Effects of Temperature on the Synthesis of SiAlON and SiAlON Composite Material from Aluminium Dross

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SiAlON and a SiAlON composite material were synthesized from aluminium dross by adding a certain amount of silicon, SiO_2 and Al using aluminothermic (silicothermic) reduction and nitridation. The effects of temperature on the synthesis were investigated. For this purpose, the apparent porosity (AP), bulk density (BD), phase composition and microstructure of specimens fired at 1000 °C for 1 h, and then heated to 1300 °C, 1350 °C, 1400 °C, 1450 °C and 1500 °C for 4 h, respectively, were determined. The results showed that single-phase β-SiAlON can be synthesized at 1000 °C / 1 h and then at 1450 °C / 4 h with an N_2 flow of 0,5 l/min. The apparent porosity of the specimens was highest at the latter temperature. In the experiments for synthesizing SiAlON composite material, SiAlONs occurred in hexagonal prisms, growing among corundum crystals or on the surface of it. The optimum temperature was between 1400 °C and 1450 °C.

1 Introduction

Aluminium dross is a by-product of aluminium production, generated during primary and secondary aluminium melting [1, 2]. The dross usually contains aluminium metal, aluminium oxide, nitride, and carbide, salts, other metal oxides such as oxide of silicon, magnesium, and others [2, 3]. Aluminium dross always contains about 5 – 20 % SiO_2 and 43 – 75 % $A1_2O_3$. Other elements and compounds contained in the dross have deleterious effects on the environment as landfill, such as the compounds Al_4C_3 and AlN, which react with water to produce CH_4 and NH_3, respectively [4]. In recent years, China contributed over 1/4 of the world aluminium production. About 1 – 3 % of this is furnace waste known as aluminium dross. The strong development of the aluminium industry has made the disposal and recycling of aluminium dross a worldwide problem.

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SiAlONs are ceramic materials based on the elements silicon, aluminium, nitrogen and oxygen derived from silicon nitride in which silicon and nitrogen are simultaneously replaced by aluminium and oxygen atoms respectively [5 – 9]. Such materials possess excellent resistance to thermal shock and corrosion by molten metals. They are used for high temperature applications such as thermocouple protection sheaths in aluminium metallurgy and are candidates for hot-zone parts in internal combustion engines [6].

Tab. 1 **Chemical analysis of aluminium dross**

Compound /element	As-received dross [mass-%]	Water-treated dross [mass-%]
Al_2O_3	64,17	52,53
SiO_2	8,63	7,72
Fe_2O_3	1,28	1,33
MgO	6,53	5,36
CaO	1,91	1,69
K_2O	1,14	0,62
Na_2O	4,04	1,85
TiO_2	0,6	0,58
C	3,2	2,32
Al	6,69	8,3
LOI	2,54	17,7

SiAlON ceramics are prepared by either reactive sintering of Si_3N_4, Al_2O_3 and AlN powders or by carbothermal (aluminothermic or silicothermic) reduction nitridation (CRN) of salic minerals such as kaolin or materials containing alumina and silica. Another way to synthesize SiAlON ceramics is self-propagating high-temperature synthesis (SHS) [7, 10]. The advantage of CRN for synthesizing SiAlON is that it is a low cost and simple process, which is why it has firmly established itself as one of the main methods to produce SiAlON ceramics.

In the work described in this report, the reduction nitridation method was used to synthesize SiAlON and a SiAlON composite material from aluminium dross, silicon, SiO_2 and Al.

2 Experimental

The aluminium dross used in this experiment was provided by a company in Henan province. Since the as-received sample contained KCl and NaCl, it was necessary to remove these salts by washing with water at room temperature for 24 h and drying at 60 °C for 24 h. The chemical analysis of the as-received water-washed aluminium dross is shown in Tab. 1.

