicide, such as FeSi and Fe_5Si_3, have much higher CTE than Si_3N_4. Xiaolin et al. [23,24] introduced FeSi particles in Si_3N_4 ceramics by adding Fe_3Al powder, and found the fracture toughness increased from 6.2 MPa·$m^{1/2}$ to 8.0 MPa·$m^{1/2}$. Hideki et al. [25] added Fe_3O_4 powder to form Fe_5Si_3 particles in Si_3N_4 ceramics, and a linear crack was observed along the boundary between Fe_5Si_3 particles and the matrix due to the different CTE. As a result, the flexural strength of the ceramics decreased from 977 MPa to 900 MPa and the fracture toughness decreased from 6.7 MPa·$m^{1/2}$ to

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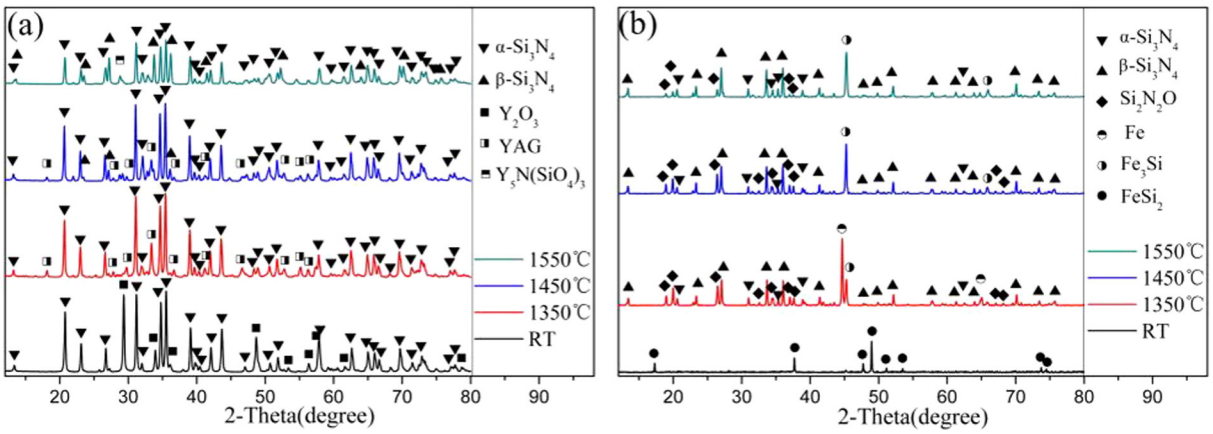

Fig. 1. The XRD patterns of SN and $FeSi_2$ powder before and after being heated in different temperatures for 2 h: (a) SN, (b) $FeSi_2$.

6.3 MPa·$m^{1/2}$. Meanwhile, they in situ formed smaller size of Fe_5Si_3 particles in Si_3N_4 ceramics by infiltrating the Si_3N_4 calcined body with iron-alcoxide solution [26], and found that the linear crack vanished and the flexural strength of Si_3N_4 ceramics reached 1187 MPa. However, the addition of Fe_3Al, Fe_3O_4 or iron-alcoxide also introduces aluminum or oxygen element, which changes the content of grain boundary phase and influences the mechanical properties.

In our research, $FeSi_2$ powder was synthesized and firstly used as an additive in preparing Si_3N_4 ceramics. β-Si_3N_4 seeds and Fe_5Si_3 reinforcing particles were formed by in situ reaction during the sintering process. Furthermore, the reaction process of $FeSi_2$ and its effects on the fracture toughness and flexural strength of Si_3N_4 ceramics were investigated.

Starting α-Si_3N_4 powder (99 wt%, E-10 grade, Ube Industries, Japan) had an average particle size of 0.33 μm, and the α-Si_3N_4 phase content was above 95 wt%. Si powder (99.9 wt%, Haotian Nano Co., Ltd., China) with an average particle size of 1.0 μm and Fe powder (99.9 wt%, Haotian Nano Co., Ltd., China) with an average particle size of 1.0 μm were used to synthesis $FeSi_2$. Al_2O_3 powder (99.9 wt%, Fenghe Ceramic Co., Ltd., China) and Y_2O_3 powder (99.99 wt%, Yuelong Materials Co., Ltd., China) were used as sintering aids.

