Synthesis of (Ca,Mg)α′-Sialon-AlN-BN powders from boron-rich blast furnace slag by microwave carbothermal reduction-nitridation

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Abstract: (Ca,Mg)α′-Sialon-AlN-BN powders were synthesized by carbothermal reduction and nitridation (CRN) method using boron-rich slag, one of the intermediate products from pyrometallurgy separation of pageit, as the staring material. The influences of synthesis temperature and holding time on phase composition and microstructure during a microwave CRN were studied by XRD, SEM and EDS. The comparison between two heating techniques, conventional and microwave heating, to the synthesized powder was presented as well. The experimental results revealed that the phase compositions and microstructures of the synthesized products were greatly affected by synthesis temperature and holding time. With an increase in the synthesis temperature and holding time, the relative amount of α′-Sialon increased and became the main crystalline phase at 1400 ℃ for 6 h. The synthesized p N and a small amount of β-SiC. Elongated α′-Sialon grains, short rod AlN grains, aggregate nanoscale BN grains were observed in synthesized powders. The reaction temperature of microwave heating method was reduced by 80 ℃, the reacti was shortened by 2h, and more elongated α′-Sialon grains with large aspect ratio were observed.

Keywords: (Ca,Mg)α′-Sialon-AlN-BN, microwave, boron-rich blast furnace slag, carbothermal reduction- nitridation, powders

1. Introduction

Boron-rich blast furnace slag is one of the major products created during the separation of iron and boron from ludwigite in a blast furnace process. Boron-rich blast furnace slag primarily contains SiO_2, Al_2O_3, MgO, CaO and B_2O_3 along with a smaller amount of iron oxide and other materials. Because of the low activity (approximately 50%) and low boron grade (B_2O_3 content of approximately 12 wt.%), it is difficult to use boron-rich blast furnace slag to directly produce boric acid and borax. Thus, the high efficiency utilisation of its is of great importance to the Chinese boron industry.

Based on this background, one innovative process to recycle the boron-rich blast furnace slag in the synthesis of α′-Sialon ($M_xSi_{12-(m+n)}Al_{(m+n)}O_nN_{16-n}$) using the carbothermal reduction–nitridation (CRN) method has been proposed in this study. In this process of CRN, SiO_2, Al_2O_3, MgO and CaO in the slag will synthesize (Ca,Mg)α′-Sialon, at the meantime B_2O_3 is converted into hexagonal boron nitride, which has a high melting point and thermal conductivity, excellent corrosion and thermal shock resistance, as well as good electric insulativity and lubricity[1,2]. These superior characteristics can improve the properties of α′-Sialon matrix composites. (Ca,Mg)α′-Sialon–AlN–BN composite can be used as break rings in the horizontal continuous casting of steel, as a nozzle refractory or in new structural ceramics.

Sialon ceramics (mainly α′-Sialon and β′-Sialon) exhibit great potential for engineering applications because of their excellent mechanical properties, such as high hardness, toughness and strength. Typically, Sialons are prepared by firing powder compacts of Si_3N_4, AlN, Al_2O_3 and some oxide sintering additives at high temperature via a reaction sintering method[3-7]. The high manufacturing costs have limited the practical application of Sialon ceramics. Some researchers have turned to the carbothermal reduction and nitridation method to synthesized Sialons powders from a wide range of low-cost precursors. There are reports that α′-Sialon and β′-Sialon powders have been synthesized by heating natural clay powders [8-13]or industrial waste slag[14-16] with carbon in flowing nitrogen. The process requires long processing time, and hence has obvious disadvantages, such as high-energy consumption. Recently, a novel synthesis method, namely microwave sintering technology has been extensively explored for the preparation of β′-Sialon、AlN、SiC ceramics powders[17-19]. Compared with most conventional synthesis processes, a microwave sintering has the advantages of even quickly heating, high thermal efficiency, safety and clean.

At present, there have been no reports about the synthesis of low-cost (Ca,Mg)α′-Sialon powders from boron-rich blast furnace slag. Therefore, the purpose of this work is to explore the feasibility of synthesizing (Ca,Mg)α′-Sialon–AlN–BN powders from boron-rich blast furnace slag by microwave CRN method. The effects of synthesis temperature and holding time on phase formation and microstructure evolution during a microwave CRN process were investigated. The comparison between two heating techniques, conventional and microwave heating, to the synthesized powder was presented as well.