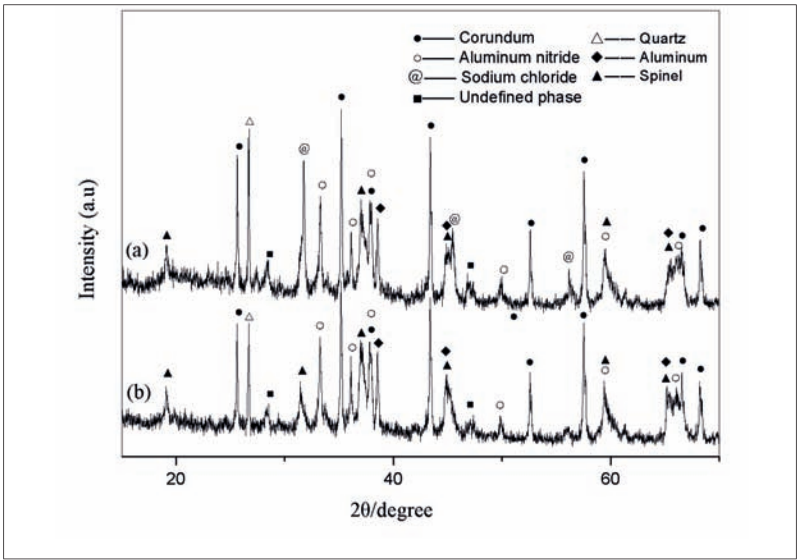

Fig. 1 X-ray diffraction patterns: a) aluminium dross; b) water-treated aluminium dross

Fig. 1 shows the effect of the water treatment. The pattern for the water-treated sample shows the absence of the NaCl peaks, while the intensity of the peaks for other phases shows almost no change. The other starting materials used were aluminium powder, SiO_2 powder and silicon powder.

The mixture was calculated in accordance with the stoichiometric reaction for the synthesis of β-SiAlON and β-SiAlON composite material. These two groups of specimens were marked A and B, respectively. Specimen A was produced according to Eq. (1), where the value of Z is 1. Specimen B was based on specimen A, but with higher aluminium dross and lower Si contents.

$$Al + AlN + Si + SiO_2 + Al_2O_3 + N_2 \rightarrow Si_{6-Z}Al_ZO_ZN_{8-Z} + O_2\uparrow \quad (1)$$

The starting materials were dry blended in a ball mill for 2 h, and then die-pressed at a pressure of 100 MPa to form cylinders of 20 mm diameter and 20 mm thick.

The specimens were placed in a graphite crucible which was placed in an atmosphere furnace and fired to 1000 °C for 1 h, followed by firing at the reaction temperature 1300 °C, 1350 °C, 1400 °C, 1450 °C and 1500 °C for 4 h, respectively, with an N_2 flow of 0,5 l/min.

The apparent porosity and bulk density of the specimens were determined using Archimedes' method, and the phase composition and microstructure by X-ray powder diffraction (XRD, X'Pert Pro, *Philips*, Netherlands) and scanning electron microscopy (SEM, Nova NanoSEM 400, *FEI*, Netherlands and SEM, XL-30w/TMP, *Philips*, Netherlands).

3 Results and discussion

3.1 Apparent porosity and bulk density

As is shown in Fig. 2, the apparent porosity of A is higher than that of B and the bulk density of A is lower than that of B at the same temperature. In the range of 1300 °C to 1350 °C, the apparent porosity of A decreases slowly with increasing temperature, while a further increase to between 1350 °C and 1500 °C leads to an increase in apparent porosity with increasing temperature. At 1450 °C, the apparent porosity of A is highest and the bulk density is lowest. Generally speaking, silicon started to react with N_2 at between 1300 °C and 1350 °C, and the full density of Si_3N_4 is higher than that of Si. So this reaction made the apparent porosity decline. In general, the formation of β-SiAlON begins at 1350 °C. At this temperature, the release of O_2 from this reaction probably increased the apparent porosity, a process which gains in intensity up to 1450 °C, as shown in the XRD patterns and SEM photographs. At between 1450 °C and 1500 °C liquid phase formed, filling some of the pores and thus reducing the apparent porosity. The apparent porosity of sample B decreases with the increasing temperature, with a sharp drop occurring at 1450 °C to 1500 °C.

