Application of spark plasma sintering for consolidation study of β-sialon ceramics

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Abstract. Investigated were the spark plasma sintering (SPS) of β-sialon ceramics according to two different schemes: the simple sintering of pure β-Si₅AlON₇ powder and the reactive sintering of mixture of α-Si₃N₄ and β-Si₂Al₂O₅N₄ powders. The high-density homogenous structure of simple sintered β-Si₅AlON₇ ceramics was achieved at maximum temperature of isothermal holding $T_{\text{max}} = 1550 \, ^\circ\text{C}$ by using submicron raw powder. While ceramics from coarse raw powder had porous structure and was subjected to thermal decomposition at $T_{\text{max}} \geq 1750 \, ^\circ\text{C}$.

Three specific temperature intervals were revealed for the reactive sintering. At $T_{\text{max}} \leq 1650 \, ^\circ\text{C}$, the shrinkage rate attained the values sufficient for densification near to a theoretical density, without any changes in the size/morphology of starting particles and without transformation of starting α-Si₃N₄ into β-sialon. At $T_{\text{max}} = 1700–1750 \, ^\circ\text{C}$, starting α-Si₃N₄ was found to undergo transformation into β-sialon but without marked changes in the size/morphology of starting particles. At $T_{\text{max}} \geq 1750 \, ^\circ\text{C}$, the sintered ceramics exhibited a marked growth in the size and change in the shape of sintered particles.

1. Introduction
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. Due to the above advantages, SPS has been widely recognized as an effective consolidation method for various materials, especially for materials with complex structure and composition: nanostructured, functionally graded and layered materials, reinforced, non-equilibrium composites containing chemically incompatible compounds, and items shaped in conditions of superplastic deformation and so on [1, 2]. Solid solutions of silicon nitride with general formula β-Si₆₋₂Al₂O₂N₈₋₂ (z = 0.0–4.2) are known for their excellent hardness, strength, and wear/corrosion/thermal shock/high-temperature creep resistance, which explains their successful use in various engineering applications such as refractory and structural materials, bearings, cutting instruments, electric welding fixture, etc. [3]. Meanwhile, processing sialon ceramics requires proper account of various factors that define the density, microstructure, and phase composition of sintered multicomponent systems [4]. Studies on the mechanism and temperature dependence of densification process, chemical reactions, and structural/phase transformations taking place during sintering are normally difficult to perform because of simultaneous occurrence of the above mutually interdependent processes. This work aimed at consolidation study of β-sialon ceramics by SPS. The use of this relatively rapid process could be expected to discern individual stages of sintering and simultaneously insure formation of fine structure without undesirable by-products.
2. Experimental

Investigated were two different schemes for sintering \( \beta \)-sialon ceramics: the simple sintering of pure \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) powder and the reactive sintering of appropriate mixture of \( \alpha \)-\( \text{Si}_{3}\text{N}_{4} \) and \( \beta \)-\( \text{Si}_{2}\text{AlO}_{4}\text{N}_{4} \) powders. All main raw powders were obtained by infiltration-mediated combustion synthesis in gaseous nitrogen according to own original methods. Combustion was performed in a 2-L reactor at \( P(\text{N}_2) = 2–4 \) MPa for synthesis \( \alpha \)-\( \text{Si}_{3}\text{N}_{4} \) and \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) fine powders with a mean particle size of 0.6–1.0 \( \mu \)m and at \( P(\text{N}_2) = 8–10 \) MPa for synthesis \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) and \( \beta \)-\( \text{Si}_{2}\text{AlO}_{4}\text{N}_{4} \) coarse powders with a mean particle size of 3.5–4.0 \( \mu \)m. In case of \( \text{Si}_{3}\text{N}_{4} \) the green mixture contained some amount of halogen-containing compounds in order to increase content of the low-temperature \( \alpha \)-phase above 95 wt. % [5]. Commercial \( \text{Y}_2\text{O}_3 \) powder was also used as a sintering aid.

Aliquot amounts of combustion synthesized raw powders were intermixed in a high-energy planetary steel-ball mill (800 rpm, ball/mill ratio 10:1, \( \tau = 5 \) 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\(^{-1} \). 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 under compressive stress at a desired temperature \( (T_{\text{max}}) \) for 5 min until the power was turned off.

