

Effect of raw materials on carbothermal reduction synthesis of γ -aluminum oxynitride spinel powder

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The effect of starting Al_2O_3 materials on synthesis of γ -aluminum oxynitride spinel (γ -AION) powder by carbothermal reduction has been investigated. Whether using $\text{Al}(\text{OH})_3$, boehmite, dried gel, or calcined alumina as an alumina source, the reaction rate is faster than that using α - Al_2O_3 . That is because the oxygen distribution in γ - Al_2O_3 is cubic close packed as the non-metal arrangement in AION spinel is whereas that in α - Al_2O_3 is hexagonal close packed. When hydrated aluminas used lose structural water and transform into γ - Al_2O_3 in heating cycle, γ - Al_2O_3 is easily reduced and nitrated into AION spinel after a slight adjustment in the cation positions and proportions is made in the reduction process of alumina. The particle morphology of the product after carbothermal reduction was strongly influenced by the type of alumina source employed, which suggests the mechanism of $\text{Al}_2\text{O}_3/\text{C}$ powder mixtures in a flowing N_2 stream is the absorption of aluminum-containing gas, such as $\text{Al}(\text{g})$, $\text{Al}_2\text{O}(\text{g})$, etc., on the surface of aluminum oxide in the initial stages, followed by reaction with N_2 gas to form AION and AlN phases with nucleation, and growth on Al_2O_3 particle surfaces. © 1999 Kluwer Academic Publishers

1. Introduction

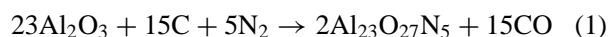
γ -Aluminium oxynitride spinel (γ -AION) has attracted much attention as a high temperature window material because of its optical, dielectric and mechanical properties [1, 2]. In addition to this, AION material has other excellent properties such as resistance to oxidation and chemical attack; it is moreover a potential engineering ceramic [3]. In order to make this material commercially viable, it is important to develop routines for manufacturing fine, high-purity AION powders [2]. Several methods have been used to synthesize AION powder, including reaction sintering of AlN and Al_2O_3 , and carbothermal reduction of Al_2O_3 [4–6], etc. In fact, reduction of Al_2O_3 is the most popular method for preparing AION powder. However, so far, almost no researchers have investigated the effects of different raw materials on the product powder.

The present work does this and compares the reaction rate and the morphologies of the samples by SEM before and after nitridation.

2. Experimental

Five kinds of Al_2O_3 raw materials and one type of carbon black were used in our experiments. The properties of the starting powder are shown in Table I, with the

exception of the alumina sol-gel, which was obtained by dissolving boehmite powder in acid solution, stirring the slurry and then depositing it for 24 hours. The average particle sizes of alumina powders were measured using a particle-size analyzer (MasterSizer Serial No.6100. Malvern Instrument Ltd. Malvern, UK). Samples of the alumina sources were analyzed with DTA and TGA (7 Series Thermal Analysis System, Perkin Elmer, USA). The powders were mixed with carbon using anhydrous ethanol as the dispersion medium in a corundum blender; however carbon black was mixed directly with deposited alumina sol-gel. The ratio of $\text{Al}_2\text{O}_3/\text{C}$ was calculated from reaction (1):



based on the work of McCauley, who reported $\text{Al}_{23}\text{O}_{27}\text{N}_5$ as the ideal spinel composition for AION spinel [7]. The mixtures were reacted in a perforated graphite crucible in a furnace using a graphite element heater at 1550 and 1800 °C for 0.5–3 h in a flowing nitrogen stream. After the reaction, the products were heated at 700 °C for 3 h in air to remove residual carbon.