3.2 Phase characteristics

O'-SiAlON, β-SiAlON, silicon and Si_3N_4 were detected in sample A at 1300 °C (Fig. 3a). The peaks of O'-SiAlON and β-SiAlON were lower at this temperature. At 1350 °C, 1400 °C and 1500 °C, only O'-SiAlON and β-SiAlON as the main phase were present. It

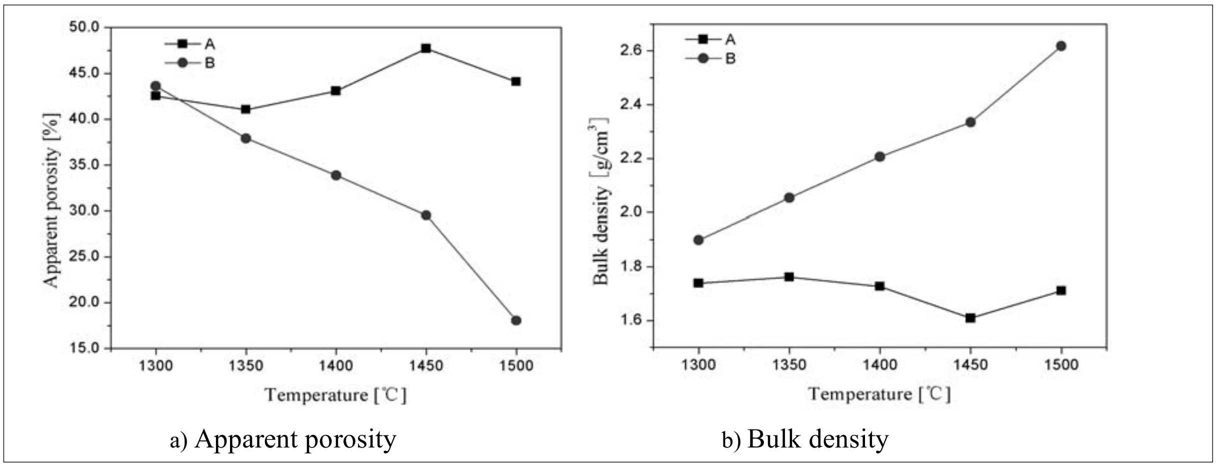

Fig. 2 Apparent porosity and bulk density of specimens at different nitriding temperatures