The particle size distribution of used powders was determined with Fritsch Analysette 22 device. The BET analysis (\( \text{N}_2 \) sorption) was performed by surface area analyzer (Sorbi-M). 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 \( (\sigma_f) \) was measured for bending a thin disk on a ring base in a testing machine Instron-5966 [6].

3. Results and discussion

According to XRD results, the all starting powders of \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \), \( \beta \)-\( \text{Si}_{2}\text{AlO}_{4}\text{N}_{4} \) and \( \alpha \)-\( \text{Si}_{3}\text{N}_{4} \) did not contain any impurity phases. According to SEM results, the combustion synthesized powders appeared largely as agglomerates. The specific surface was about 1.1–1.3 \( \text{m}^2\text{-g}^{-1} \) for \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) and \( \beta \)-\( \text{Si}_{2}\text{AlO}_{4}\text{N}_{4} \) coarse powders, and from 4.2 to 10.8 \( \text{m}^2\text{-g}^{-1} \) for \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) and \( \alpha \)-\( \text{Si}_{3}\text{N}_{4} \) fine powders. After crushing agglomerates by ball milling, their specific surface increased by a factor of 2–3.

![Figure 1. Relative density \( \rho_{\text{rel}} \) as a function of temperature \( T \) for 1 – \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) \( (d_{\text{av}} = 0.6–1.0 \mu \text{m}) \), 2 – \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) \( (d_{\text{av}} = 3.5–4.0 \mu \text{m}) \) and 3 – \( \beta \)-\( \text{Si}_{5}\text{AlON}_{7} \) \( (d_{\text{av}} = 3.5–4.0 \mu \text{m}) \) – \( \text{Y}_2\text{O}_3 \) (5 wt. %) ceramics; \( T_{\text{max}} = 1650 \degree \text{C} \).](image-url)
most intensive densification was registered for systems using fine grained raw materials. For fine pure \( \beta\)-Si5AlON7 high-density homogenous structure of sintered ceramics was already achieved at \( T_{\text{max}} = 1550 \, ^\circ\text{C} \) (curve 4 in figure 2). While relative density of coarse \( \beta\)-Si5AlON7 sintered at same condition was about 0.75–0.77 and gradually grows up to 87 % upon further increase in \( T_{\text{max}} \) (curve 1 in figure 2). According to SEM data, the coarse particles remained practically unchanged (figure 3b) and only the formation of bottle necks in contact points was observed. According to XRD data, coarse \( \beta\)-Si5AlON7 sintered above 1750 °C exhibits the traces of AlN formed upon thermal decomposition of \( \beta\)-Si5AlON7. This is also evidenced by some increase in gas pressure in the SPS chamber observed above 1600 °C caused by the release of appropriate gaseous decomposition products, N$_2$ and SiO [7]. The addition of sintering additive improved the efficiency of sintering and the density close to theoretical for coarse \( \beta\)-Si5AlON7 ceramics was attained at \( T_{\text{max}} = 1750 \, ^\circ\text{C} \) upon addition of 5 wt. % Y$_2$O$_3$ (curve 3 in figure 2). Simultaneously the formation of a high-density structure completely suppressed thermal decomposition at \( T_{\text{max}} \geq 1750 \, ^\circ\text{C} \).

Three specific temperature intervals were revealed for the reactive sintering of \( \alpha\)-Si$_3$N$_4$ and \( \beta\)-Si$_2$Al$_4$O$_4$N$_4$ powders in presence of Y$_2$O$_3$. At \( T_{\text{max}} \leq 1650 \, ^\circ\text{C} \), the shrinkage rate attained the values sufficient for densification near to a theoretical density, without any changes in the size/morphology of

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**Figure 2.** Relative density \( \rho_{\text{rel}} \) as a function of \( T_{\text{max}} \) for \( \nabla - \beta\)-Si5AlON7 (\( d_{\text{av}} = 0.6–1.0 \, \mu\text{m} \)), \( \square - \alpha\)-Si$_3$N$_4$ (80 wt. %)-\( \beta\)-Si$_2$Al$_4$O$_4$N$_4$ (15 wt. %)-Y$_2$O$_3$ (5 wt. %), \( \blacksquare - \beta\)-Si5AlON7, (\( d_{\text{av}} = 3.5–4.0 \, \mu\text{m} \)) \( \blacktriangle - \beta\)-Si$_5$AlON$_7$ (\( d_{\text{av}} = 3.5–4.0 \, \mu\text{m} \))-Y$_2$O$_3$ (2.5 wt. %), \( \bullet - \beta\)-Si$_5$AlON$_7$ (\( d_{\text{av}} = 3.5–4.0 \, \mu\text{m} \))-Y$_2$O$_3$ (5 wt. %).