The products were characterized by X-ray powder diffractometry (D/Max-III A, manufactured by Rigaku

TABLE I Raw materials used

Code	Name	Al ₂ O ₃ (%)	K ₂ O (%)	Na ₂ O (%)	Ignition loss (%)	Average particle size <i>d</i> ₅₀ (μm)
A	Gibbsite	64.81	0.02	0.14	34.70	~6
B	Boehmite	76.78	0.03	0.33	22.78	~7
C	α-Alumina	99.19	Trace	0.03	0.18	~6
D	Calcined alumina	99.2	0.03	0.21	—	~4
E	Carbon black	Fixed carbon (%)	Ash (%)	Volatimatter (%)	Ignition loss (%)	Residual sulphur (%)
		97.68	1.14	1.18	0.69	0.36

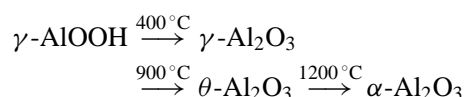
Corporation, Japan) and scanning electron microscopy (SEM). The relative quantities of phases were based on the XRD intensity of the product powders. The experimental procedure has been described in detail previously [8, 9].

3. Results and discussion

3.1. The thermal behavior of raw materials

TGA and DTA heating curves for gibbsite, calcined alumina, boehmite, and the dried gel are shown in Fig. 1. Curve (a) is consistent with the expected thermal behavior of gibbsite. When heated to 247 °C, gibbsite began to dehydrate part of the structural water, and then transformed into boehmite after further dehydration at 331 °C. Up to 538 °C, the weight loss was 35.0%, almost equal to the theoretical weight loss of 34.6%. Subsequently, γ-Al₂O₃ formed and transformed into α-Al₂O₃ at 1249 °C. For Curve (b), alumina was produced by calcination of gibbsite at 600 °C, so it only lost absorbed water at 100 °C. Curves (c) and (d) seemed to show similar thermal weight changes, with total weight

losses of 33.0% for boehmite and 35.0% for dried gel. This may be because the dried gel was manufactured using boehmite as its precursor, which mainly consists of boehmite with a little gibbsite phase. XRD patterns of the dried gel indicated that phase transformation occurred with increasing heating temperature (Fig. 2) and the thermal dehydration sequence can be summarized as [10]:



3.2. The reaction sequence of alumina/carbon

The results of the reaction in Al₂O₃-C-N₂ system for different alumina sources at 1550 and 1800 °C are shown in Figs 3 and 4, respectively. The temperatures selected were below and above 1650 °C, which is a controversial temperature for the stability of the AlON phase [11]. The results can be described as follows:

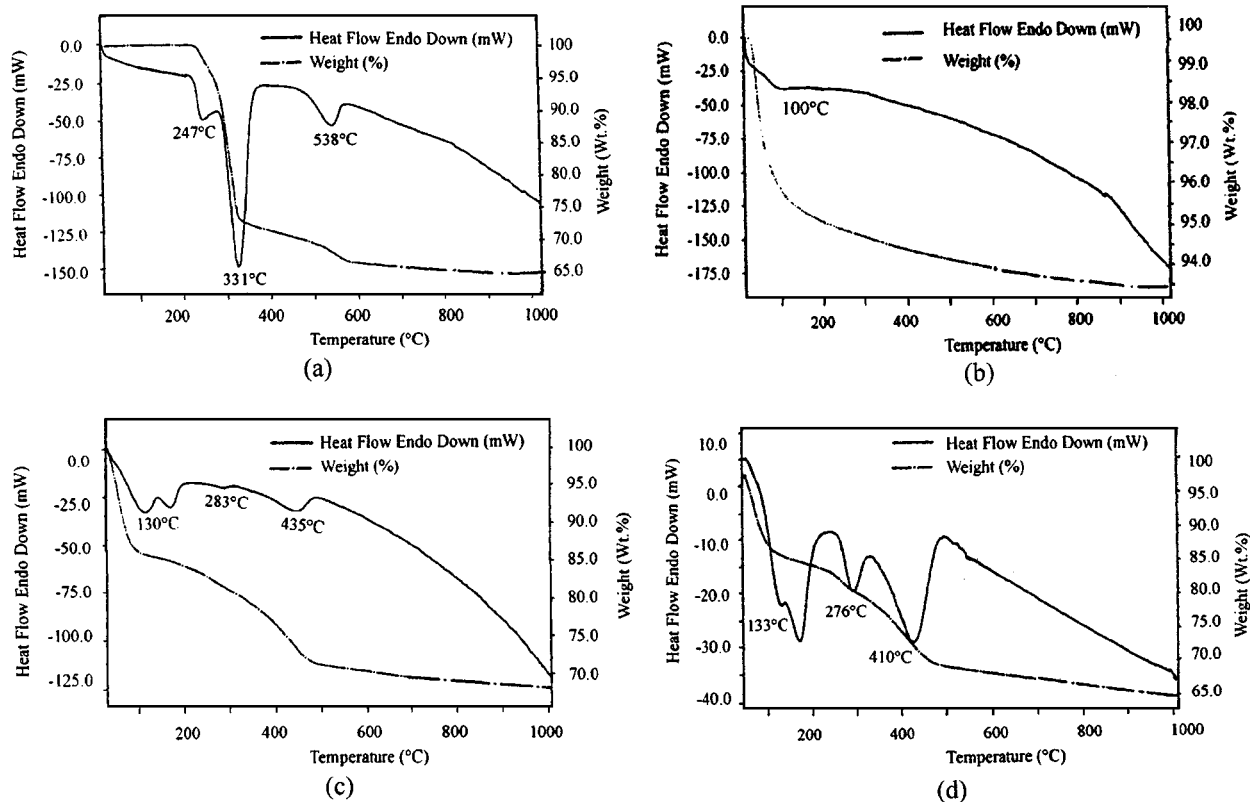


Figure 1 TGA and DTA curves of raw materials: (a) gibbsite, (b) calcined alumina, (c) boehmite and (d) dried gel.

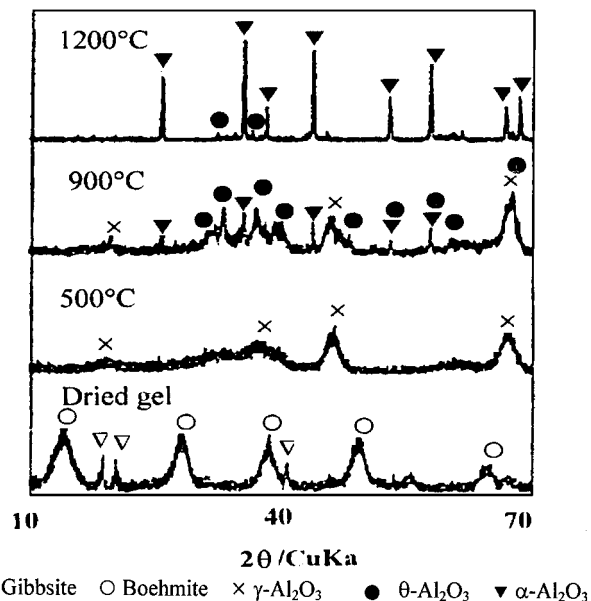


Figure 2 XRD patterns of dried gel heated at 500, 900 and 1200 °C.

1. Whether at 1550 or 1800 °C, the AION phase appeared with AlN and Al₂O₃ in the reduction process. At 1550 °C, the AION content first increased with time and then decreased as the content of AlN and corundum went up, because the formation of AION was related to P_{N_2} and P_{O_2} . In our experiments, the carbothermal reduction reaction was performed in an open furnace in a flowing nitrogen stream, so the P_{N_2} and P_{O_2} condi-

tions around the samples were not constant during the reaction. With reference to activity diagrams for P_{N_2} and P_{O_2} [11, 12], the stable region of AION is narrower and longer in comparison with other phases and AION is easily transformed into AlN and Al₂O₃. At 1800 °C the content of AION always increased vs. time in the reaction process. This may result from the wider range of AION stability at this temperature than at 1550 °C [12].

2. It was quite evident that the type of alumina raw materials used strongly influenced the reaction evolution. Whether Al(OH)₃, boehmite, dried gel, or calcined alumina used as an alumina source, the reaction rate was faster than that for α -Al₂O₃ at 1550 or 1800 °C. The reason for this is that when aluminum oxyhydrate loses structural water, it transforms into γ -Al₂O₃, and γ -Al₂O₃ has a higher reactivity than α -Al₂O₃ [13, 14]. However, it was found in our previous experiments, that the AION phase is an intermediate compound in the carbothermal reduction process [9, 15]. This means that γ -alumina is first reduced into AION spinel, and then the AION phase is further nitrided into AlN. Such a conclusion suggests a relationship between the crystalline structural changes taking place on the alumina sources during the heating cycle and the reaction product. In the process of rapid heating, Al(OH)₃, boehmite, dried-gel, and calcined Al(OH)₃ changed into γ -Al₂O₃, then it subsequently easily reduced and nitrided into AION, which has the same cubic symmetry as γ -Al₂O₃. The situation is different for α -Al₂O₃, which has the rhombohedral symmetry. That is to say, the oxygen

