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In situ synthesis of Al₂O₃-SiC powders via molten-salt method

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Abstract

Alumina-silicon carbide (Al₂O₃-SiC) composite powder (ASCP) was synthesized by molten salt method with silicon dioxide, carbon black, and Al powder as starting materials and NaCl and KCl together as molten salt medium. Effects of temperature and holding time on the phase composition and morphology were systematically investigated. Possible reactions involved in synthesis process of Al–Si–O–C system were analyzed by thermodynamic calculation, and synthesis mechanism was discussed. As-prepared ASCP was utilized to fabricate Al₂O₃-SiC composite bulk materials by pressureless route. Results show that molten salt is an essential factor to lower synthesis temperature. ASCP was synthesized at 1300 °C by heating for 4 h and template mechanism was found to play an important role. The bulk sample obtained by sintering at 1500 °C for 4 h attained apparent porosity of 42.3%, bulk density of 1.81 g cm⁻³, and higher compressive strength of 16.4 MPa.

Keywords Silicon dioxide · Al₂O₃-SiC · Molten salt · Mechanical properties

Introduction

Alumina-silicon carbide (Al₂O₃-SiC) composite material has been extensively studied owing to its superior properties including high hardness, high melting point, good chemical stability, and excellent wear resistance in contrast to monolithic Al₂O₃ [1–4]. These merits make it an essential starting material with broad range of applications in high-speed machining [5], wear-resistant coatings [6], refractories [7], and many other fields.

Several conventional ways are used to fabricate Al₂O₃-SiC composite powders (ASCPs). However, all these synthesis methods have some demerits. For example, pressureless sintering, hot-pressing sintering, and carbothermal reduction method require high synthesis temperature (> 1450 °C) [8–10]. Although the preparation process is simple, a large amount of energy is consumed in these processes. In contrast, although sol–gel method [11] can be used to synthesize powder at a lower temperature, its preparation process is complex and requires expensive precursor powders. Therefore, it is vital to explore a promising method with high efficiency, low cost, and simple process to prepare Al₂O₃-SiC composite powders.

Currently, the molten salt method is widely used to prepare high-melting inorganic powder. It can provide a liquid environment for the substance involved in the reaction, which in turn can significantly lower the synthesis temperature compared to the solid-phase reaction. For instance, Fazli et al. [12] used molten-salt method to fabricate nano-sized MgAl₂O₄ powder by heating at 850 °C for 4 h in LiCl. Liu et al. [13] utilized molten-salt and microwave co-assisted carbothermal reduction to prepare ZrB₂ powder using ZrO₂, BC, and amorphous carbon as starting materials. Their result manifested the synthesis of pure ZrB₂ powder by firing at 1200 °C for 20 min, and these processing conditions were remarkably milder than those required for traditional carbothermal reduction. Gu et al. [14] synthesized Si₃N₄ powder in NaCl-NaF molten salt at 1200 °C under N₂ atmosphere, which clearly indicates that the molten-salt method can obviously reduce the synthesis temperature and acquire high-purity products.

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In this study, pure ASCP was synthesized at 1300 °C for 4 h by the molten-salt method using silicon dioxide (SiO_2), carbon black, Al powder, NaCl, and KCl as raw materials. The effect of synthesis temperature and holding time on phase composition and microstructure was systematically investigated. The powder product was consolidated by pressureless sintering, so as to obtain Al_2O_3-SiC ceramic inherited from raw powders with the resulting mechanical properties.

Experimental procedure

Materials

SiO_2 (analytical grade purity; Sinopharm Chemical Reagent, Shanghai Co., Ltd., China) was used as Si source. Al powder (> 99% purity; particle size: ~ 2.6 μm; Gongyi Borun Refractory Materials Co., Ltd., China) was used as a reducing agent and source of Al. The carbon source used in the experiment was carbon black (> 99.9% purity; particle size ~ 15 μm; Zhengzhou Xinke Chemical Products Co., Ltd., China). NaCl and KCl (99.5% purity; Sinopharm Chemical Reagent, Shanghai Co., Ltd., China) were together employed as molten salt medium.

