

β -SiAlON-Based Ceramic Composites from Combustion-Synthesized Raw Materials by Spark Plasma Sintering

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Abstract

Spark plasma sintering of β -SiAlON-based ceramic composites from powders – β -Si₅AlON₇, h-BN, β -SiC, and TiN – prepared by combustion synthesis (CS) method was investigated. The process parameters for the CS of ceramic composites containing 0–30 wt. % h-BN, 0–40 wt. % β -SiC, and 0–40 wt. % TiN and exhibiting high relative density (> 95 %) and flexural strength (up to 400 MPa) were optimized.

Keywords

Combustion synthesis; spark plasma sintering; ceramic composites; sialon; boron nitride; titanium nitride; silicon carbide.

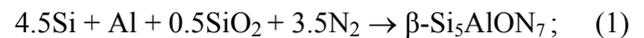
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Introduction

Solid solutions of general formula Si_{6-z}Al_zO_zN_{8-z} (z = 0.0–4.2) are known for their excellent hardness, strength, and wear/corrosion resistance, which explains their wide use in various engineering applications [1]. The addition of hexagonal boron nitride (**h-BN**), TiN, and SiC to ceramic composites is known to improve their fracture toughness, thermal shock resistance, tribological properties, thermal/electrical conductivity, and machinability. Combustion synthesis (CS) is a rapidly developing research area oriented on fast and energy efficient production of high-melting compounds and materials. For example, infiltration-mediated CS in nitrogen is a convenient technique for production of α - and β -SiAlON powders with different phase and elemental composition, particle size, and morphology [2]. Spark plasma sintering (SPS) is a newly developed process that uses dc pulses for sample heating. As compared to conventional hot pressing, SPS ensures higher heating rates and very short holding times and has been widely recognized as an effective method for densification of various materials [3]. Therefore, the combination of CS and SPS techniques seems rather promising for R & D of β -SiAlON-based ceramics with widened functionality.

Experimental

Infiltration-mediated CS of β -Si₅AlON₇ and h-BN powders in nitrogen gas was carried out by the following schemes:



Green mixtures also contained some amount of homemade diluents, β -Si₅AlON₇ and h-BN respectively, in order to improve extent of conversion. Combustion was performed in a 2-L reactor at $P(\text{N}_2) = 8\text{--}10$ MPa. The CS of β -SiC was carried out by using multistep chemical reactions in the Si–C–N system [4] and TiN fine powders with added NH₄Cl as a gasifying agent [5].

Aliquot amounts of combustion-synthesized raw powders were intermixed in a high-energy planetary steel-ball mill. Ball milling time (800 rpm, ball/mill ratio 10 : 1) was 5 min. Then milled powders were placed into a graphite die and sintered in a Labox 625 SPS facility under vacuum (below 10 Pa). The heating rate was 50 deg/min. The sintered compacts were heated from room temperature to 600 °C without

applied load and then to 1550–1800 °C at a compressive stress of 50 MPa. The compacts were held at a desired temperature for 5 min.

The BET analysis (N₂ sorption) and particle size distribution of used powders was determined with Sorbi-M surface area analyzer and Fritsch Analysette 22 device. The raw powders and sintered compacts were characterized by XRD (DRON-3.0) and SEM (JEOL 6610L). Sample densities were determined by hydrostatic weighing. Flexural strength σ_f was measured for bending a thin disk on a ring base in a testing machine Instron-5966.

Results and discussion

According to XRD results, the raw powders of β -Si₅AlON₇, h-BN, and TiN did not contain impurity phases while β -SiC had trace amounts of Si₃N₄. According to SEM results, all as-synthesized powders appeared largely as agglomerates. Their specific surface was about 1.3 m²/g for β -Si₅AlON₇ powders, and from 9.8 to 22.8 m²/g for h-BN, β -SiC, and TiN fine powders. After ball milling, the specific surface increased by a factor of 4–6.

