Fabrication of dense Si$_3$N$_4$ ceramics via coating amorphous Si$_3$N$_4$ nano-powders by sodium reduction in liquid ammonia

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Commercial Si$_3$N$_4$ powders coated with 0–30% amorphous Si$_3$N$_4$ nano-powders were fabricated successfully. Amorphous Si$_3$N$_4$ nano-powders coating were prepared through the reduction of silicon tetrachloride (SiCl$_4$) by sodium in liquid ammonia at $-45^\circ$C. Dense Si$_3$N$_4$ ceramics with 97.2% relative density of theoretic value were obtained from Si$_3$N$_4$ micro-powders coated with 30% nano-powders sintered by spark plasma sintering at 1500$^\circ$C without sintering additives.

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1. Introduction

Silicon nitride (Si$_3$N$_4$) ceramics have attracted much attention because of its several obvious advantages, such as low density, low thermal conductivity, high-temperature stability, low dielectric constant and high resistance to chemical attack. However, preparing fully dense Si$_3$N$_4$ ceramics is still a challenge. These fully dense ceramics composites are made conventionally from powder mixtures with required amounts of metal oxides like Al$_2$O$_3$ or Y$_2$O$_3$ as sintering additives and a high sintering temperature, such a procedure gives rise to relatively large agglomerates and inclusions of one phase resulting in an inhomogeneous microstructure. Moreover, the grain boundary and triple point phases that formed from the remains of the sintering additives after densification play a critical role in many high temperature properties including oxidation and corrosion. Considering this, the sintering of silicon nitride ceramics without additives is an important approach to reducing impurity phases in the densified bodies achieving Si$_3$N$_4$ ceramics with the intrinsic properties. Ceramics sintered without additives exhibited improved mechanical properties at high temperature compared to those sintered with additives.

Nano-powders is an effective ingredient to improve the sintering ability of Si$_3$N$_4$ ceramics due to its high surface energy. Here, we provide a new method to prepare dense Si$_3$N$_4$ ceramics by coating amorphous Si$_3$N$_4$ nano-powders on micro-powders. Liquid ammonia is a good reaction medium to prepare nitrides. Here, we provide a new method to prepare dense Si$_3$N$_4$ ceramics by coating amorphous Si$_3$N$_4$ nano-powders on micro-powders. Liquid ammonia is a good reaction medium to prepare nitrides. Liquid ammonia was used as the reaction medium to prepare Si$_3$N$_4$ from SiCl$_4$ was nearly 100% effective. In the present work, commercial Si$_3$N$_4$ micro-powders coated with amorphous Si$_3$N$_4$ nano-powders were in-situ fabricated via the reduction reaction between the solution of SiCl$_4$ and sodium in liquid ammonia. The coated powders were sintered by spark plasma sintering (SPS) without sintering additives.

2. Experimental procedure

Commercial Si$_3$N$_4$ powders with a broad range of particle size from several hundred nanometers to several microns were used as sintering material. SiCl$_4$ (Beijing Shuanghuan Chemical Factory, ≥99.0%), Na (Beijing Shuanglong Chemical Factory, ≥99.5%) and NH$_3$ (Beijing Haipu Gas Company, China, 99.9%) were used as raw materials to prepare Si$_3$N$_4$ nano-powders. All manipulations to synthesize Si$_3$N$_4$ nano-powders was carried out under high purity argon atmosphere in order to avoid the oxidation of the samples. Firstly, commercial Si$_3$N$_4$ powders were weighed with predetermined quantity. Then SiCl$_4$ was dripped into the commercial Si$_3$N$_4$ powders with continuous stirring to make sure the surface of Si$_3$N$_4$ particles coated with a uniform SiCl$_4$ layer, stirring was confined to the container to prevent SiCl$_4$ from evaporation. Subsequently, metal Na was weighed with reaction ratio and put into a reactor. The reactor was immersed in a cryostat (model FP50-MV, Julabo, Germany) maintained at around $-45^\circ$C. Argon gas in the reactor was taken out by a vacuum pump and ammonia gas was guided into the reactor condensed to form a blue solution of sodium in liquid ammonia. Then, Si$_3$N$_4$ particles coated with the solution of SiCl$_4$ were put into the solution of sodium in liquid ammonia. The route was similar to the previous works of our research group. The reduction reaction took place immediately and the product powders were extracted by Soxhlet extraction method with liquid ammonia as the extraction solvent to eliminate the by-products. The Si$_3$N$_4$ micro-powders coated with Si$_3$N$_4$ nano-powders were finally obtained. Based on our previous research, the yield of Si$_3$N$_4$ from SiCl$_4$ was nearly 100%. In the present work, the content of Si$_3$N$_4$ nano-powders range from 0 percent to 30 percent. Figure 1 shows a conceptual schematic of Si$_3$N$_4$ nano-powders coated Si$_3$N$_4$ micro-powders.
The synthesized coated Si$_3$N$_4$ powders were put in a graphite die sintered by SPS at 1500°C under pressure of 50 MPa for 5 min.