To synthesis $FeSi_2$ powder, Fe and Si powder were mixed according to Fe:Si = 1:2 (molar ratio) and heated at 1200 °C for 1 h in argon. Si_3N_4 powder with 0.2 wt% $FeSi_2$, 9.0 wt% Y_2O_3 and 3.0 wt% Al_2O_3 were mixed and milled in ethanol with Si_3N_4 and then dried in draught drying cabinet. The composite powders were sieved through a 100-screen sieve and uniaxially dry pressed at 60 MPa, following by cold isostatic pressing at 200 MPa (named SN-F). As a comparison, Si_3N_4 powder with 3.0 wt% Al_2O_3 and 9.0 wt% Y_2O_3 were also prepared (named SN). The green compacts were sintered at 1780 °C for 2 h in nitrogen in furnace (SIP300/500-2000-10, Cisri, China). To study the phase transformation and reactions during sintering process, the green compacts and $FeSi_2$ powder were also heated at 1350 °C, 1450 °C, 1550 °C in nitrogen for 2 h, respectively.

Phase analysis of the composites was determined by X-ray diffraction (XRD) using a Guinier-Hagg camera (Expectron XDC-1000, Jungner Instrument, Solna, Sweden) with Cu K_α radiation. The microstructure of powder was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The phase identification of microscopic particles [27,28], grain size distribution and cracks introduced by indentation in hardness test on polished surface were analyzed by scanning electron microscopy (Magellan 400, FEI, Hillsboro, American) equipped with EBSD and EDS (INCA SERIES, Oxford Instrument, UK) attachments. The EBSP (Electron backscatter diffraction pattern) was acquired at an angle of 60° and an acceleration voltage of 15 kV, and Aztec software was used to clarify the phase. The cross section area and the aspect ratio distribution of Si_3N_4 grains were counted by Image-Pro Plus 6.0 software after grain boundary were retouched by Paint.NET v3.5.10 software. A minimum of 1000 grains were counted in each sample.

Bulk density was measured by Archimedes method with distilled water as the immersion medium. The theoretical density of the specimen was calculated according to the rule of mixtures. Flexural strength was measured by three point bending method, and a minimum of 6 rectangular bars with dimensions 3 mm × 4 mm × 36 mm were tested to take average value as the flexural strength. Fracture toughness was measured by single-edge notched beam method, and a minimum of 6 rectangular bars with dimensions 3 mm × 6 mm × 36 mm were tested after a V-shaped notch with a crack depth of 2 mm was introduced into 3 mm × 36 mm surface. Vickers' hardness was measured by Vickers indentation (Model 2100B, Tukon, Canton, MA) on a polished surface of the sample using a load of 10 Kg. A minimum of 5 indentations were tested.

The XRD results for SN samples and $FeSi_2$ powder before and after being heated at different temperatures for 2 h are shown in Fig. 1. It

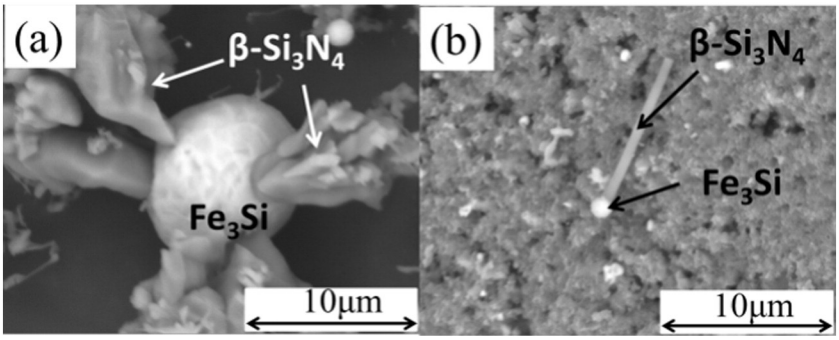

Fig. 2. The microstructure of $FeSi_2$ powder and SN-F after being heated in 1550 °C for 2 h: (a) $FeSi_2$, (b) Fracture of SN-F.