Figures 1 and 2 show relative density ρ_{rel} of sintered samples as a function of temperature T . The sintering of pure β -Si₅AlON₇ was accompanied by marked intensification of the consolidation process at temperatures above 1400 °C (curve 1 in Fig. 1) probably due to formation of SiO₂ and Al₂O₃ eutectics. Upon further increase in T , relative density of sintered β -Si₅AlON₇ gradually grows up to 87 % (curve 1 in Fig. 2). According to XRD data, pure β -Si₅AlON₇

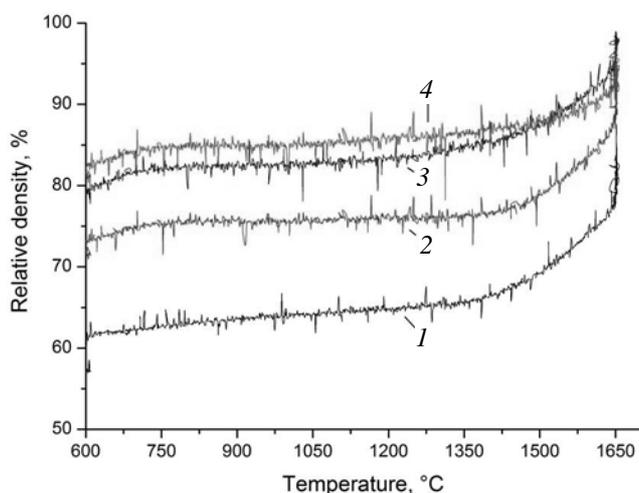


Fig. 1. Relative density ρ_{rel} as a function of temperature T :
 1 – β -Si₅AlON₇; 2 – β -Si₅AlON₇-BN (10 wt. %);
 3 – β -Si₅AlON₇-BN (20 wt. %); 4 – β -Si₅AlON₇-BN (30 wt. %);
 $T_{max} = 1650$ °C

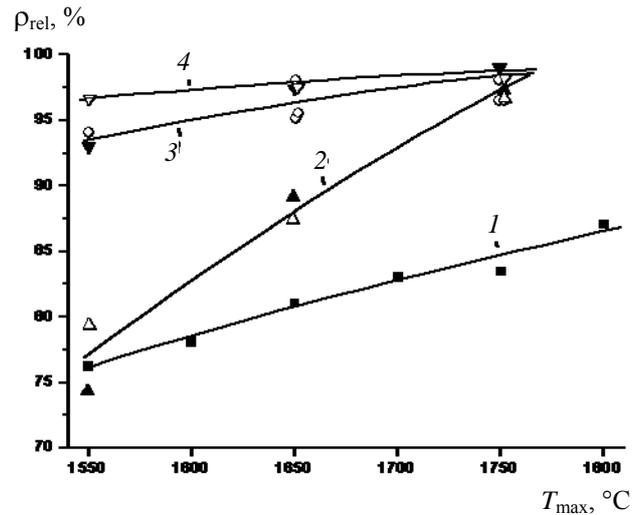


Fig. 2. Relative density ρ_{rel} as a function of T_{max} :
 ■ – β -Si₅AlON₇ – curve 1; ○ – β -Si₅AlON₇-BN (10–30 wt. %) – curve 2;
 ▼ – β -Si₅AlON₇-TiN (20 wt. %)-BN (10 wt. %) – curve 3;
 ▽ – β -Si₅AlON₇-TiN (40 wt. %)-BN (10 wt. %) – curve 4;
 ▲ – β -Si₅AlON₇-SiC (20 wt. %)-BN (10 wt. %) – curve 2;
 △ – β -Si₅AlON₇-SiC (40 wt. %)-BN (10 wt. %) – curve 2

sintered above 1750 °C exhibits the traces of AlN formed upon thermal decomposition of β -Si₅AlON₇. The addition of h-BN improves the compactibility of sintered powder mixtures. Under compressive stress of 50 MPa at 600 °C, the initial value of ρ_{rel} exceeds 80 % for the compact containing 30 wt. % BN and 60 % for that of pure β -Si₅AlON₇ (Fig. 1). In parallel, an increase in h-BN content suppresses the consolidation processes due to formation of liquid eutectics. At 30 wt. % BN (curve 4 in Fig. 1), the temperature dependence of ρ_{rel} becomes much more aligned. The small flaky h-BN particles are uniformly distributed over the surface of larger β -Si₅AlON₇ particulates. At 30 wt. % BN, the h-BN particles (unwettable with oxide melt) fully separate the β -Si₅AlON₇ particles apart. It is clear that in such systems a contribution from liquid-phase processes to consolidation cannot be important. In case of 10 and 20 wt. % h-BN, the processes associated with formation of liquid eutectics are more or less pronounced, so that high relative density can be attained (curve 3 in Fig. 2). The addition of fine β -SiC and TiN powders worsens the compactibility of sintered powder mixtures under a compressive stress at the initial stage. As a result, the highest value of relative density for sintered ceramic composites containing β -SiC can only be achieved at 1750 °C (curve 2 in Fig. 2). Meanwhile, the addition of TiN powder facilitates the efficiency of sintering above 900 °C and the highest values of ρ_{rel} can be achieved already at 1550 °C (curve 4 in Fig. 2).