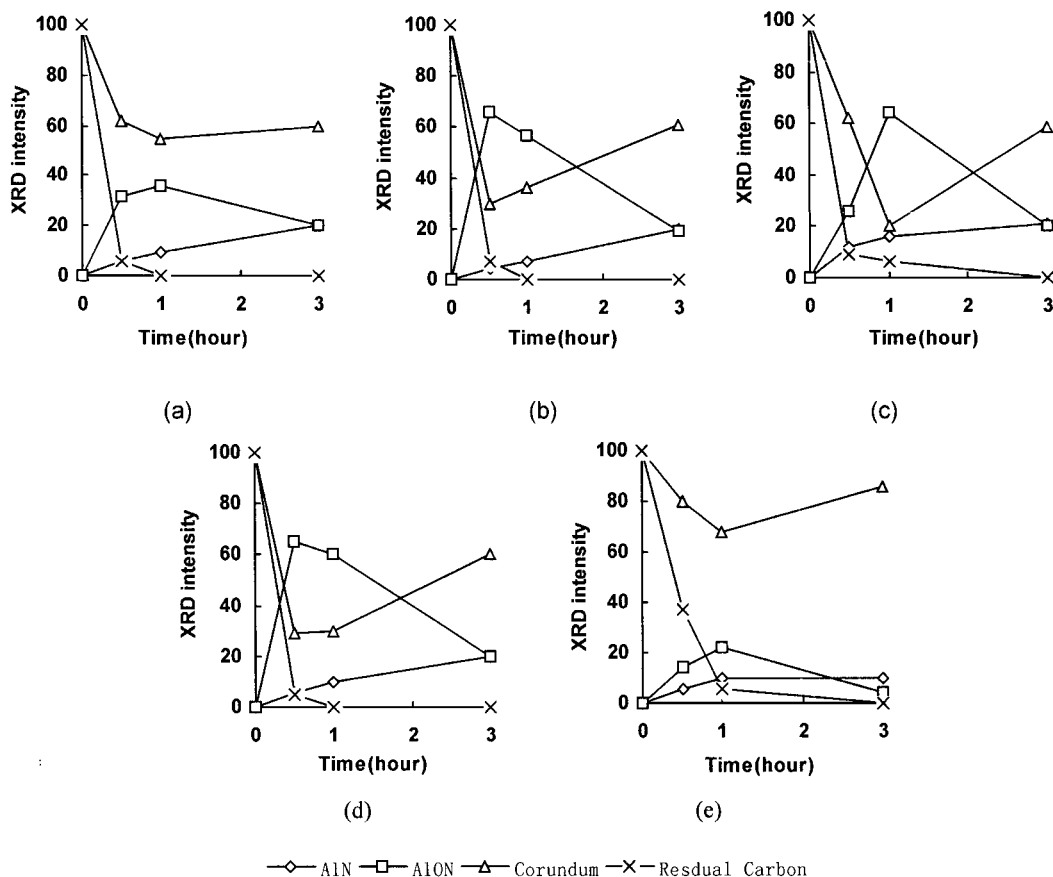


Figure 3 Reaction rates for different alumina sources and carbon: (a) Al(OH)₃, (b) boehmite, (c) dried gel, (d) calcined alumina, (e) α -alumina. N₂ flowrate: 0.04 m³/h, heating temperature: 1550 °C.