Sample preparation

Equation (1) expresses the total reaction equation for synthesizing ASCP through molten-salt method.

$$4Al + 3SiO_2 + 3C = 2Al_2O_3 + 3SiC \tag{1}$$
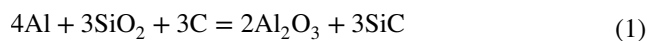
The theoretical molar ratio of the reactants (Al/SiO_2/C) was 4:3:3 if the reactants were completely converted to products. In order to ensure the completion of the reaction, excess carbon black and Al powder were added, and the ratio of starting materials was eventually determined to be 8:3:12. The starting materials were weighed according to the designed molar ratio of NaCl and KCl, i.e., 1:1. The weight ratio of salts to reactant was 2:1. Then, the raw materials were mixed through ball milling. Next, the mixture was placed in an Al_2O_3 crucible, and in turn placed in a high-temperature tubular furnace. Next, high-purity argon gas was pumped into the furnace at a flow rate of 20 mL min^{-1}, and the reaction temperature was increased up to 1100, 1150, 1200, and 1300 °C at a heating rate of 5 °C min^{-1} and then held at the highest temperature for 4–6 h. After the products were cooled down to room temperature, they were taken out and ground into powder. Furthermore, the powders were cleaned a few times with hot water to eliminate the residual salts from the product. Finally, the resultant powders were dried overnight at 100 °C in a drying oven. The optical ASCP was pressed at 200 MPa for 4 min using a stainless-steel die to form a specimen with dimension of φ20 mm × 5 mm. The samples were dried at 100 °C and pressure-less-sintered in a vacuum-sintering furnace at 1500 °C for 4 h at the rate of 5 °C min^{-1} under argon atmosphere.

Characterization

The phase composition of the composite powder was analyzed via X-ray diffraction (XRD; Cu$K\alpha$ radiation; PANalytical X´Pert Powder, Netherlands). Microstructure of the powders was characterized via field-emission scanning electron microscopy (FESEM; SUPRA™ 55, Germany), and energy-dispersive X-ray spectroscopy (EDS) analysis was also conducted. The apparent porosity and bulk density were determined by Archimedes' method. The compressive strength of the cylindrical specimen with size of Φ20 mm × 5 mm was measured by utilizing a digitally controlled tester (Longsheng Precision Testing Co., Ltd., LM-02, China) at a crosshead speed of 0.5 mm min^{-1}.

