

# Formation mechanism of 21R AlN-polytypoids in aluminothermic reduction and nitridation process

Y. W. Li · G. H. Zhou · S. L. Jin · N. Li

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**Abstract** Synthesis of 21R AlN polytypoids was investigated using Al and ultrafine SiO<sub>2</sub> powder in a flowing nitrogen atmosphere by means of thermal gravity (TG), differential scanning calorimeter (DSC), X-ray diffractometer (XRD) and scanning electronic microscope (SEM) linked with energy dispersive spectrometer (EDS). The results showed that the formation mechanism of AlN polytypoids was different from that in reaction sintering process using Si<sub>3</sub>N<sub>4</sub>, AlN, Al<sub>2</sub>O<sub>3</sub> and other sintering additive as raw materials. It was suggested that firstly Al reduce SiO<sub>2</sub> into Si and is also nitrided into AlN, then AlN, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> dissolve into silicon liquid until the AlN polytypoids precipitate in saturated liquid in a flowing nitrogen atmosphere at lower than 1700 °C.

## Introduction

It is well known that sialon ceramics are a family of materials that possesses high performance properties at elevated temperatures and are very useful materials for high temperature application. Among sialon family, at the compositions between  $\beta$ -sialon and AlN in the corner of Si–Al–O–N system, there exist six structurally related phases having compositions represented as  $M_mX_{m+1}$  ( $M = \text{Al, Si}$ ;  $X = \text{N, O}$ ), which were observed by Jack and Gauckler et al in 1973 and 1975, respectively, assigned to be AlN polytypes or polytypoids based on the tetrahedral layer

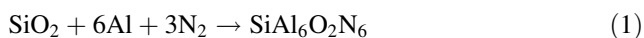
structure of the AlN wurtzite type and designated with Ramsdell symbols (8H, 15R, 12H, 21R, 27R and 2H<sup>δ</sup>) [1, 2]. Since the establishment of the Si–Al–O–N phase diagram, most of studies on AlN-polytypoids have been concentrated on their crystal structures and are scarcely involved in considering them as structural materials because of their poor mechanical properties. However, recently, their formation and mechanical properties of the AlN-polytypoids are also greatly intrigued owing to their needle or elongated platelet morphology and the compatibility with  $\beta$ -sialon (except 8H) and  $\alpha$ -sialon (except 8H, 15R), which offers the possibility to incorporate polytypoids phase into  $\alpha$ -and/or  $\beta$ -sialons forming composite ceramics where an in situ strengthening and toughening effect could be achieved [3–5]. Generally, in order to obtain these dense AlN polytypoids and their composite ceramics, the high pure Si<sub>3</sub>N<sub>4</sub>, AlN, Al<sub>2</sub>O<sub>3</sub>, and rare earth sintering additives such as Y<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, etc, were adopted as raw materials, and compacted pellets were hot-pressed or gas-pressed at high temperatures (above 1700 °C) in the process [6–9]. Mazzoni et al. reported an alternative method to obtain phases of Si–Al–O–N system via aluminothermic reduction and nitridation of high silica minerals such as diatomite and bentonite at the range of 1250–1650 °C. A great deal of AlN polytypoids accompanying with corundum,  $\beta$ -sialon phases occurred in the final product fired at 1350–1650 °C. Although the reaction sequence was also discussed, the formation mechanism was emphatically pointed out [10]. In fact, AlN polytypoids, together with other nitride ceramics are promising candidates for advanced refractories, which theoretically have good thermo-chemical stability and low solubility in liquid steel at high temperatures, so in-situ nitridation process as a feasible approach has been widely taken to synthesize nitride ceramics for advanced refractories [11–14].

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The aim of this paper is to report emphatically the precipitation of AlN polytypoids from the silicon-richened melt in aluminothermic reduction and nitridation process at lower than 1700 °C, which is different from formation mechanisms in reaction sintering process where AlN polytypoids precipitate from transient liquid at higher than 1700 °C using Si<sub>3</sub>N<sub>4</sub>, AlN, Al<sub>2</sub>O<sub>3</sub> and other sintering additive as raw materials.

## Experimental

The starting materials in this experiment were SiO<sub>2</sub> ultra-fine powder (98.3%SiO<sub>2</sub>, Elkem company, Norway) and aluminium powder (99%Al, Wuhan Iron and Steel company, China) and α-Al<sub>2</sub>O<sub>3</sub> reactive powder (99.9%Al<sub>2</sub>O<sub>3</sub>, Kaifeng special refractory factory, Henan province, China). The Al/SiO<sub>2</sub> ratio in the mixture was based on the following reaction Eq. (1) in order to synthesize the 21R AlN polytypoids.



