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Pressureless sintering of TiN/Y-(α/β)-sialon ceramics from SHS powder

Jianguang Xu *, Baolin Zhang, Wenlan Li, Hanrui Zhuang, Guojian Jiang

Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

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Abstract

TiN/Y-(α/β)-sialon ceramics with good mechanical properties were successfully obtained by pressureless sintering from SHS powder. XRD results showed the main phases of SHS powder to be α-sialon (68.5 wt.%) and β-sialon (29.3 wt.%). The microhardness, flexural strength and fracture toughness of the pressureless densified sialon ceramic reached 14.22 GPa, 651 MPa and 5.09 MPa $m^{1/2}$, respectively.

Keywords: A. Sintering; B. Composites; C. Mechanical properties; D. Sialon; SHS

1. Introduction

Sialon ceramics (mainly α′ and β′) have attracted intensive attention for more than 30 years because of their excellent mechanical properties for engineering applications especially at high temperatures [1,2]. They offer advantages of easier fabrication compared with Si_3N_4 ceramics because of the lower viscosity of the M-Si-Al-O-N liquid phase, where M is one of the cations Li, Mg, Ca, Y, Sc and some other rare earths, which facilitates easier densification at sintering temperatures.

Typically, sialons are prepared by firing powder compacts of Si_3N_4, AlN, Al_2O_3 and some oxide additives for sintering at high temperatures via a liquid phase sintering mechanism [3]. Both the expensive starting powders and the complex manufacturing process (compared with most oxide ceramics) have limited the practical application of sialon ceramics. And also, this process requires a high-temperature furnace and long processing times, and hence has obvious disadvantages, such as low-productivity and high-energy consumption.

On the other hand, the development of α-sialon ceramics has received little attention. This has primarily been due to the poor fracture toughness and processing difficulties associated with the fabrication of these materials. Conversely, β-sialon ceramics are easier to densify than α-sialon by pressureless sintering and possess a good combination of properties [4]. However, α-sialon has the advantage of a significantly higher hardness than that of β-sialon. Though some researchers obtained densified α-sialon in some certain conditions [5–9], the high cost and poor fracture toughness limited their application. So it is important to find a cost-effective process to synthesize α-sialon with good mechanical properties for extensive application.

Recently, a novel synthesis method, namely self-propagating high-temperature synthesis (SHS) has been extensively explored for the preparation of AlN, TiN and $MoSi_2$ powders. This technique involves the ignition of a compressed powder mixture, in either air or an inert atmosphere, producing an exothermic chemical reaction, with sufficient heat release so that it becomes self-sustaining. During an SHS process, the temperature may reach several thousand degrees in seconds. Therefore, compared with most conventional synthetic processes, SHS has the advantages of low cost, high-productivity and low energy consumption. Products of high purity can be obtained owing to the vaporization of the volatile contaminants at the extremely high temperatures. The fast cooling in SHS can produce some metastable phases with better sinterability.

* Corresponding author. Tel.: +86 21 5241 1036; fax: +86 21 5241 3903.
E-mail addresses: jgxu@163.com, jgxu@mail.sci.ac.cn (J. Xu).

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This last feature makes it especially appealing for the production of α-sialon powders, as α-sialon is known to have poor sinterability. On the other hand, it is known that TiN is a good second reinforced phase for α-sialon matrix. In this work, TiN/Y-(α/β)-sialon ceramics (mainly α′ phase) has obtained from low-cost SHS powder during pressureless sinter process. It exhibits good mechanical properties for future application.

2. Experimental procedures

Starting materials for synthesizing Y-(α/β)-sialon powders by SHS included Si_3N_4 (UBE E10, Japan, 2 wt.% O), Si (Si > 98 wt.%, 20 μm), Al (Al > 98 wt.%, 25 μm). NH_4Cl (99.9 wt.%) as an additive was added to some samples for the fabrication of pure sialon powders. The samples were prepared according to the composition shown in Table 1. The mixtures were milled with Si_3N_4 balls in absolute ethanol for 24 h. After milling, the resultant slurry was dried with a rotary evaporator in a drying box at 80 °C for at least 5 h until the powders were completely free of alcohol. The dried powders were then passed through 60 mesh sieve to obtain an agglomerate-free powder mixture for following SHS procedure. Then the mixed powders were pressed into a cylindrical graphitic crucible and covered with a top layer of titanium powders. A tungsten heating coil was connected to ignite the Ti powder, which then induced the spontaneous SHS process. The powders were combusted on a steel chamber under 30 MPa N_2 pressure. The purity of the N_2 gas was reported as 99.9%.