Results and discussion

Effects of temperature and holding time on the phase composition

Figure 1 shows the XRD patterns of ASCPs prepared through molten-salt method at different temperatures for 4–6 h. When the temperature is in the range of 1100–1150 °C, the main crystalline phases are α-Al_2O_3 with a small quantity of β-SiC and 6H-SiC; at the same time, a few quartz can also be detected, which indicates incomplete reduction of SiO_2. With the increase in the synthesis temperature to 1200 °C, the diffraction peak of α-Al_2O_3 becomes significantly stronger, and the intensity of quartz obviously becomes weaker. At 1300 °C, the quartz phase almost disappeared, and only a little amount was left in the product. The quartz phase might have formed during the synthesis process (because the purity of Ar is about 99%) [15] or the melting point of SiC is much higher than that of quartz, and a thin amorphous quartz layer was formed and wrapped the crystalline SiC particles during the cooling stage [16]. Besides, Fig. 1 exhibits that there exist two types of SiC. Yang et al. [17, 18] reported that Al promotes the transformation of β-SiC to 6H-SiC. Therefore, 6H-SiC and 3C-SiC types of SiC still exist in the products. This phenomenon manifests that the pure ASCP can be synthesized by heating at 1300 °C for 4 h. With the increase in the holding time from 4 to 6 h, the peak intensity of α-Al_2O_3, β-SiC, and 6H-SiC remains basically unchanged. For economic consideration, 4 h was selected as the most suitable holding time. Compared with previous studies [19, 20], ASCP fabricated
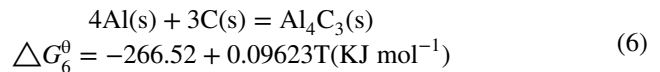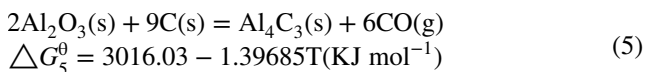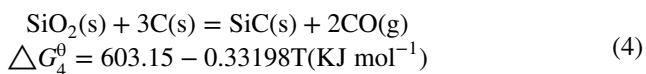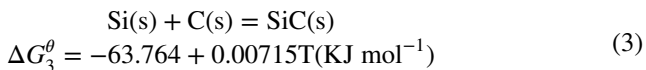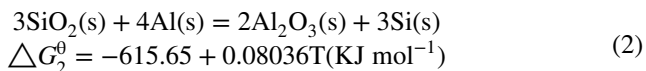
Fig. 1 XRD patterns of ASCPs fabricated via molten-salt method at different temperatures for 4–6 h
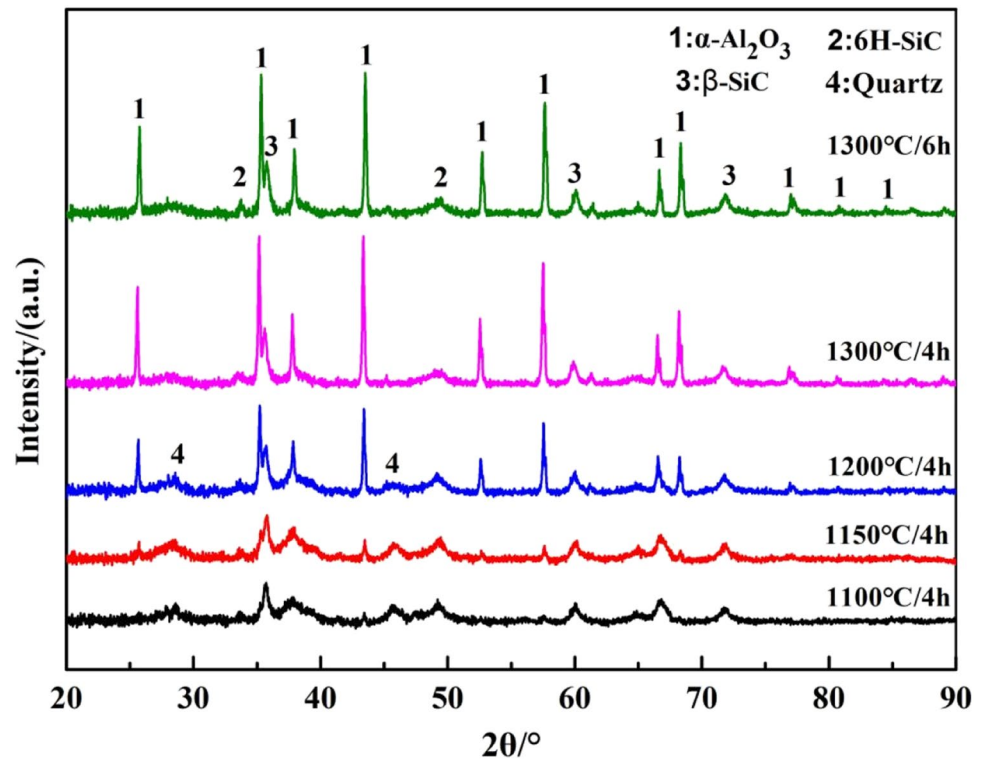
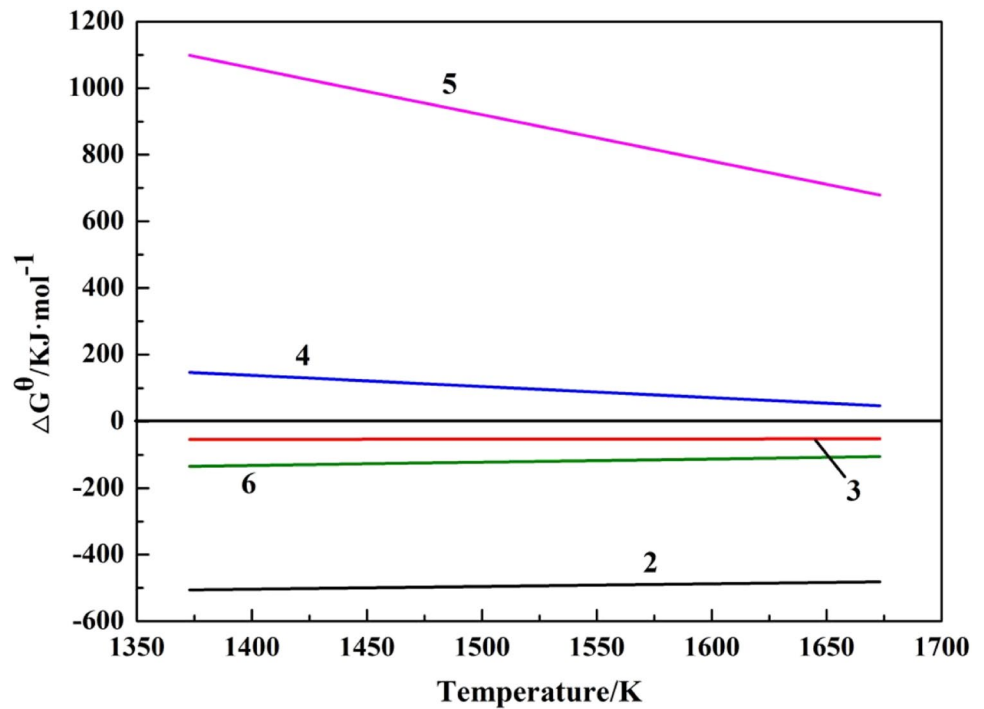by the molten-salt method can effectively lower the synthesis temperature by at least 200 °C.