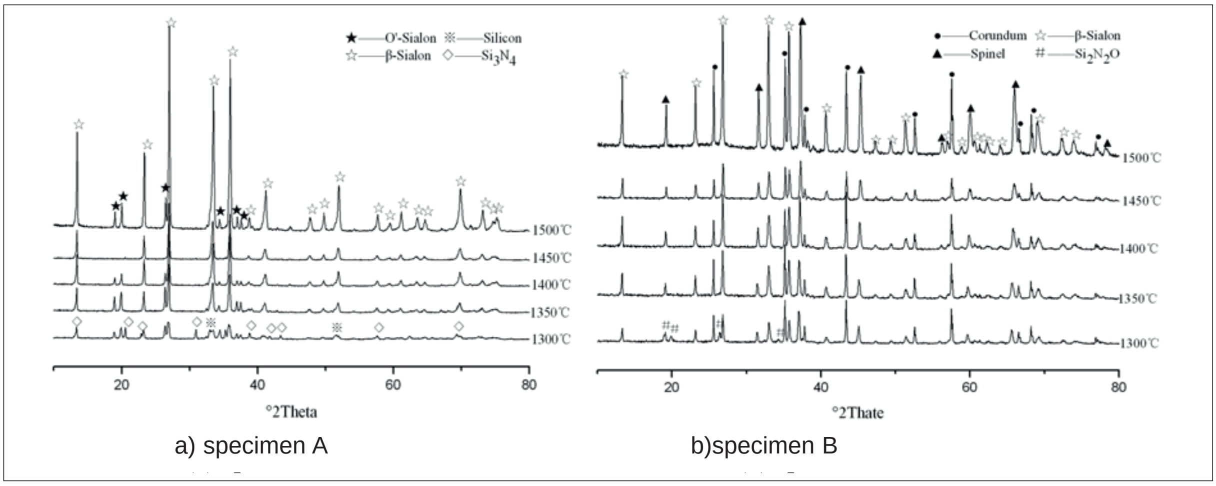

Fig. 3. XRD patterns of specimens at different nitriding temperature

is worthy to mention that, at 1450 °C, only β-SiAlON was found. The relative O'-SiAlON content decreased between 1350 °C and 1450 °C, disappeared altogether at 1450 °C, and then re-appeared at 1500 °C. The reason for this might be that O'-SiAlON reacted with N_2 to produce β-SiAlON. But this is a reversible reaction, and when the temperature increases beyond a certain limit, O'-SiAlON will appear again. As is shown in Fig. 3b, β-SiAlON, corundum, spinel ($MgAl_2O_4$) and Si_2N_2O were found in the XRD pattern of sample B at 1300 °C. At 1350 °C to 1500 °C, only β-SiAlON, corundum and spinel ($MgAl_2O_4$) were present. While the relative content of these phases shows no change with higher temperatures, the XRD peak increases significantly. This means increasing the temperature properly would be favourable for the crystal development.