2. Experimental

Boron-rich blast furnace slag, silica fume and bauxite chamote were used as the starting materials. Table 1 lists the characteristics of these there materials. In addition, carbon black, containing 96.7wt% carbon, was used as a reducing agent. The carbon content in the all samples was fixed at 1.2 times the required stoichiometric value.

The compositions of all of the samples were designed to nominally lie on the two-dimensional α′ plane. In all of the samples, the m:n ratio was 2:1. Thus, their compositions were nominally located on the tie line between Si_3N_4 and RO:3AlN (where R=Ca or Mg) in the α′ plane with the formula $(Ca,Mg)_xSi_{12-3x}Al_{3x}O_xN_{16-x}$. In this work, the compositions with an x value of 4 were designed.

Table 1 Compositions of the starting material powders (mass fraction, %)

Compound	Boron-rich BF slag	Silica fume	Bauxite chalmette
SiO2	28.03	94.50	13.28
Al2O3	7.30	0.64	79.30
CaO	15.03	0.33	0.35
MgO	34.55	1.27	0.04
B2O3	12.01		
Na2O	0.34		0.2
K2O	0.53		0.21
Fe2O3	0.21	0.87	2.97
TiO2			3.07
Burning loss		1.86	
Total	98.00	99.47	99.42

First, the mixtures were placed in a polyurethane pot and ball-milled in ethanol for 24 h using agate-milling media. After milling, the slurry was dried and mixed again for 4 h. Approximately 1.5 g of powder was then uniaxially pressed into a pellet with a diameter of 15 mm. The pellets were then pressureless sintered in a microwave heating furnace in a nitrogen atmosphere with a N_2 flow rate of 1 L/min at 1300 to 1480 ℃ for 0 to 8 set to approximately 15 ℃/min below 1000℃ and 6℃/min in ab ℃. The resid burning the synthesised powders at 700 ℃ for 2 h in air.

Phase identification was performed by x-ray diffractometry (XRD, D/MAX-RB) using nickel-filtered Cu Kα radiation. The relative amount of the mainly crystalline phases in the samples was estimated as:

$$w\% = \frac{A_i}{\sum A_{ij}} \times 100 \tag{1}$$

where A_i is the relative integral area of the strongest peak of a crystalline phase, and A_{ij} is the sum of the relative integral area of the strongest peak of all the crystalline phases in the sample.

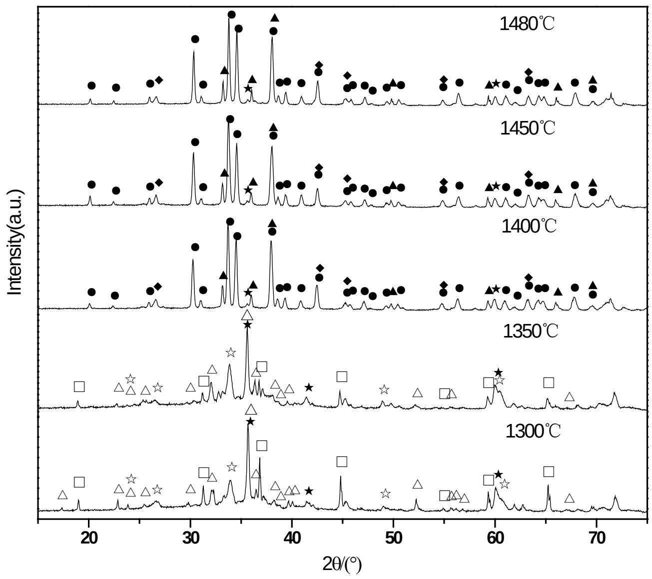
The morphology of the samples was characterised by scanning electron microscopy (SEM, SSX-550). The specific microstructural features of synthesised powders were analysed by energy dispersion spectroscopy (EDS, SSX-550) and SEM.