Thermal analysis of Al$_2$O$_3$-SiC composite powder

The reduction process of SiO$_2$ is a complex process. The ASCP was synthesized in flowing argon ($\geq 99\%$) atmosphere; thus, it was not required to consider reactions involving oxygen. The following reactions occur during the generation of ASCP, and the relationship between standard Gibbs-free energy and temperature of related reactions should meet the following requirements [21]:

$$3SiO_2(s) + 4Al(s) = 2Al_2O_3(s) + 3Si(s)$$
$$\triangle G_2^\theta = -615.65 + 0.08036T(KJ\ mol^{-1}) \tag{2}$$

$$Si(s) + C(s) = SiC(s)$$
$$\Delta G_3^\theta = -63.764 + 0.00715T(KJ\ mol^{-1}) \tag{3}$$

$$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$$
$$\triangle G_4^\theta = 603.15 - 0.33198T(KJ\ mol^{-1}) \tag{4}$$

$$2Al_2O_3(s) + 9C(s) = Al_4C_3(s) + 6CO(g)$$
$$\triangle G_5^\theta = 3016.03 - 1.39685T(KJ\ mol^{-1}) \tag{5}$$

$$4Al(s) + 3C(s) = Al_4C_3(s)$$
$$\triangle G_6^\theta = -266.52 + 0.09623T(KJ\ mol^{-1}) \tag{6}$$

