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New synthesis route for Si_2N_2O ceramics based on desert sand

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Abstract

A new approach for synthesis and sintering of silicon oxynitride starting from a unique natural raw material, desert sand is described. The sand in a mixture with silicon metal is combusted under pressurized nitrogen gas into pure silicon oxynitride powder. Then, this powder is densified in the presence of 5 wt.% calcia-alumina mixture to a compact with about 99% of theoretical density within 6 min heating up and holding by using the spark plasma sintering technique. The dense silicon oxynitride has 18.7 GPa Vickers hardness, 3.3 MPa $m^{1/2}$ fracture toughness, and 363 MPa strength. Morphology of a fractured surface shows that the grains are equiaxed and the fracture occurs in transgranular mode. The material exhibited excellent oxidation resistance at high temperatures up to 1500 °C as well as outstanding chemical resistance in acidic, alkaline and salt mediums at room temperature.

Keywords: Nitrides; SHS; Sialons; Sintering; SiO_2; Spark plasma sintering

1. Introduction

Silicon oxynitride, Si_2N_2O, is a non-toxic material consisting of three elements which are the most abundant elements in the earth's crust. It is truly a unique technical ceramic with superior chemical and oxidation resistance in many environments at high temperatures.[1] Reported applications include cutting tools, wear parts and heat engine components.[2] But, in practice, this ceramic is limited in use and this is because of difficulties encountered in its conventional synthesis and densification methods.[3,4] These difficulties can be summarized as: (1) high temperature heating processes are used with long periods of time, and (2) secondary phases mainly α- and β-silicon nitride as well as unreacted materials like silicon and silica are frequently present. These reasons also greatly hindered the accurate investigation of the physical properties of phase pure Si_2N_2O until now.[5–7] To avoid these problems, new potential processes are therefore necessary.

Here we describe a new route for the synthesis of silicon oxynitride powder and its subsequent sintering. We selected desert sand as a starting material. It is abundant in the earth's crust in pure forms and is very cheap. Two advanced rapid processes are used. The self-propagating high-temperature synthesis or SHS method is used for the conversion of the desert sand into silicon oxynitride powder. SHS method which was discovered in late 1967 by professor Merzhanov[8] and his colleagues was applied successfully for the synthesis of many advanced ceramic materials.[9,10] It is characterized by high exothermicity (self-propagation) and extremely rapid propagation. SHS processed silicon oxynitride powder is densified in presence of 5 wt.% $CaO–Al_2O_3$ additives by using the advanced spark plasma sintering, SPS, technique. The amount of the alumina additive is less than its solubility limit in the silicon oxynitride.[11] SPS is a new powerful pressure sintering method which applies high electrical energy in a short time directly to voids between powder particles and utilizes the high energy of spark plasma (generated momentarily by spark discharges between the particles) to achieve high thermal diffusion.[12] It is therefore capable of producing highly dense compacts at temperatures lower than those of conventional sintering methods in a short period of time which ranges between 5 and 20 min including heating up and holding time.[12]

2. Experimental procedure

Fig. 1 describes a general flowchart of the new approach. Natural desert sand obtained from Egypt and

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reclaimed silicon (8 μm in size) from Toho Zinc Co. Ltd., Japan, were used as raw materials. The purity of each was 99.7 and 94%, respectively. Sand was pulverized at first to −40 μm size by using a vibration mill. The starting composition can be described by the following equation (in molar ratio):

$$3(1-X)/2\ \mathrm{Si} + (1-X)/2\mathrm{SiO_2} + X\mathrm{Si_2N_2O} + (1-X)\mathrm{N_2} \rightarrow \mathrm{Si_2N_2O} \tag{1}$$

The mixing ratio X was determined as 0.075. Presynthesized Si_2N_2O was added as a diluent. The reaction components were mixed using a ball mill for 2 h. The SHS experiment was performed in a combustion furnace under 3 MPa nitrogen gas. Fifty grams of the reaction mixture was placed in a porous carbon crucible. The reaction was initiated at the bottom from burning 5 g thermite mixture placed beneath the reaction burden by passing 50–60 A current through a carbon ribbon (heater) as schematically illustrated in Fig. 2. The temperature profile and the average combustion temperature, $T_{\max}$, of the reaction were recorded by using W-5%Re/W-26%Re thermocouple placed in the middle of the reaction burden. Phase identification for the synthesized powder was carried out by X-ray powder diffraction analysis with Cu-K_α radiation.