3. Results and discussion

3.1 Effect of synthesis temperature on the reaction

Fig. 1 shows the XRD patterns of the powders that were synthesised after sintering at 1300 ℃–1480 ℃ for 6 h, and Fig. 2 presents the relative amount of the crystalline phases. As shown in Fig. 1 and Fig. 2, Mg_2SiO_4, $MgAl_2O_4$, $Ca_2Al_2SiO_7$ and less SiC were found in the products when the synthesis temperature was 1300℃. The presence of these products reveals that under these conditions, the Mg_2SiO_4 in the boron-rich blast furnace slag was not reduced and did not decompose, and solid-phase reactions occurred between SiO_2, Al_2O_3, CaO and MgO to generate compound oxides. At 1300℃, the reaction products contained amorphous phases as a result of which the eutectic temperature in the Ca–Mg–Si–Al system is 1250℃[20]. Above this temperature, the reaction system generates many liquid phases, which were maintained as amorphous phases during decreasing temperature due to the lower reaction temperature. A thermodynamic analysis indicated that SiC is formed only at higher temperatures under standard conditions. However, the presence of impurity elements, such as iron, alters the phase equilibria by changing the thermodynamic activity, resulting in the formation of liquid phases at lower temperatures. Because the starting materials in the present work were composed of natural minerals and metallurgical waste slag, which contains many impurities, the formation temperature of the liquid phases decreased, resulting in the generation of SiC at the low temperature of 1300℃, and its amount increased then decrease with increasing temperature.

When the temperature reached 1350℃, the phase compositions of the synthesized products were the same as that of at 1300℃, however, the amounts of $MgAl_2O_4$, Mg_2SiO_4 and $Ca_2Al_2SiO_7$ decreased and amorphous phases increased.



●α′-Sialon ◆BN ▲AlN ★SiC □$MgAl_2O_4$ △Mg_2SiO_4 ☆$Ca_2Al_2SiO_7$

Fig.1 XRD patterns for samples prepared at different synthesis temperature

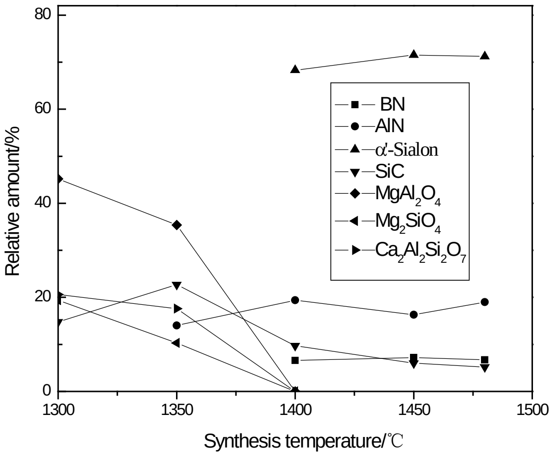


Fig. 2 Variation of phase compositions of samples with synthesis temperature

At a synthesis temperature of 1400℃, the amount of α′-Sialon increased rapidly to become the primary crystalline phase. Meantime, other oxides disappeared entirely, which revealed that these oxides were generated as transitional phases in the preparation of α′-Sialon. Hewett et al.[21] also reported that $Ca_2Al_2SiO_7$ was generated as a transitional phase in the preparation of Ca–α′-Sialon by the reaction sintering method at temperatures between 1200 and 1400℃, which is the same as that of the present work. And contrasting the diffraction standard card of Ca–α′-Sialon (x=0.8), all the diffraction peaks of α′-Sialon formed were deviated to the direction of big diffraction angles. It indicated that the small amount of Ca^{2+} and Mg^{2+} was incorporated into α′-Sialon structure at the moment. In addition, AlN were also produced at 1400℃, and the results revealed that the CRN reaction of Al_2O_3 happened, yielding AlN, then some of the AlN participated in the synthesis of α′-Sialon. Based on the phase relationship of the Ca–Si–Al–O–N system[20], the upper limit of Ca–α′-Sialon on the link Si_3N_4–CaO:3AlN is at an x value of 1.4, beyond which there is a multi-phase region, composed of α′-Sialon, a liquid phase and AlN polytypoids or AlN. Moreover, the partial SiO_2 in the initial materials was reduced to SiO gas and removed from the reaction system with the flowing N_2, which resulted in an excess of Al_2O_3 in the starting materials. Subsequently, the Al_2O_3 surplus was converted to AlN by the CRN process. The typical diffraction peak of h-BN occurred at a temperature of 1400℃, and did not change significantly through a temperature of 1480℃, which was the maximal temperature used the present work. Yoon et al.[22] reported that the optimal synthesis temperature of h-BN was between 1300 and 1400℃, using B_2O_3 and carbon mixtures as the starting materials, which is consistent with the present work.