The relationship between standard Gibbs-free energy and temperature related to reactions (2)-(6) is shown in Fig. 2. In the experimental temperature range, ΔG_2^θ is far less than zero; thus, the reaction can occur easily. ΔG_3^θ is also less than zero in the experimental temperature range and the reaction can occur spontaneously; however, increase in temperature is not significantly beneficial for the reaction to occur. The high-positive value of Gibbs-free energy prevents the occurrence of reaction (5). Though ΔG_6^θ remains negative over the entire temperature range, we cannot find Al$_4$C$_3$ in Fig. 1; the reason is that Al$_4$C$_3$ can easily dissolve in water and be washed away. For reaction (4), because of the existence of molten salt, both the diffusion activation energy and diffusion distance can be reduced, which leads to the occurrence of reaction (4) under experimental conditions [22]. To sum up, the synthesis process of ASCP includes the following three stages: (I) reduction of SiO$_2$ by Al to form Al$_2$O$_3$ and Si in molten salt through reaction (2); (II) reaction of the reduced Si with C to generate SiC particles via reaction (3) and the reaction of a small proportion of SiO$_2$ with C to produce SiC through reaction (4); (III) when SiC is supersaturated in liquid phase, it precipitates and promotes the continuous dissolution of undissolved reactants into molten salt until all the reactants are consumed, and eventually, the reaction stops.

Microstructures and reaction mechanism of Al₂O₃-SiC composite powder

Figure 3a, b, c, d, e shows the SEM images of ASCP synthesized by heating at different temperatures for 4 h through the molten-salt method. When the temperature was in the range of 1100–1300 °C, the as-obtained product consisted of small particles and a certain number of agglomerates with the size in the range from a few tenths to a few microns, and sheets were also present. With the increase in the temperature, it was clearly observed that the growth of the particles increased and more agglomerations were present. This phenomenon is attributed to the nucleation of some small particles in the molten salt at early stage, which makes the aggregation easier, resulting in the formation of agglomerations [19]. Moreover, with the increase of temperature, the
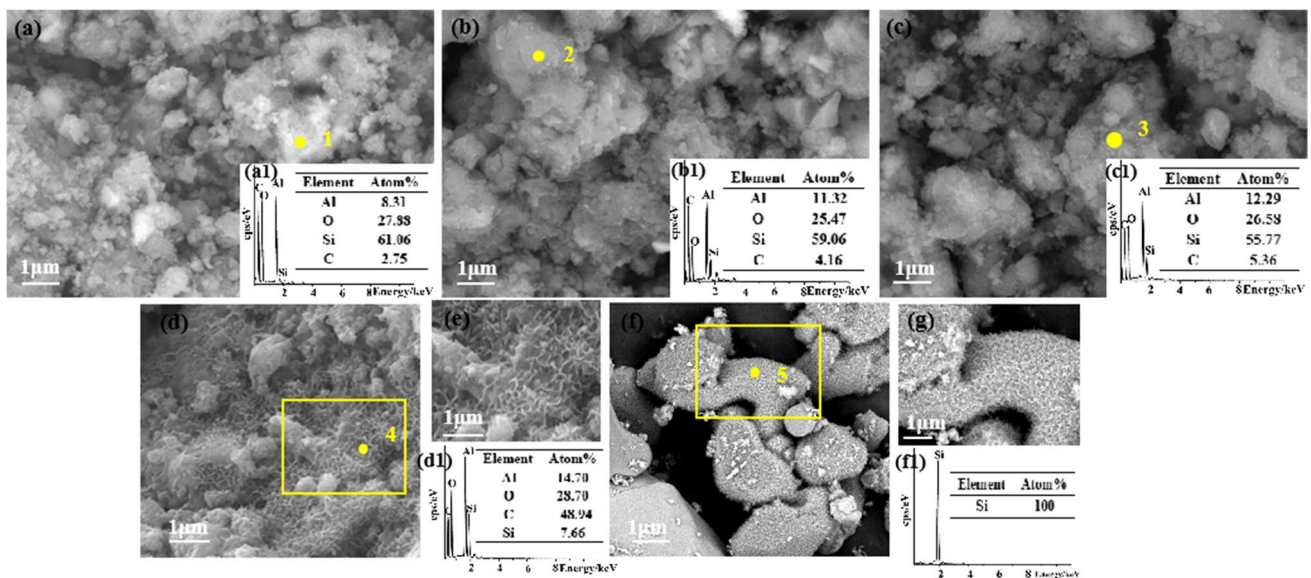