The resultant silicon oxynitride powder was mixed thoroughly with 5 wt.% calcia-alumina additive by the planetary mill for 1 h in ethanol using agate milling balls. Ethanol was evaporated and the powder mixture was dried by heating under vacuum at 110 °C. Ten grams of the dried powder mixture was pressed into 30 mm diameter compacts by cold isostatic pressing at 200 MPa. The sintering experiments were carried out using Dr. Sinter® Model 1050 SPS apparatus (Sumitomo Coal Mining Company, Ltd., Japan). Fig. 3 shows the schematic diagram of the SPS apparatus. The green compact was placed inside 30 mm diameter graphite die and BN powder was used to surround this compact. The temperature was increased up to 1600 °C (the optimum sintering temperature from preliminary experiments) with a heating rate of 400 °C/min. The sintering is kept for 2 min under a pressure of 30 MPa which was applied from the beginning of the heating. The cooling rate was the same as the heating rate. The temperature was measured by means of an optical pyrometer focused on a hole on the die surface centered on the sintering sample. The sintered samples were approximately 28 mm in diameter and 5 mm thick.

The density of the sintered compacts was measured in distilled water by the Archimedes' method. The sintered compacts were cut into rectangular bars and ground by using rotating diamond wheel in two steps as mentioned in the ASTM method (C 1161- 94). Final hand polishing for the lateral sides and corners was performed using diamond slurries with subsequent appropriate sizes.

The hardness was measured at 1 kg test load and 15 s dwell time by Vickers indentation. The calculated hardness was the mean value of five accepted indentations. The fracture toughness was evaluated under the same load using the indentation fracture method.[13]

The flexural strength at room temperature was measured by three-point bending on bars with dimensions of 2×4×10 mm under loading speed of 0.5 mm/min.

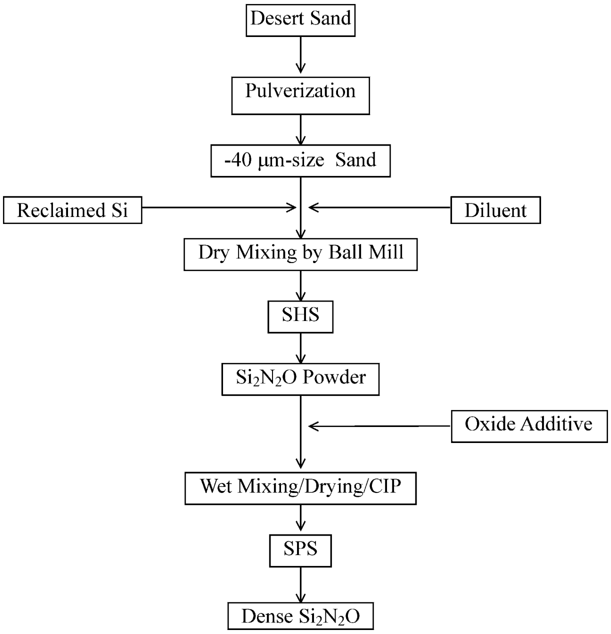

Fig. 1. A flowchart of the new approach for the preparation of dense Si_2N_2O ceramic from desert sand.

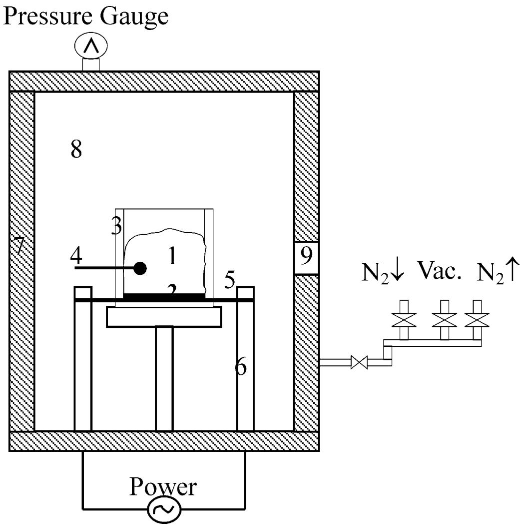

Fig. 2. Schematic diagram of SHS apparatus (combustion furnace): (1) burden, (2) ignition agent, (3) porous container, (4) thermocouple, (5) carbon ribbon, (6) electrodes, (7) high-pressure chamber, (8) nitrogen gas atmosphere, and (9) glass window for observation.

Oxidation resistance tests were performed in a muffle furnace at 1200, 1400 and 1500 °C in dry air for 10 h. The heating rate was 20 C/min. The weight and the volume of the specimens were measured after the test for each temperature and time. The resistance to chemical solutions at room temperature was measured by soaking the specimens in 1 M sulfuric acid, 2 M sodium hydroxide and 2 M sodium chloride solutions. The specimens were weighed thoroughly, after washing and drying, after 24, 48, 100 and 200 h soaking times.