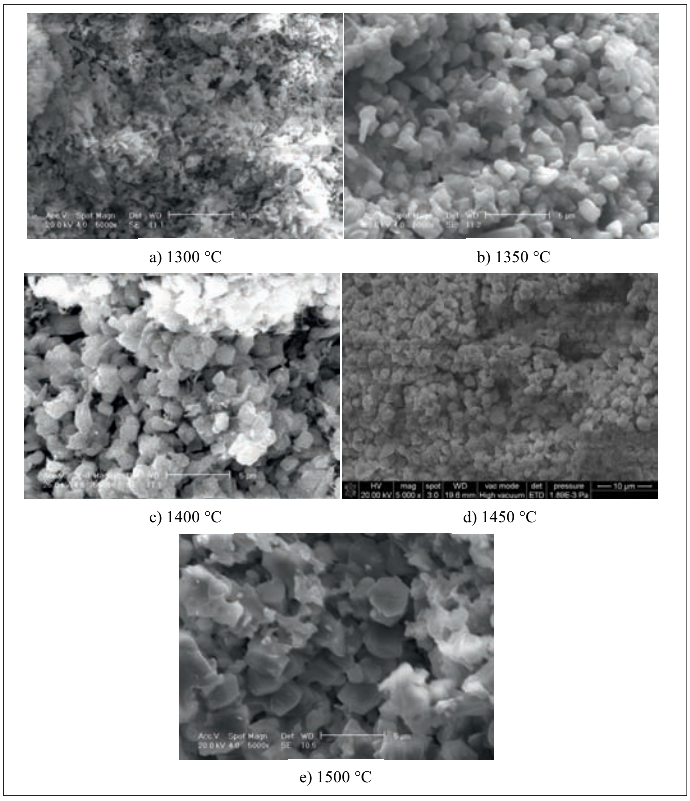

Fig. 4 SEM images of specimen A at different nitriding temperatures

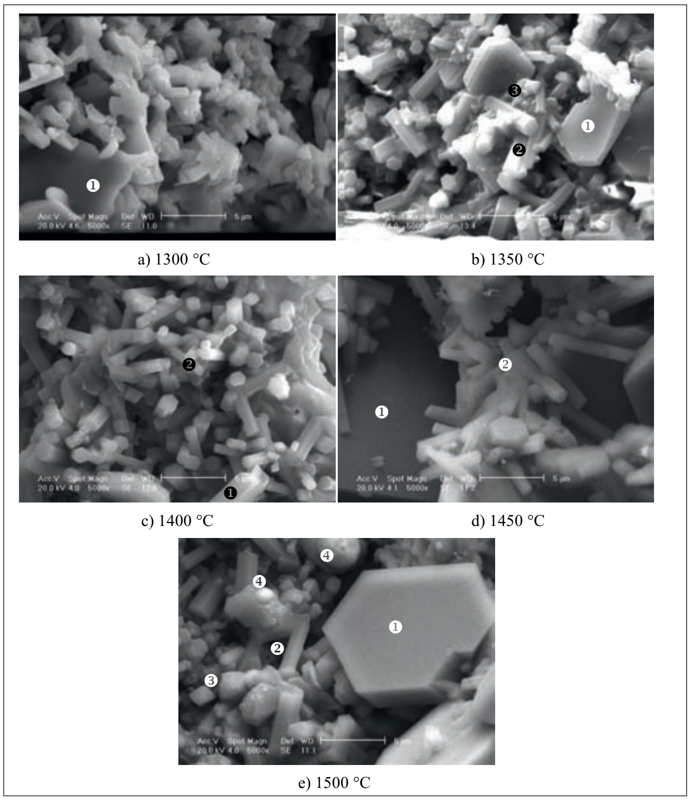

Fig. 5 SEM images of specimens B under different nitriding temperatures: 1 – corundum, 2 – SiAlON, 3 – $MgAl_2O_4$, 4 – fused drop

3.3 Microstructure

As is shown in Fig. 4a, at 1300 °C the size of the crystals is less than 0,5 µm and the shape is not uniform. At 1350 °C and 1400 °C, the size of SiAlON is up to 1,0 – 1,5 µm (Figs. 4b and 4c). Figure 4d shows that the SiAlON crystal has developed to form short prisms in sizes of 1,5 – 2,5 µm at 1450 °C (SEM, Nova NanoSEM 400, FEI, Netherlands). At 1500 °C, the SiAlON crystals occur as hexagonal prisms with a diameter of 3,0 – 3,5 µm (Fig. 4e); however, they also coalesce to form aggregates of irregular shape. This phenomenon is probably attributable to the high temperature.

The shape of the SiAlON crystals in sample B is not uniform at 1300 °C (Fig. 4a). At 1350 °C, they occur as hexagonal prisms associated with corundum and spinel crystals; their length is 3,0 – 3,5 µm and the diameter is 0,5 – 1,0 µm (Fig. 4b). At 1400 °C, the SiAlON crystals are growth interlaced and serried, with a length of 3,5 – 4,0 µm (Fig. 4c). After a further increase to 1450 °C (Fig. 4d), the length of SiAlON crystals is > 5,0 µm and they grow among or on the surface of corundum crystals. A temperature of 1500 °C causes further growth of the SiAlON crystals to between 1,5 and 2,0 µm (Fig. 4e), with some fused drops measuring 1,0 – 3,0 µm. At the same time, the crystals form aggregates at this high temperature. In all of the SEM images of sample B, corundum developed to plate-like crystals and spinel crystals with regular octahedral morphology.

4 Conclusions

The experiments for synthesizing SiAlON and a SiAlON composite material from aluminium dross allow some conclusions to be drawn as follows:

- In the experiment for synthesizing SiAlON, single-phase β-SiAlON was successfully generated by firing the specimens to 1000 °C for 1 h and then at 1450 °C for 4 h, with an N_2 flow of 0,5 l/min. At this temperature, the apparent porosity of the specimens was highest.
- In the experiments for synthesizing SiAlON composite material, SiAlONs crystallized as hexagonal prisms, growing among or on the surface of corundum crystals. The optimum temperature was between 1400 °C and 1450 °C.

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