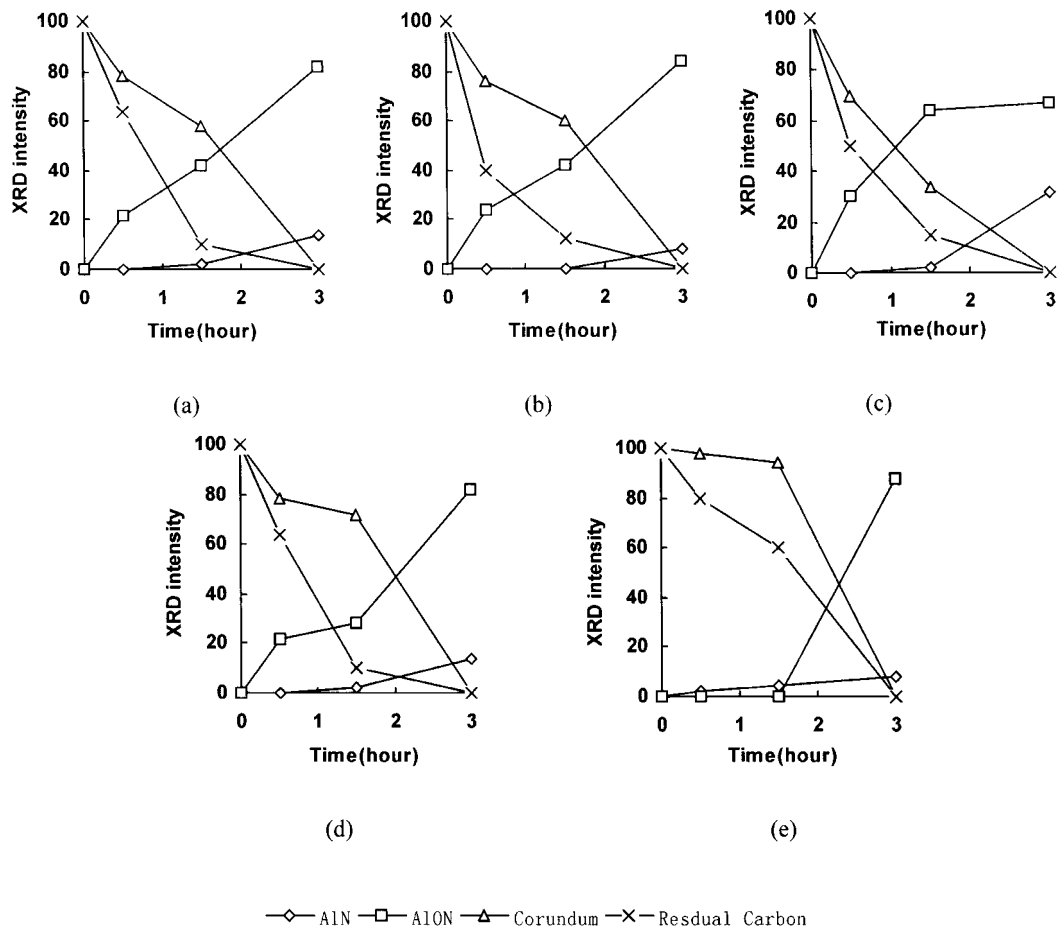


Figure 4 The evolution of the reaction of different alumina sources and carbon: (a) Al(OH)₃, (b) boehmite, (c) dried gel, (d) calcined alumina, (e) α -alumina. N₂ flowrate: 0.05 m³/h, heating temperature: 1800 °C.

distribution in their dehydrated alumina, γ -Al₂O₃ is cubic close packed, and that in α -Al₂O₃ is hexagonal close packed. And since the non-metal arrangement in AION is cubic close packed, essentially the non-metals do not need to move, and all that happens is a slight adjustment in the cation positions and proportions in the reduction of alumina into AION.

3. When dried gel was used, the reaction rate was faster than for other mixtures and a lot of AIN remained in the final product because the dried gel was of high reactivity. In this case much more aluminum containing gases, e.g. Al(g), Al₂O(g), AlO(g), etc. were easily produced in the reduction process in a time comparing with other alumina sources used. Some of these gases possibly escaped with flowing N₂ into the air, leading to excess carbon in the mixture in contrast with reaction (1), and the excess carbon further reduced and nitrated as-produced AION into AIN.