3. Results and discussion

The synthesis of the silicon oxynitride from a mixture of sand and silicon under pressurized nitrogen can be considered to proceed through two sub-reactions:

$$\text{first: } 3/2\mathrm{Si}_{(s)} + \mathrm{N}_{2(g)} \rightarrow 1/2\beta\text{-}\mathrm{Si}_3\mathrm{N}_{4(s)}$$

$$\Delta H_r^\circ = -393.90 \ \mathrm{kJ}/0.5 \ \mathrm{mol} \tag{2}$$

$$\text{second: } 1/2\beta\text{-}\mathrm{Si}_3\mathrm{N}_{4(s)} + 1/2\mathrm{SiO}_{2(s)} \rightarrow \mathrm{Si}_2\mathrm{N}_2\mathrm{O}$$

$$\Delta H_r^\circ = -98.33 \ \mathrm{kJ}/0.5 \ \mathrm{mol} \tag{3}$$

On initiating the reaction, silicon is quickly combusted to silicon nitride phase which is thermodynamically favorable and highly exothermic. The resultant heat is enough to activate a further reaction between the formed silicon nitride (β-phase) and the silica sand to synthesize a stable silicon oxynitride structure.

Fig. 4 shows a typical temperature profile of the combustion synthesis reaction measured by a thermocouple in the middle of the burden. The reaction is complete in about 2 min. It can be observed that the combustion temperature of this reaction, $T_{\max}$, is approximately 1500 °C. The diffraction pattern is shown in Fig. 5 and reveals the existence of the silicon oxynitride structure as the main phase. Meanwhile, a minor amount of β-Si_3N_4 is observed. Although the nitride phase could not be avoided, the pattern reflects high phase purity of silicon oxynitride. This pattern is close to the JCPDS-file 47-1627 of Larker.[14]

The results of the spark plasma sintering and the properties of the dense Si_2N_2O are summarized in Table 1. The density of the sintered sample was 99% of theoretical density (calculated based on the silicon oxynitride crystal

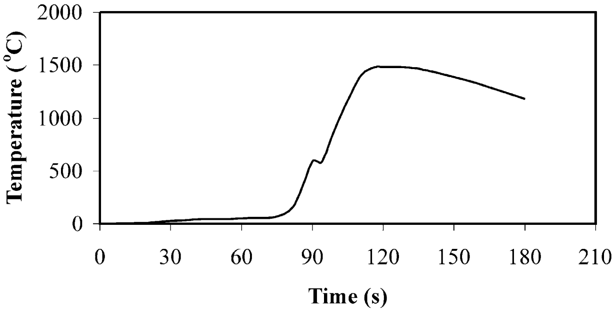

Fig. 4. Typical temperature profile of the SHS of Si_2N_2O.

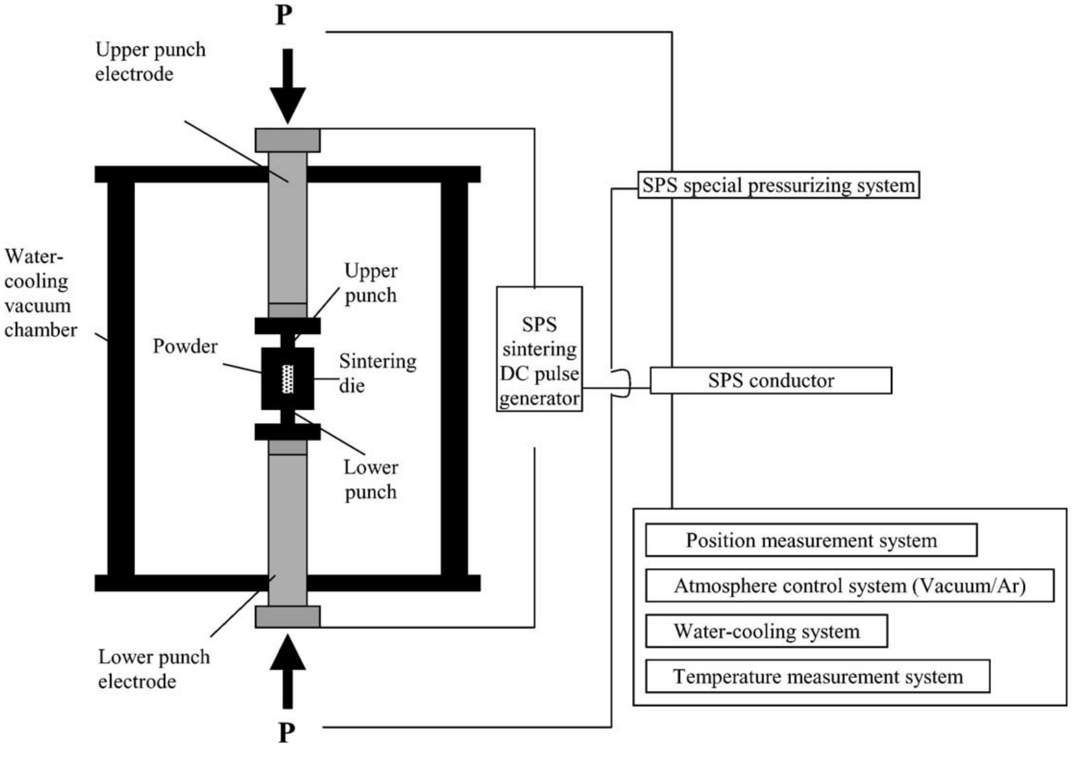

Fig. 3. Schematic diagram of SPS apparatus.