When the synthesis temperature was increased to 1450℃, the amount of α′-Sialon increased gradually, and AlN decreased. At this time, the microwave CRN reaction proceeded completely. At 1480℃, the amount of α′-Sialon decreased, but the AlN phases increased at the same time, suggesting that α′-Sialon had decomposed at this temperature.

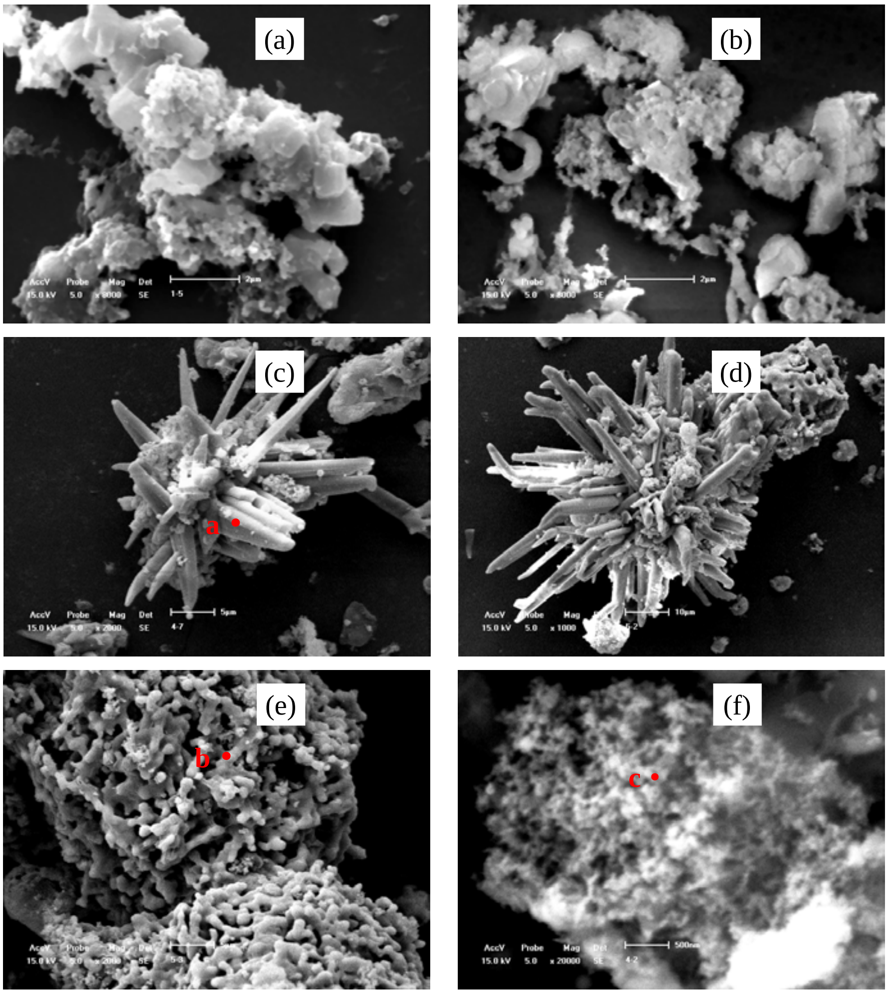


Fig. 3 SEM micrographs of the synthesized powders and characteristic grains at different temperatures
(a) 1300℃; (b) 1350℃; (c) 1400℃; (d)1480℃; (e)AlN grains; (f)BN grains

Fig. 3 contains SEM micrographs of the powders that were synthesised at temperatures ranging from 1300 to 1480℃ for 6 h. Fig. 4 shows the EDS spectra of the characteristic grains in the synthesized powders. As shown in Fig.3 and Fig.4, the grains in the powders synthesised at 1300℃ and 1350℃ were flaky and irregular and formed large agglomerates. It suggested that the reaction system generated many liquid phases, which promoted the formation of aggregates. A large quantity of elongated α′-Sialon with higher aspect ratios increased rapidly with the increase of synthesis temperature, and displayed obviously crystallization orientation, which indicated that the microwave field could promote preferred orientation of the α′-Sialon grains. The AlN grains were in the form of short rods, and agglomerates of nano-sized grains that are thought to be BN grains were observed as well.