Fig. 3 SEM images of ASCP obtained via molten-salt method at different synthesis temperatures: (**a**) 1100 °C, (**b**) 1150 °C, (**c**) 1200 °C, and (**d, e**) 1300 °C for 4 h and EDS spectra of (**a1**) point 1, (**b1**) point 2, (**c1**) point 3, and (**d1**) point 4; (**f, g**) SEM images of monatomic silicon synthesized by heating at 1300 °C for 4 h by the molten-salt method and (**f1**) EDS spectrum of point 5

appearance of more sheets was also observed. EDS spectra of points 1, 2, 3, and 4 exhibit that the sheets consist of C, O, Al, and Si elements. At 1100 °C, the content of Si and Al was low, indicating that the reduction of Al was insufficient. The EDS spectra of points 2, 3, and 4 show that the content of Si and Al increases with the increase in the temperature, indicating that Al_2O_3 and SiC grains are well developed, which is in accordance with the XRD results. As Al_2O_3 and SiC phase can be detected in the same grain; they are difficult to distinguish. The morphology of ASCP was attributed to the reaction mechanism due to molten-salt method with NaCl–KCl as molten salt medium.

When the reaction occurs in molten salt, the reaction process and mechanism are very different due to the properties of molten salts; in particular, the effects of molten salts on the melting capacity of reactants are different. The formation mechanism of molten salt method can be explained in terms of the following two mechanisms, the dissolution–precipitation mechanism and the template-growth mechanism [23]. To a large extent, the solubility of reactants in molten salts determines the growth mechanism. According to the thermodynamic analysis, carbon black is almost insoluble in molten salt; therefore, Al with high activity reacts first with SiO_2 to form monatomic Si (reaction (2)). The reduced monatomic Si with high reactivity migrates and diffuses to the surface of C particles. Si atoms and C atoms form SiC on the liquid–solid interface of carbon black particles according to reaction (3). SiC particles nucleate and grow in molten salt

and precipitate out of molten salt after reaching saturation as shown in Fig. 4. Based on the abovementioned reaction process, the images showing the production of monatomic Si at 1300 °C for 4 h by molten-salt method were analyzed in this study. Figure 3g demonstrates that the morphology of ASCP is similar to that of reduced Si. EDS analysis manifests that only Si element can be detected, which further confirms that the template-growth mechanism plays a leading role in the synthesis process.

Properties of Al₂O₃-SiC composite bulk materials

The Al_2O_3-SiC ceramic sample was fabricated by sintering at 1500 °C for 4 h, using raw powders, i.e., ASCPs synthesized at 1300 °C for 4 h. The weight ratio of salt to reactants was 2, and the mechanical properties of sintered Al_2O_3-SiC ceramics were characterized and tested, respectively. Table 1 presents that after sintering at 1500 °C for 4 h, the porosity (42.3% vs. 67.2%), bulk density (1.81g·cm^{-3} vs. 1.05g·cm^{-3}), and compressive strength (16.4 MPa vs. 2.6 MPa) of the sample fabricated herein were improved compared to those of the Al_2O_3-SiC ceramics fabricated by traditional carbothermal reduction at equal forming pressure followed by sintering at 1600 °C [24]. It is well known that the mechanical properties of ceramics are affected by the sintering temperature and forming pressure. At similar forming pressure and lower sintering temperature, a relatively high compressive strength for the Al_2O_3-SiC ceramics