3.3. Sample morphology before and after nitridation

Fig. 5 shows SEM micrographs of samples, before and after nitridation at 1550 °C for 1 h in a nitrogen flowrate of 0.4 m³/h. In all samples before nitridation, the finer particles were carbon black that adhered to the surface of the alumina powder particles. After nitridation, the particle morphologies of the samples were homogeneous and strongly correlated with that of the alumina

powder used [13, 14, 16], when the same carbon black was used as the source of carbon, even though XRD analysis revealed that the products consisted of AIN, AION and corundum. Asoke, Chaklader *et al.* [17] found similar results in their experiments on carbothermal reduction of aluminosilicate precursors to manufacture Al₂O₃/SiC composites. The morphology of the SiC particles formed *in situ* depended on the nature of the carbon source added, and involved a reaction between SiO gas absorbed on the surface of the carbon resulting in the nucleation and growth of SiC on carbon particles.

Considering the phenomenon of AIN whiskers appearing on samples after nitridation [18], which indicated that gases containing aluminium were being produced during the carbothermal reduction process [6, 12, 19, 20] and the fact of AION as an intermediate phase in this process, the mechanism of Al₂O₃/C powder mixtures in a flowing nitrogen stream is suggested as being the absorption of Al(g), Al₂O(g), etc., on the surface of aluminum oxide in the initial stages, followed by reaction with N₂ gas to form AION and AIN phases with nucleation, and growth taking place on Al₂O₃ particle surfaces. Fig. 6 shows the equilibrium temperature dependence of log P_{Al_xO_y} in the Al₂O₃-C-N₂ system. Al(g) and Al₂O(g) are the highest partial pressure gases to be produced in the reaction system [12, 19], which is different from a previous report that Al₂O(g) and AlO(g) are the possible gases [20].