Meanwhile, 14.3% of α-Al<sub>2</sub>O<sub>3</sub> as a diluent was added in the mixture. The powders were mixed with alcohol and milled in a corundum container for 1 h, dried and then pressed into cylindrical samples (20 mm in diameter, 20 mm in length) under 50 MPa. The samples were placed in a graphite crucible, and treated within the range of temperatures (700–1600 °C) for the same duration of 3 h in vertical corundum tube heated by a MoSi<sub>2</sub> element at a rate 3 °C/min. The nitrogen used was an industrial gas with nitrogen content of 99.9%. Before heating, the chamber was flushed with N<sub>2</sub> gas for several minutes. The pressure of a flowing nitrogen was maintained slightly above 1 atm in the furnace through the reactions. Differential thermal analyses and gravimetric analyses were carried out in Netzsch STA 449C in N<sub>2</sub> at a flow rate of 30 ml/min. The reaction products were examined by X-ray diffractometer (XRD, X'Pert Pro, Philips) and the microstructure of composites was observed under scanning electron microscope (SEM, XL-30TMP, Philips) linked with energy dispersive spectrometer (EDS). Moreover, in order to find out the phase evolution of Al/SiO<sub>2</sub> mixture in N<sub>2</sub> atmosphere during 700–1600 °C, all the phases in the reaction progress were quasi-quantitatively estimated according to the intensity of the phase to be characterized. For example, 21Rwt% in the products was based on Eq. (2) by using the intensities of the diffraction lines of [*d* = 3.48 (012)] for α-Al<sub>2</sub>O<sub>3</sub>, [*d* = 3.13 (111)] for Si, [*d* = 2.02 (200)] for Al, [*d* = 2.49 (002)] for AlN, [*d* = 3.32 (020)] for Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> and [*d* = 2.60–2.80] for AlN-polytypoids. Similar

equations were used to estimate the relative contents of α-Al<sub>2</sub>O<sub>3</sub>, Si, AlN, and Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> phases.

$$21\text{Rwt}\% = \frac{I_{21\text{R}}}{I_{21\text{R}} + I_{\alpha\text{-Al}_2\text{O}_3} + I_{\text{Si}} + I_{\text{Al}} + I_{\text{AlN}} + I_{\text{Si}_3\text{Al}_3\text{O}_3\text{N}_5}} \times 100\% \quad (2)$$

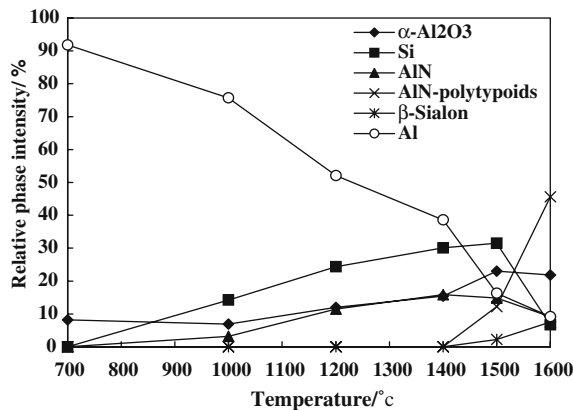
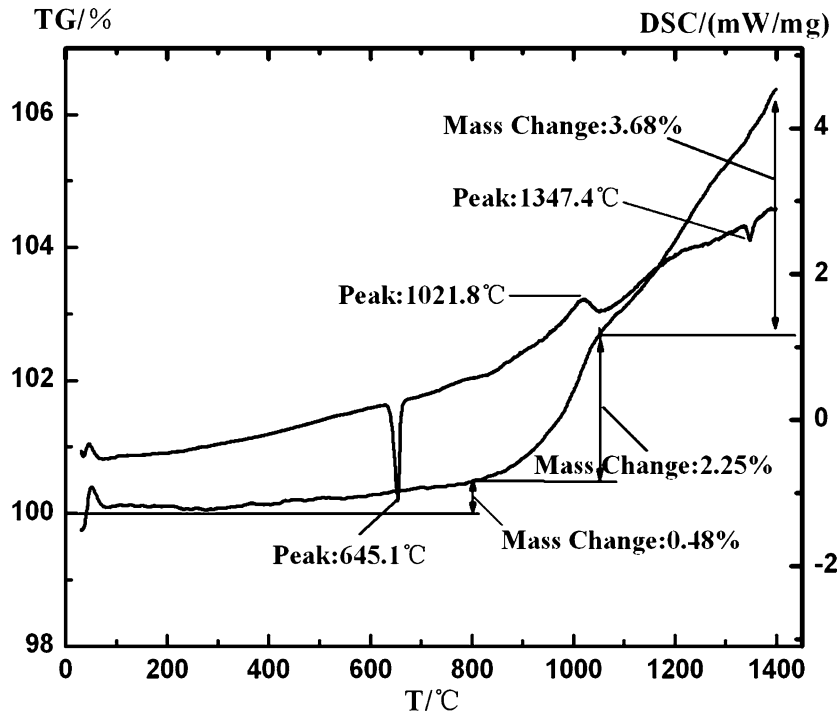
## Results and discussions