The phase composition of the samples was characterized by X-ray diffraction (XRD, Dmax-RB, Rigaku, Japan). Density of the sintered ceramics we measured by the Archimedes method. Microstructure of fracture surface was observed by scanning electron microscopy (SEM: JSM-6480LV, JEOL, Japan). Vickers hardness of the samples was detected by a microhardness tester (Wilson-Wolpert Vickers 430SVD, China) under a load of 5 kg for a dwelling time of 10 s. The three-point bending strength was tested by a servo-hydraulic testing machine (MTS810, USA) and Si$_3$N$_4$ samples were cut into a dimensions of $15 \times 2 \times 1$ mm$^3$ employed an upper loading span length of 12 mm.

3. Results and discussion

Figure 2 is SEM images of Si$_3$N$_4$ micro-powders coated with various contents of nano-powders. It shows that the commercial Si$_3$N$_4$ powders are coarse particles with size from several hundred nanometers to several microns. It is clearly seen that Si$_3$N$_4$ micro-particles were not covered completely when the nano-powders amount was less than 10%. When the nano-powders amount reached to 30%, Si$_3$N$_4$ particles were well coated with Si$_3$N$_4$ nanoparticles.

Figure 3 shows XRD patterns of the commercial Si$_3$N$_4$ micro-powders coated with various contents of amorphous nano-powders. The phase composition of the commercial Si$_3$N$_4$ micro-powders consisted of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$. Amorphous Si$_3$N$_4$ nano-powders were prepared via reaction in liquid ammonia and covered the surface of Si$_3$N$_4$ micro-powders. Therefore, it can be seen that there is a very broad diffraction peak at 10–50° observed in the XRD pattern of Si$_3$N$_4$ micro-powders coated with 30% nano-powders, which indicates that amorphous phase existed in the coated powders. It is not obvious of the broad diffraction peak because the strength of the peak for amorphous phase is very weak relative to that of Si$_3$N$_4$ crystals.

The commercial Si$_3$N$_4$ micro-powders coated with various contents of nano-powders were sintered by SPS at 1500°C without sintering additives. Figure 4 shows the variation of temperature and shrinkage along with time during SPS process. It can be seen that there was a slight decrease of shrinkage for the commercial
Si₃N₄ micro-powders in the sintering process which was caused by expansion of the sample with the increase of temperature until 1500°C, which indicated that the densification of Si₃N₄ micro-powders had not taken place yet. Different from that, there was an obvious increasing of shrinkage for coated-powders which indicated that sintering ability of the commercial Si₃N₄ micro-powders was greatly improved by coating Si₃N₄ nano-powders. The reason for this is that amorphous nano-powders have high surface energy and high formation enthalpy, and this energy can be transformed into driving force for the sintering.

The amorphous structure was stable up to 1200°C and turned to the crystal structure of α-Si₃N₄ at 1300°C, and then to β-Si₃N₄ structure when heated at temperatures higher than 1450°C. It can be seen that the sample coated with 30% nano-powders transforms into β-crystal phase after SPS sintering (Fig. 5) (card number 82-702). Figure 6 shows the relative density of the samples by SPS at 1500°C. The commercial Si₃N₄ micro-powders showed poor sintering ability and the relative density of the sintered ceramic was only 75.3% of theoretical density of β-Si₃N₄ (3.188 g·cm⁻³). The sintering ability was significantly improved when the coated-powders were used as raw materials. The relative density of the sample increased with the rise of nano-powders. The relative density reached to 97.2% when Si₃N₄ micro-powders was coated with 30% nano-powders, it is quite near to the density of sample sintered by 100% nano-powders (97.9%). These results clearly demonstrated that the densification behavior of coarse Si₃N₄ micro-powders could be significantly enhanced via coating with amorphous Si₃N₄ nano-powders.

Figure 7 shows SEM images of profile of the samples sintered by SPS at 1500°C from Si₃N₄ micro-powders coated with nano-powders range from 0 percent to 30 percent, respectively. It can be seen that the sample sintered by the commercial Si₃N₄ micro-powders contained numerous large pores, which explained its low density and indicated that it had not been sintered completely. However, there were nearly no visible pores observed in the structure of the samples sintered by the micro-powders coated 30% nano-powders which confirmed that it had a compact structure and is dense.

Figure 8 shows the mechanical properties of the samples sintered with various nano-powders content. The three-point bending strength and Vickers hardness (Hv) of specimens were tested respectively. The Vickers hardness (Hv) increase from 8.3 to 16.7 GPa and the bending strength increase from 216 to 1103 MPa, respectively as nano-powders content increase from 0 to 30%. The strength is higher than Si₃N₄ ceramic prepared with the sintered catalyst of rare earth oxides. Compared to our previous work, the mechanical properties of the sample is closed to the Si₃N₄ ceramics obtained by sintering of 100% amorphous Si₃N₄ nano-particles. The result indicate that the oxide-free high dense Si₃N₄ ceramics bulks were successfully obtained and have better performance.

4. Conclusions

Commercial Si₃N₄ micro-powders coated with Si₃N₄ amorphous nano-powders were in-situ prepared via the reduction reaction of the solution of SiCl₄ by sodium in liquid ammonia. The sintering ability of Si₃N₄ micro-powders was significantly improved by coating Si₃N₄ nano-powders and dense Si₃N₄.
ceramic was obtained from powders with 30% nano-powders sintered by SPS at 1500°C without any sintering additives. Compared with Si$_3$N$_4$ ceramic sintered by commercial Si$_3$N$_4$ micro-powders, Si$_3$N$_4$ ceramic sintered by coated powders exhibit outstanding mechanical property.

References