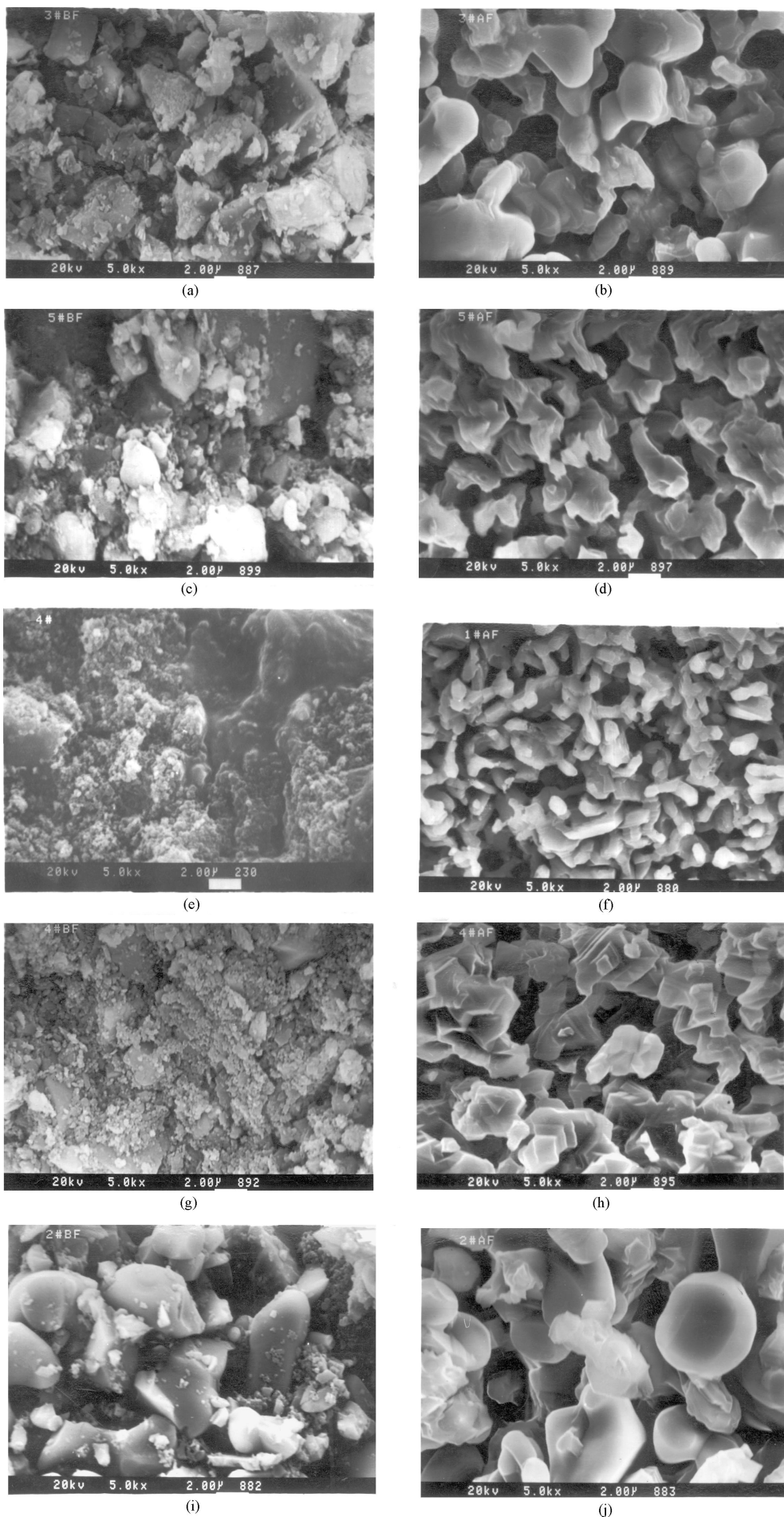


Figure 5 SEM micrographs, before (left) and after (right) nitridation (1550 °C): (a, b) Al(OH)₃, (c, d) boehmite, (e, f) dried gel, (g, h) calcined alumina, (i, j) α-alumina.

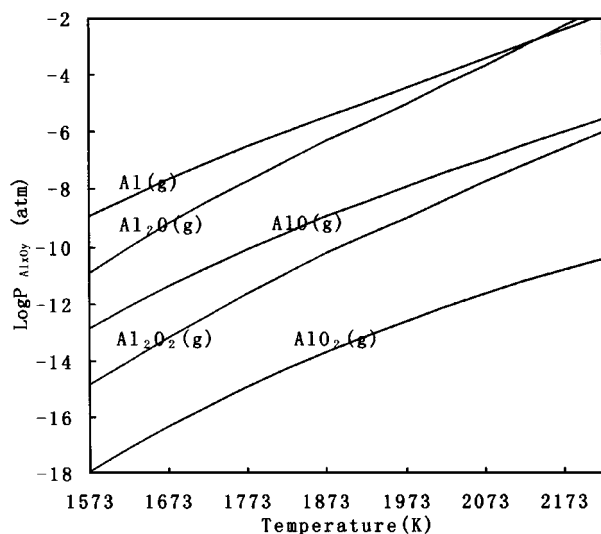


Figure 6 The equilibrium temperature dependence of $\log P_{Al_xO_y}$ in the Al_2O_3 -C- N_2 system [12].

4. Conclusions

1. The type of alumina source used significantly influenced reaction progress in Al_2O_3 -C- N_2 systems. Whether $Al(OH)_3$, boehmite, dried gel, or calcined alumina were used as the alumina source, the reaction rate was faster than that using α - Al_2O_3 . That is because the oxygen distribution in γ - Al_2O_3 is cubic close packed, and that in α - Al_2O_3 is hexagonal close packed. Similarly, the non-metal arrangement in AlON spinel is cubic close packed. When hydrated aluminas used lose structural water and transform into γ - Al_2O_3 , it is easily reduced and nitrided into AlON spinel after a slight adjustment in the cation positions and proportions is made in the reduction process of alumina into AlN.

2. The particle morphology of the product after carbothermal reduction was strongly influenced by the type of alumina source employed, which suggests the mechanism of Al_2O_3 /C powder mixtures in a flowing N_2 stream is the absorption of aluminum-containing gas, such as $Al(g)$, $Al_2O(g)$, etc., on the surface of aluminum oxide in the initial stages, followed by rea-

ction with N_2 gas to form AlON and AlN phases with nucleation, and growth on Al_2O_3 particle surfaces.

Acknowledgements

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