DSC-TG curves of metal Al and SiO<sub>2</sub> mixture in N<sub>2</sub> atmosphere given in Fig. 1 shows that the first endothermic peak appears at 654.1 °C corresponding to aluminium melting and a broad exothermic band between 700 °C and 1021.8 °C, with weight gains of 0.48% and 2.25%, respectively, which is associated with the remarkable aluminothermic reduction and nitridation reactions. Such the phenomena are confirmed by the formation of Si and AlN phases and increase of α-Al<sub>2</sub>O<sub>3</sub> in the product by XRD analysis. From 1030 °C to 1400 °C, there is a second exothermic band resulting from that reactions proceed strongly with much weight gain of 3.68%. At 1347.4 °C, it seems as if the endothermic peak were indicative of silicon melting, which is lower than the melt-point of silicon (1412 °C) due to mainly containing silicon in its complicated composition instead of pure silicon at that time.

The phase variation of the Al/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixtures in N<sub>2</sub> atmosphere during 700–1600 °C is semi-quantitatively plotted in Fig. 2 according to Eq. (2), especially its XRD patterns at 1400–1600 °C are also shown in Fig. 3. Up to 1000 °C little amount of Si and AlN begin to occur in the product. At 1200 °C and 1400 °C still only silicon, AlN, corundum and residual Al are presented in the sample; however, the amount of different phases varies at elevated temperatures. Up to 1500 °C, 21R phase begins to appear with little amount of β-sialon phase in the products. At 1600 °C, the peak of 21R and β-Sialon phase continues to intensify with the formation of two other AlN-polytypoids 15R and 12H while the amount of Si and Al, AlN and Al<sub>2</sub>O<sub>3</sub> decrease obviously in the reaction process. So, it is regarded that the above system is still in a non-equilibrium state, even if at 1600 °C, as the number of crystalline phases in the compositions of the present work is only 3 phases, for example, a beta sialon and two AlN polytypoids phases according to the sialon phase diagram.

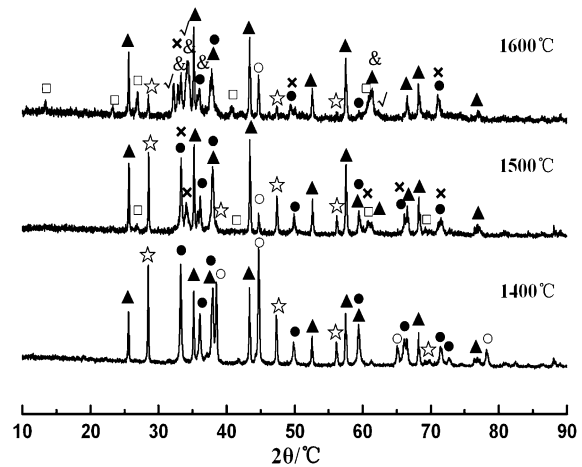
After all the samples are cleaved, it is found that the edge area is much denser than the center area at the cross sections, especially in the samples treated at higher than 1400 °C. The center area of the samples is loose and almost separated from the different size of the pores;