**Figure 3.** Fracture surface of SPSed ceramics: a – \( \beta\)-Si5AlON7 (\( d_{\text{av}} = 0.6–1.0 \, \mu\text{m} \), \( T_{\text{max}} = 1550 \, ^\circ\text{C} \)); b – \( \beta\)-Si5AlON$_7$ – (\( d_{\text{av}} = 3.5–4.0 \, \mu\text{m} \), \( T_{\text{max}} = 1550 \, ^\circ\text{C} \)); c – \( \beta\)-Si$_5$AlON$_7$ (\( d_{\text{av}} = 3.5–4.0 \, \mu\text{m} \), \( T_{\text{max}} = 1750 \, ^\circ\text{C} \))-Y$_2$O$_3$ (5 wt. %).

Three specific temperature intervals were revealed for the reactive sintering of \( \alpha\)-Si$_3$N$_4$ and \( \beta\)-Si$_2$Al$_4$O$_4$N$_4$ powders in presence of Y$_2$O$_3$. At \( T_{\text{max}} \leq 1650 \, ^\circ\text{C} \), the shrinkage rate attained the values sufficient for densification near to a theoretical density, without any changes in the size/morphology of
starting particles and without transformation of starting $\alpha$-Si$_3$N$_4$ into $\beta$-sialon. At $T_{\text{max}} = 1700–1750 \, ^{\circ}\text{C}$, starting $\alpha$-Si$_3$N$_4$ was found to undergo transformation into $\beta$-sialon but without marked changes in the size/morphology of starting particles. At $T_{\text{max}} \geq 1750 \, ^{\circ}\text{C}$, the sintered ceramics exhibited a marked growth in the size and change in the shape of sintered particles. The above features of SPS are illustrated in figure 4 and 5, respectively. The formation of the $\beta$-sialon is seen to be practically accomplished at $T_{\text{max}} = 1700 \, ^{\circ}\text{C}$. The grains of $\beta$-sialon ceramics sintered at $T_{\text{max}} = 750 \, ^{\circ}\text{C}$ were larger in their size and acquired a shape of elongated hexagonal prisms with a high aspect ratio (about 1:6).

![Figure 4. XRD patterns of $\alpha$-Si$_3$N$_4$ (80 wt. %) – $\beta$-Si$_2$Al$_4$O$_9$N$_4$ (15 wt. %)–Y$_2$O$_3$ (5 wt. %) sintered at $T_{\text{max}}$: a – 1650 °C; b – 1700 °C; c – 1750 °C.](image)

![Figure 5. Fracture surface of $\alpha$-Si$_3$N$_4$ (80 wt. %) – $\beta$-Si$_2$Al$_4$O$_9$N$_4$ (15 wt. %)–Y$_2$O$_3$ (5 wt. %) sintered at $T_{\text{max}}$: a – 1650 °C; b – 1700 °C; c – 1750 °C.](image)
caused by dissociation the flexural strength $\sigma_f$ clearly came down (120–150 MPa). Conversely, a marked increase in $\sigma_f$ (450–600 MPa) was registered for fine grained dense $\beta$-sialon ceramics obtained by two different schemes mentioned above.

4. Conclusions
SPS was successfully used to analysis of main consolidation features of $\beta$-sialon ceramics for two different sintering schemes. For simple and reactive sintering experimentally established were (a) the maximum temperatures of isothermal holding that ensure a required density, phase composition, and microstructure of sintered ceramics, (b) the specific stages of sintering process, (c) the effect of quality of raw powders on the phase composition, microstructure, and strength properties of sintered $\beta$-sialon ceramics.

Acknowledgments
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