As shown in Fig. 4(a), both Ca^{2+} and Mg^{2+} were incorporated into the α′-Sialon structure, but the Ca^{2+} was present to a greater extent than the Mg^{2+} in the lattice. In this study, the compounds in the synthesised products that include Mg were not observed by the XRD characterisation, even though the amount of MgO in the boron-rich blast furnace slag was very high. This lack of Mg detection suggests that much of the magnesium oxide may have been reduced and lost during the carbothermal reduction process. The results of some studies noticed that the volatile phenomenon during the CRN process of MgO at higher temperature, which resulted in the loss of magnesium[23-25].

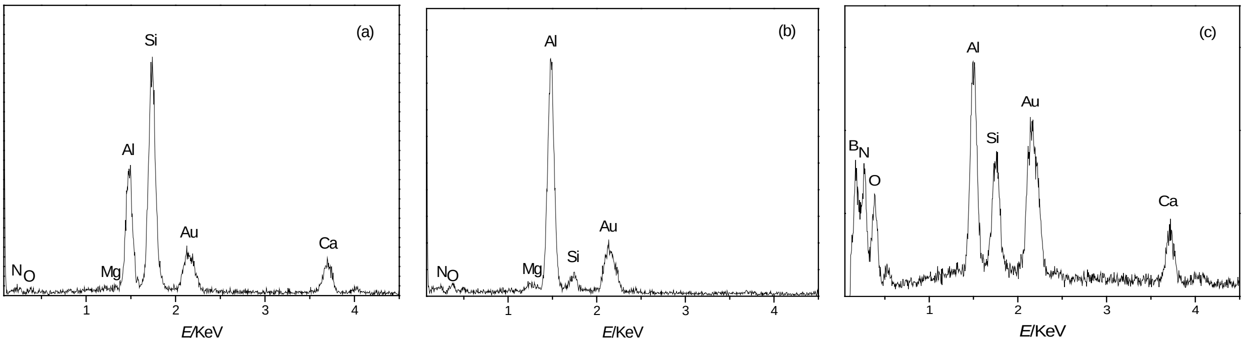


Fig. 4 EDS spectra of the characteristic grains: (a) elongated α′-Sialon; (b)short rod-shaped AlN and (c) h-BN

3.2 Effect of holding time on the reaction

The phase assembly of the samples as a function of the holding time at a temperature of 1400℃ is shown in Fig. 5. As shown in this figure, the phases of the products were composed of $MgAl_2O_4$, Mg_2SiO_4 and SiC at 1400℃ with a holding time of 0 h. Prolonging holding time to 1 h, Mg_2SiO_4 vanished and $Ca_2Al_2SiO_7$ and little β′-Sialon occurred, which showed that the reduction-nitridation reactions have proceeded at this time. After 2 h, AlN was formed. With a holding time of 4 h, $MgAl_2O_4$ and $Ca_2Al_2SiO_7$ vanished entirely and the amounts of AlN and β′-Sialon decreased continuously, α′-Sialon was generated. The amount of α′-Sialon increased with an increase in the holding time and reached its maximum with a holding time of 6 h. Subsequently, α′-Sialon content decreased and AlN content increased slightly. BN was formed after 4 h, and its content did not changed nearly.

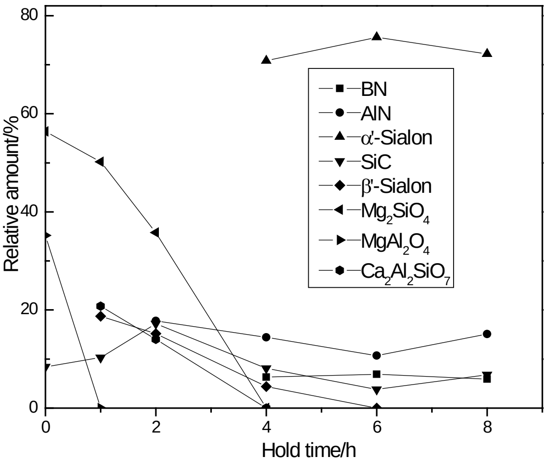


Fig.5 Variation of phase compositions of reaction products with holding time at 1400 ℃

3.3 Comparison between conventional and microwave heating

The XRD pattern of the (Ca,Mg)α′-Sialon−AlN−BN powders that were synthesised by conventional heating method at 1480 ℃ for 8h is shown in Fig. 6. As shown in Fig. 6, the synthesis products were of basically the same phase compositions by conventional and microwave heating, both of which were mainly composed of α′-Sialon, AlN, BN and a small amount of SiC.