The SHS powders were mixed with Al_2O_3, TiN, SiO_2, TiO_2 powders and then milled with Si_3N_4 balls in absolute ethanol for 24 h. The Al_2O_3, TiN, SiO_2, TiO_2 powders were local products of high purity (>99.2 wt.%). The detail composition of mixtures is shown in Table 2. After drying, the powder mixtures were sieved and uniaxially pressed at 20 MPa, and then cold isostatically pressed at 200 MPa. The isostatically pressed green compacts were placed in a graphite crucible and sintered at a temperature of 1720 °C for 0.5 h and 1760 °C for 0.5 h then 1800 °C for 3 h in 0.1 MPa N_2 atmospheres. The as-received samples were machined into 3 mm × 4 mm × 36 mm bars.

The phase compositions of the powders were investigated by X-ray diffraction (XRD) using Cu Kα radiation. The morphologies of powders and sintered products were studied by using scanning electron microscopy (SEM). Sintered sample densities were measured by the Archimedes method. The Vickers hardness (H_V) and fracture toughness (K_{IC}) were measured on polished specimens using Vicker's diamond indentor under 98 N for 15 s. The flexural strength was measured at room temperature using the three-point bending test with a span length of 30 mm and a cross-head speed of 0.5 mm/min.

3. Results and discussion

3.1. Characteristics of the Y-(α/β)-sialon powders

The results of XRD patterns of the three samples A, B, C are shown in Table 1. The main phases of SHS powders are α-sialon and β-sialon with a little free Si. It can be seen by the increasing of NH_4Cl additive, β-sialon increased and free Si decreased. Unfortunately, the reaction could not carry out when the NH_4Cl additive had been increased to 3 wt.%. Because of the volatilization of NH_4Cl, it absorbed some heat and made the reaction temperature lower. Lower temperature is better for the synthesis of β-sialon [10]. Also, the volatilization of NH_4Cl left a great deal of voids in the reactants and let the contact among powders less. It could be predicted the propagation rate is lower and reaction time is longer, then the free Si transported more.

Because sample C powders include the least free Si phase, it had been used as sinter starting material. Fig. 1 shows SEM photograph of sample C powders. A few grains have large elongated shape and the others show a fine equiaxed morphology. These could be β-sialon and α-sialon, respectively.

3.2. Mechanical properties of pressureless sintered Y-(α/β)-sialon ceramics

The density, flexural strength, fracture toughness and Vickers hardness were listed in Table 3. Significant improvement in flexural strength and fracture toughness were obtained by incorporating SiO_2, TiN or TiO_2 powders into sialon. Generally, TiN had a much higher thermal expansion coefficient than sialon so that after sintering the residual strain state in the matrix close to the interface was radial tensile and tangential compressive stresses, which tended to deflect the crack path around the particle and benefited the increase in toughness [11]. Of all investigated ceramics composites, the SNT ceramic with the TiN and

Table 1
Phase composition of combustion products for different starting powder

Sample	Phase composition of starting powders (wt.%)					Phase composition of combustion products (wt.%)		
	Y_2O_3	Al	Si_3N_4	Si	NH_4Cl	α-Sialon	β-Sialon	Free Si
A	11.7	8.1	65	15.2	0	70.7	16.5	12.8
B	11.6	8.0	64.4	15.0	1	69.9	22.4	7.7
C	11.5	7.9	63.7	14.9	2	68.5	29.3	2.2
D	11.4	7.8	63.1	14.7	3	Not combusted		

Table 2
Composition of different materials

Materials	Sample C (wt.%)	Al_2O_3 (wt.%)	SiO_2 (wt.%)	TiN (wt.%)	TiO_2 (wt.%)
Sialon	96.8	3.2	0	0	0
SN	92.2	3.0	0	4.8	0
SSN	90.5	3.0	1.9	4.7	0
SNT	91.7	3.0	0	2.5	2.8

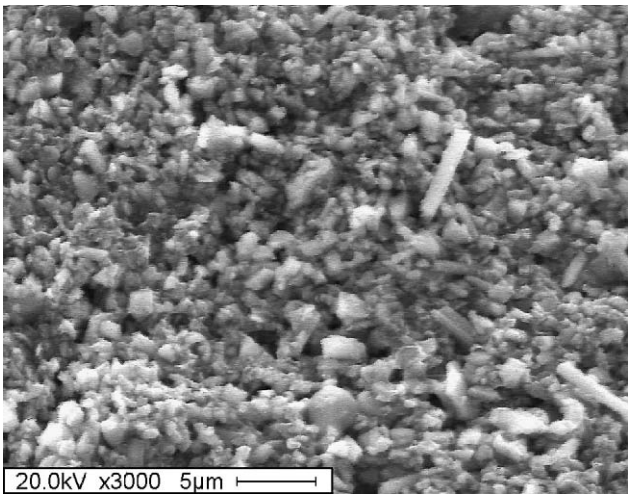

Fig. 1. SEM microstructure of sample C powders.