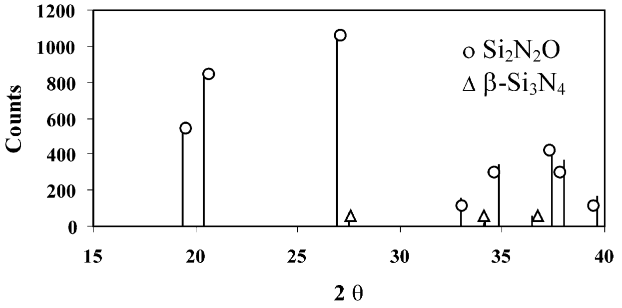

Fig. 5. X-ray diffraction pattern of synthesized Si_2N_2O powder.

Table 1
Properties of the sintered Si_2N_2O

Density (%)	99.0
Vickers hardness (GPa)	18.7
Fracture toughness (MPa $m^{1/2}$)	3.3
Flexural strength (MPa)	363

Table 2
Weight gain due to oxidation resistance of dense Si_2N_2O

Test condition	Weight gain (mg/cm^2)
1200 °C, 10 h	0.387
1400 °C, 10 h	0.641
1500 °C, 10 h	1.0

density, 2.82 g/cm^3, with the volume fraction of the calcia-alumina added). The SPS heating up and holding time are 6 min. This density is only achieved by the conventional sintering methods at higher temperatures and much longer times, for example at 1900 °C for about 4 h holding only by HIP,[14] 1750 °C for 4–5 h heating up and holding by HP,[15] and 1650–1670 °C for 3 h holding only by PLS but in presence of large sintering additives (about 16 wt.%).[16] The sintered compact (at this stage of experiments) has comparable mechanical properties to the conventional materials. The Vickers hardness and fracture toughness of the sintered sample are 18.7 GPa and 3.3 MPa $m^{1/2}$, respectively. In the literature, hardness values for conventionally sintered silicon oxynitride are 15–22 GPa[14–16] and fracture toughness values are 2.5–6 MPa $m^{1/2}$.[14–16] The three-point flexure strength measured at room temperature is 363 MPa. Reported values in the literature are 300–750 MPa.[14–17]

Fig. 6 shows a micrograph for the fractured surface. The structure has equiaxed grains and the fracture occurred in transgranular mode. The oxidation resistance results of the sintered samples heated in dry air at 1200, 1400 and 1500 °C for 10 h are shown in Table 2. The sintered material showed excellent resistance at the temperatures up to 1500 °C. Room temperature, chemical resistance to the solutions 1 M sulfuric acid, 2 M sodium hydroxide and 2 M sodium chloride are almost infinite for soaking periods up to 200 h.

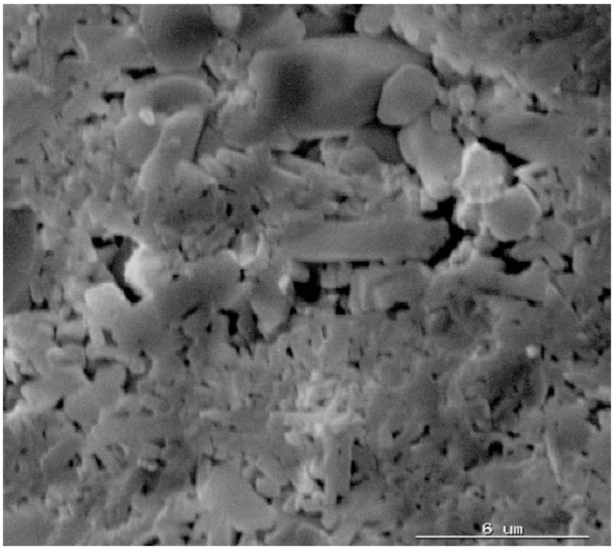

Fig. 6. SEM micrograph of fractured surface of dense Si_2N_2O.

4. Summary

Pure silicon oxynitride powder was prepared from desert sand by using the self-propagating high-temperature synthesis, SHS, method under pressurized nitrogen gas. Near full dense silicon oxynitride was obtained from this powder by using the spark plasma sintering, SPS, method. Both methods can represent a new approach for the synthesis of silicon oxynitride ceramic.

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