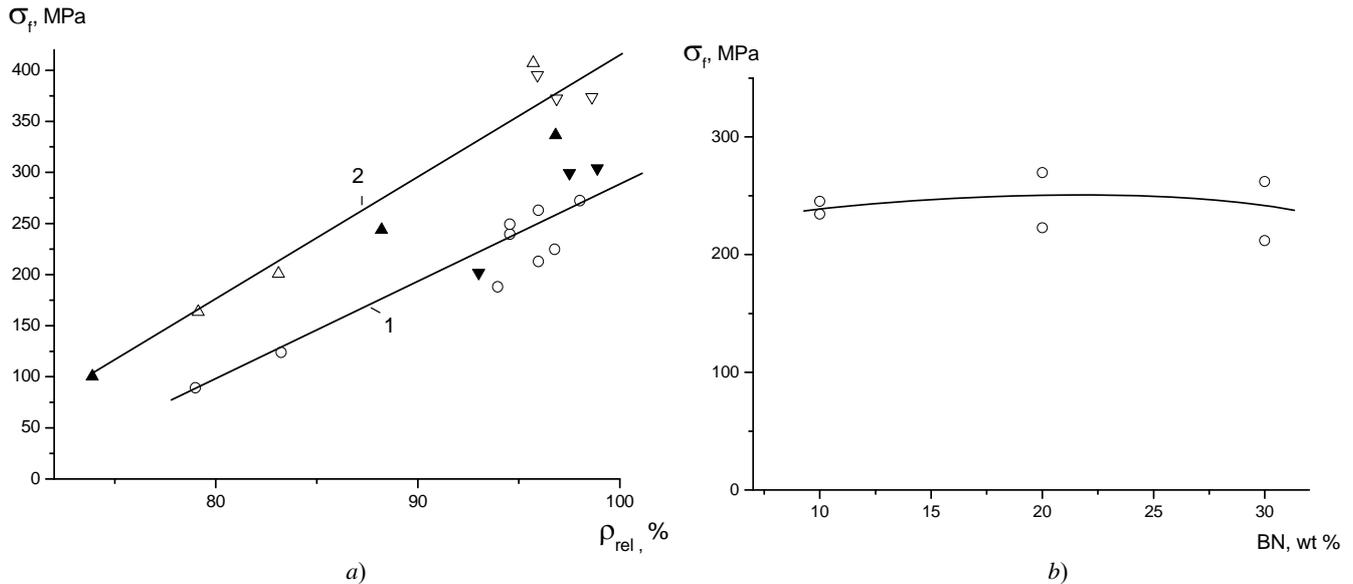


Fig. 3. Flexural strength σ_f as a function:

- a* – relative density ρ_{rel} for (○) β -Si₅AlON₇-BN (0–30 wt. %) – curve 1; ▼ – β -Si₅AlON₇-TiN (20 wt. %)-BN (10 wt. %);
 ▽ – β -Si₅AlON₇-TiN (40 wt. %)-BN (10 wt. %) – curve 2; ▲ – β -Si₅AlON₇-SiC (20 wt. %)-BN (10 wt. %);
 △ – β -Si₅AlON₇-SiC (40 wt. %)-BN (10 wt. %) – curve 2;
b – BN content in β -Si₅AlON₇-BN (10–30 wt. %); ρ_{rel} = 95–98 %

Fig. 3a illustrates flexural strength σ_f as a function of ρ_{rel} . Our results well agree with those reported for similar ceramic composites prepared by other techniques [6, 7]. SPS method affords to produce ceramic composites with higher relative density and flexural strength (up to 400 MPa). In our case, the flexural strength of sintered ceramic composites was found to depend on the BN content only slightly (Fig. 3b). A marked increase in σ_f (up to 40 %) can be achieved upon replacement of 40 wt. % of relatively coarse β -SiAlON particles in sintered ceramic composites by finer β -SiC and TiN particles (curve 2 in Fig. 3a).

Conclusions

High-density β -SiAlON-based ceramic composites can be prepared by fast and energy efficient techniques: CS of raw powder materials and subsequent SPS. Thus obtained ceramics seem promising for fabrication of items for operating in severe conditions of strong thermal shock and in highly corrosive media.

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