**Fig. 1** DSC-TG of Al/SiO<sub>2</sub> mixture in a flowing N<sub>2</sub> atmosphere



**Fig. 2** The phase evolution of Al/SiO<sub>2</sub> mixture against different temperatures

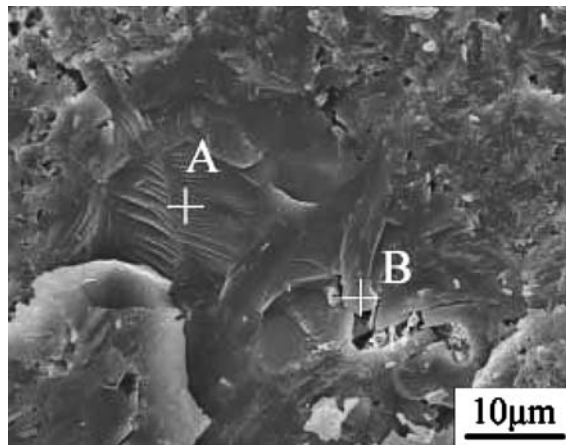
however, the conchoidal fractured dense area at the edge is connected with each other. The phenomena are well explained by mass transport from the center to the edge in these samples. In fact, the primary green sample containing large amount of Al content is heated up over 700 °C, Al particles in the samples become coherent, subsequently the pores are sealed in internal compact instead of immediate remove out of the samples with a parallel to aluminum reduction of SiO<sub>2</sub>. With the increase of temperatures, the gas in pores will tend to expand and its high pressure will drive the melt containing Al and Si around pores moving from the center to the edge and filling the space between



**Fig. 3** X-ray diffraction patterns of samples nitrided at different temperatures. ▲-αAl<sub>2</sub>O<sub>3</sub> ○-Al ●-AlN ☆-Si □-Si<sub>3</sub>Al<sub>3</sub>O<sub>3</sub>N<sub>5</sub> √-15R(SiAl<sub>4</sub>O<sub>2</sub>N<sub>4</sub>) &-12H(SiAl<sub>5</sub>O<sub>2</sub>N<sub>5</sub>) ×-21R(SiAl<sub>6</sub>O<sub>2</sub>N<sub>6</sub>)

the particles. Such mass migration causes the inhomogeneous structure and chemical compositions in the samples.

By means of scanning electronic microscope it is not difficult to observe many plate-like grains located around the dense area in the samples heated at 1500 °C and 1600 °C. The morphology of the dense area of sample heated at 1600 °C and the result of EDS analysis are shown in Fig. 4 and Table 1, respectively. The dense area consists of mainly Si element (Point A) with less Al, O, N elements, and plate-like grains (Point B) contains more Al, O, N

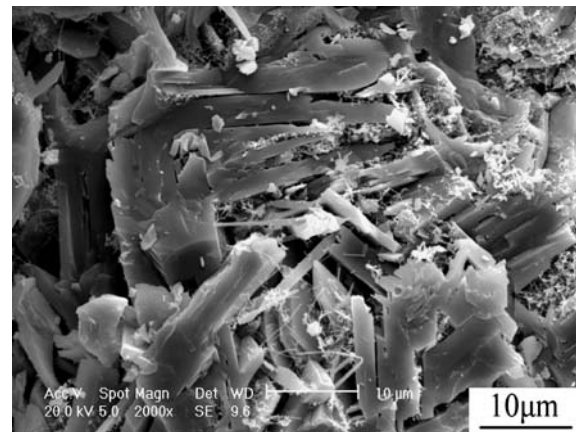


**Fig. 4** The micrographs of the samples heated at 1600 °C

**Table 1** EDS analysis of t Points A and B

Element	A		B	
	Wt%	At%	Wt%	At%
NK	06.44	11.91	11.54	19.50
OK	02.48	04.01	06.64	09.83
AlK	01.73	01.66	50.30	44.12
SiK	89.35	82.41	31.52	26.56

elements as if it were much nearly identical with the composition of the AlN-polytypoids. Typical plate-like grains located in other part of sample is presented in Fig. 5. Although it is difficult to determine which AlN polytypoids it is in the sample combining with the results of XRD, it is undoubtedly concluded that the formation of the AlN polytypoids is closely associated with the conchoidal substance containing a great amount of Si element around them. It is well known that the formation mechanism of the AlN polytypoids belong to dissolution—precipitation process reported in the literature. So, it is deduced that in a flowing nitrogen atmosphere firstly Al reduce  $\text{SiO}_2$  into Si and also is nitrided into AlN, then AlN,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  dissolve into silicon liquid until the AlN polytypoids precipitate in saturated liquid. Such liquid is at least related to silicon phase in samples because there is still a great



**Fig. 5** The micrographs of the samples heated at 1600 °C

amount of silicon phase in the samples heated at 1500 or 1600 °C, at which Si is in molten state, although it is still in research to know clearly what is the chemical composition of liquid.

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