Fig. 7 shows SEM micrographs of the powders that were synthesised by conventional heating method at 1480 ℃ for 8 h. As seen in Fig. 7, elongated and equiaxed α′-Sialon grains were observed in synthesized powders, but elongated α′-Sialon grains did not crystallized completely and the quantity and aspect ratio of the grains were less than microwave synthesize powders.

The optimal parameters for powders synthesized by microwave sintering and conventional sintering are shown in Fig. 8. As shown in Fig.8, The reaction temperature of microwave heating method was reduced by 80 ℃ and the re time was shortened by 2h. The results indicated that microwave sintering method can obviously reduce energy consumptions.

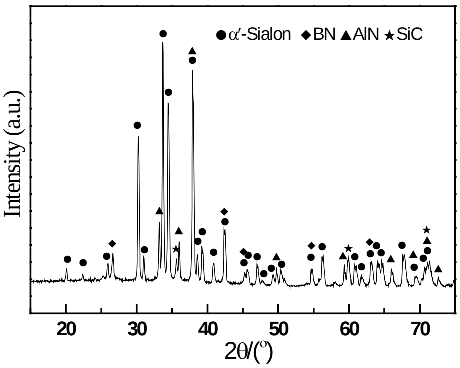


Fig.6 XRD pattern of powder synthesized by resistance heating

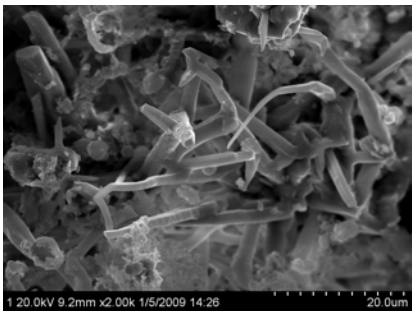


Fig.7 SEM micrograph of powder synthesized by resistance heating

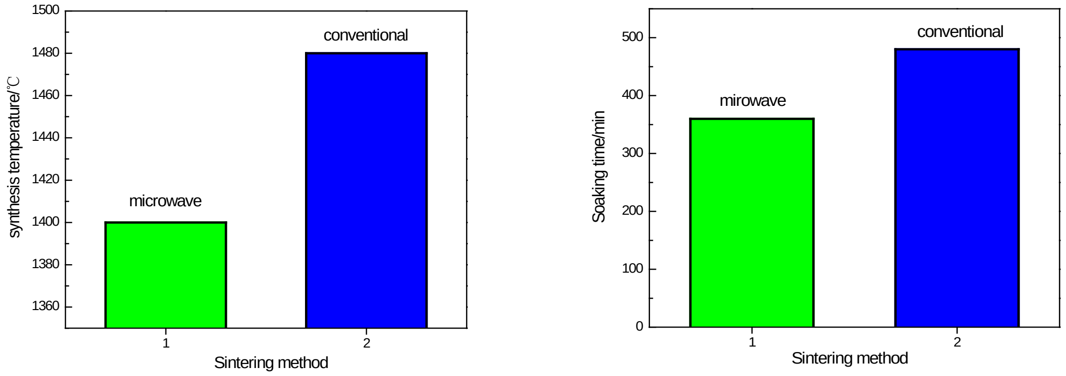


Fig. 8 Microwave sintering parameters vs. conventional sintering parameters of powders

4. Conclutions

The synthesis of (Ca,Mg)α′-Sialon–AlN–BN powders by microwave CRN method using boron-rich blast furnace slag as a starting material was greatly affected by the process conditions. With an increase in the synthesis temperature and holding time, the CRN reactions were promoted, and the production of α′-Sialon increased. The optimal conditions for powder synthesis were a temperature of 1400℃ and a holding time of 6 h, under which the crystalline phases of the products included α′-Sialon, AlN, BN and a small amount of SiC. A large amount of elongated α′-Sialon grains were produced at higher temperatures. AlN grains were in the form of short rods or had an irregular morphology. Some nano-sized h-BN grains were also observed in synthesised powders. The reaction temperature of microwave heating method was reduced by 80 ℃ and the reaction time was shortened by 2h tha the optimal conditions for powders synthesis by conventional heating method, and more elongated α′-Sialon grains with large aspect ratio were observed.

Acknowledgement

This work was supported by Chinese National Programs for High Technology Research and Development (2006AA06Z368) and the Fundamental Research Funds for the Central Universities (N100402007) in China.

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