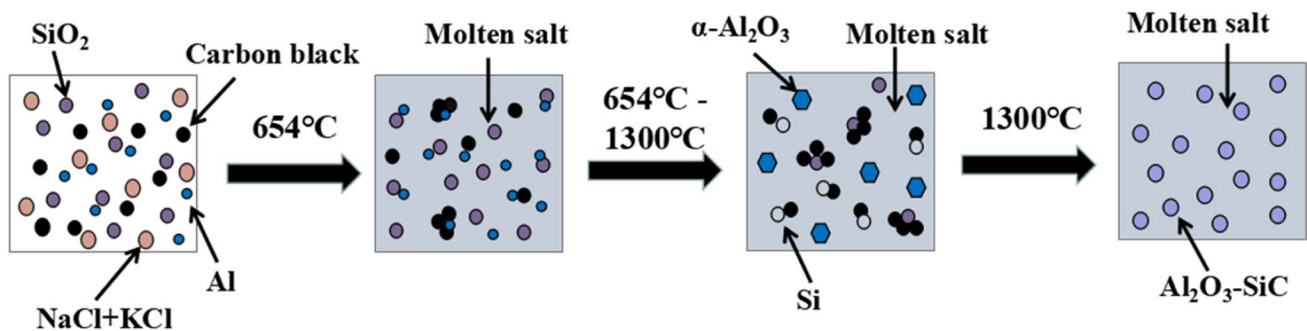**Fig. 4** Schematic illustration of synthesis mechanism of ASCP by molten-salt method

Table 1 Comparison of properties of ASCP obtained in this study and from other related literature studies

Type	Preparation method	Forming pressure/ MPa	Apparent porosity/%	Bulk density/ g·cm^{-3}	Compressive strength/MPa	Specific Strength/MPa/ (kg·m^{-3})	Sintering temperature/°C	Reference
Al_2O_3-SiC	Pressureless method	200	67.2	1.05	2.6	2.48×10^{-3}	1600	[24]
Al_2O_3-SiC	Pressureless method	20	60.8	–	15.6	–	1600	[25]
SiC	Pressureless method	22	43.1	1.5	7.5	5×10^{-3}	1000	[26]
Al_2O_3-SiC	Pressureless method	200	42.3	1.81	16.4	9.06×10^{-3}	1500	This study

was obtained herein. Comparative analysis of Al_2O_3-SiC ceramics formed by the pressureless method in this study and literature study [25] indicates that although in the literature study the forming pressure is 22 MPa, which is lower than that in this study, the value of compressive strength is similar. This is attributed to the fact that in addition to Al_2O_3 and SiC, some mullite phase also exists in the product according to the report [25], which improves the strength of Al_2O_3-SiC ceramics. The compressive strength of our samples (42.3%/16.4 MPa) is two times higher than that of SiC ceramics (43.1%/7.5 MPa) [26]. Moreover, the specific strength (9.06×10^{-3}) is better than that of other reported Al_2O_3-SiC ceramics and SiC ceramics.

Conclusions

The molten-salt method was successfully applied to synthesize Al_2O_3-SiC composite powder in NaCl–KCl under argon atmosphere. The presence of molten salt provides a liquid environment, which decreases the diffusion activation and further effectively reduces the reaction temperature by nearly 200 °C compared with the traditional synthesis method. The optimum process parameters for preparing pure Al_2O_3-SiC composite powder include temperature of 1300 °C and holding time of 4 h. The thermodynamic analysis and reaction mechanism indicate that the template-growth mechanism plays an important role in the synthesis process. The bulk materials prepared in this study exhibit a high compressive strength value of 16.4 MPa by pressureless method. As a result, the molten-salt method is a promising approach for fabricating high-melting composite ceramic material.

Declarations

Conflict of interest The authors declare no competing interest.

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