TiO_2 powders additives provided best combination of hardness (14.22 GPa), flexural strength (651 MPa) and fracture toughness (5.09 MPa $m^{1/2}$). This was due to the TiO_2 of the SNT starting powders transformed to TiN when the starting powders had been heated to 1150 °C during sintering process, which generally was smaller and distributed more homogeneous in sialon matrix than the TiN particles in SN and SSN ceramics [12,13]. The pure sialon ceramic show the highest microhardness (14.70 GPa), because in TiN–Si3N4 composites, the microhardness generally decreased with the addition of TiN since TiN was softer than the Si3N4 matrix [14].

SEM micrographs of fractured surface of pure sialon and SNT ceramics were shown in Fig. 2a and b, respectively. From Fig. 2, it could be observed that the fractured surface of SNT ceramic was more tortuous than pure sialon and the grains of SNT ceramic were smaller than pure sialon. It was

Table 3
Densities and mechanical properties of different materials

Materials	Density (g cm^{-3})	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	H_{v10} (GPa)
Sialon	3.27 ± 0.01	343 ± 35	3.51 ± 0.27	14.70 ± 0.16
SN	3.30 ± 0.01	522 ± 50	4.74 ± 0.35	14.00 ± 0.19
SSN	3.24 ± 0.01	531 ± 44	4.89 ± 0.34	13.84 ± 0.15
SNT	3.25 ± 0.01	651 ± 48	5.09 ± 0.22	14.22 ± 0.04

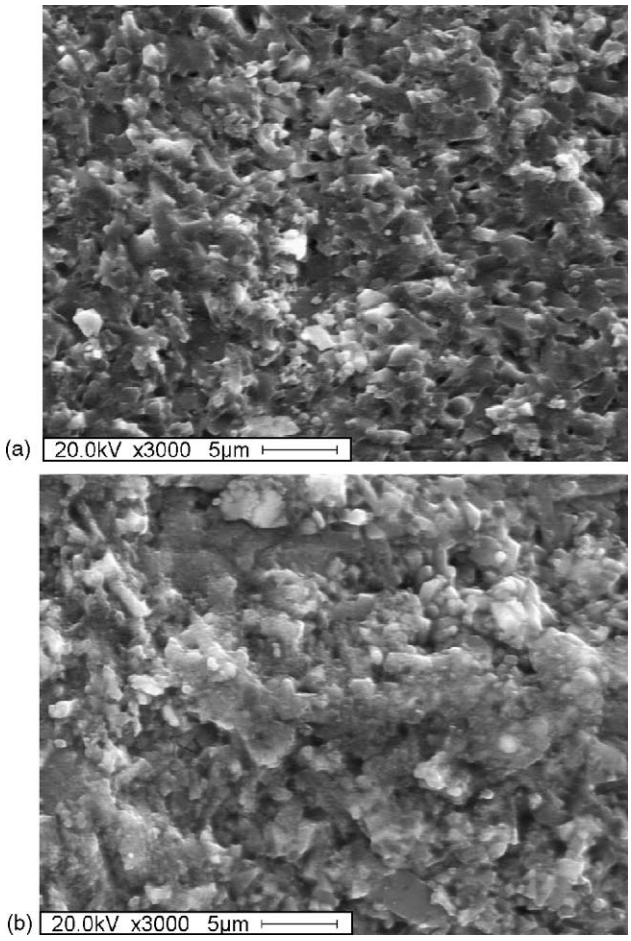

Fig. 2. SEM micrograph of fractured surface: (a) pure sialon and (b) SNT ceramic.

due to the TiN grains deflected the crack and prohibited the growth of sialon grains, which was resulting in the significant improvement of flexural strength and fracture toughness.

4. Conclusion

TiN/Y-(α/β)-sialon ceramics with good mechanical properties were successfully obtained by pressureless sintering from SHS powder. α-Sialon was the mainly phase of SHS powder and β-sialon was the second phase. NH_4Cl was used as an additive for SHS process and effectively decreased the free Si of SHS powder. Though there were slightly decrease of microhardness, the TiN additive significantly increased the flexural strength and fracture toughness. Specially, the SNT ceramic exhibits the best combination of mechanical properties, which the TiN grains in SNT ceramic were obtained from TiO_2 in situ reaction during sintering process. Because the low cost of SHS process, pressureless sintering process and the starting powder, future applications of the material by industry is therefore anticipated.

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