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The formation and stability of γ-aluminium oxynitride spinel in the carbothermal reduction and reaction sintering processes

LI YAWEI, LI NAN
School of Materials Science and Engineering, Wuhan Yejin University of Science and Technology, 430081, People's Republic of China

YUAN RUNZHANG
Institute of Advanced Materials, Wuhan University of Technology, 430070, People's Republic of China

Several methods of manufacturing γ-aluminium oxynitride spinel (ALON) powder are discussed in this paper. In the carbothermal reduction process, ALON is an intermediate compound, and powders with a high ALON content may be produced in flowing nitrogen below 1650 °C if process parameters are carefully controlled. In addition, ALON may be produced when Al_2O_3/C mixtures are heated in a coke powder bed above 1650 °C. In the reaction sintering process, ALON is unlikely to form below 1600 °C in a flowing nitrogen atmosphere or in a coke powder bed, owing to the instability of ALON and the fact that the solid–solid reaction does not readily occur unless additives, e.g. MgO, $MgAl_2O_4$, are employed.

1. Introduction

γ-Aluminium oxynitride spinel (ALON) is a new material in the AlN–Al_2O_3 system, which was first found by Yamaguchi, and colleagues in 1946 [1]. Since then, much attention has been paid to its phase diagram, composition and structure, synthesis, mechanical, dielectric, optical and chemical properties [2]. However, there is still much work needed to optimize this material. Willems, *et al.* [3] conducted experiments using carbothermal reduction of alumina and reaction sintering of AlN–Al_2O_3 mixtures to investigate the stability of the ALON phase and found that in their experiments it indeed appeared in carbothermal reduction or reaction sintering processes only above 1650 °C. It seemed that ALON produced by reduction synthesis above 1650 °C resulted from reaction at inner AlN/Al_2O_3 interfaces [4]. This confirms the difficulty of producing ALON powders at temperatures below 1650 °C, and it is difficult to explain other results which suggest that a high content of ALON powder can be obtained at 1580 °C [5].

The present work repeats previous experiments on the carbothermal reduction of alumina and reaction sintering of AlN–Al_2O_3 mixtures in order to elucidate the temperature of formation of ALON in different systems.

2. Experimental procedure

The starting materials used were calcined alumina, AlN and carbon black, whose chemical compositions are listed in Table I. The calcined alumina was prepared by dehydration of $Al(OH)_3$ at 600 °C for 3 h and then wet-grinding in a blending mill. AlN and carbon black powders are as-received. Carbothermal reduction of alumina and reaction sintering of AlN and Al_2O_3 were employed to prepare ALON powders.

In carbothermal reduction of alumina experiments, the ratio of Al_2O_3/C in the mixture was chosen to lie in a certain range. Two groups of mixtures were batched according to Reactions 1 and 2. All the mixtures were treated in a flowing stream of nitrogen at 1550, 1600 and 1650 °C, or in a coke powder bed.

$$Al_2O_3 + 3C + N_2 \rightarrow 2AlN + 3CO \quad (1)$$

$$23Al_2O_3 + 15C + 5N_2 \rightarrow 2Al_{23}O_{27}N_5 + 15CO \quad (2)$$

In the reaction sintering experiments, the ratio of AlN to Al_2O_3 in the mixture was based on the ideal composition of the ALON ($5AlN \cdot 9Al_2O_3$) [6].

The products were characterized by means of X-ray powder diffraction analysis. The relative quantities of phases were based on the XRD intensity of the product powders. The experimental procedure has been described in detail previously [7].

3. Results and discussion

3.1. The Al_2O_3–C–N_2 reaction system

In this experiment, samples of Al_2O_3/C mixtures were heated under two different conditions, one in a reaction chamber in nitrogen gas, and the other in a coke powder bed.

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TABLE I Raw materials used

Calcined alumina:	Al_2O_3, 99.2% K_2O, 0.03% Na_2O, 0.21% Ignition loss, 0 Particle size, d_{50}, 4 μm
Carbon black:	Free carbon, 97.68% Ash, 1.14% Volatile matter 1.18% Ignition loss, 0.69% Residual sulphur, 0.36%
AlN: N > 32%, Al > 64%, O < 1% C < 0.2%	Na < 0.005% Fe < 0.16% Si < 0.1%

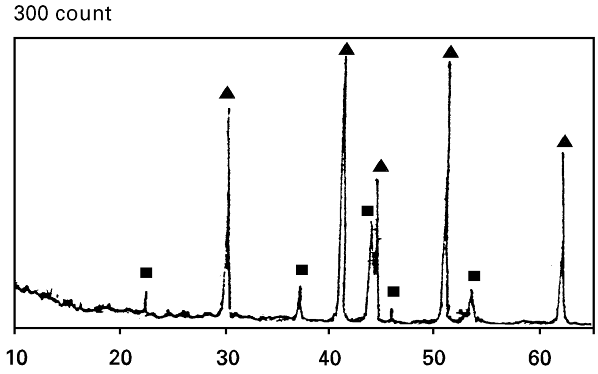

Figure 2 XRD pattern of the product of heating Al_2O_3/C powders in a coke powder bed at 1650 °C. (■) ALON, (▲) corundum.

Comparing Fig. 1a and c, the content of ALON phase in the different mixtures was different at 1650 °C. For the mixture according to Reaction 2, the ALON content in the product powder increased gradually with soaking time. However, for mixtures of an Al_2O_3/C ratio of 1/3, the ALON phase initially appeared and subsequently disappeared in the process. The AlN content in the powder was higher than that of ALON, and always increased with time. This indicated that when excess carbon was present in the mixture, ALON phase was easily nitrided into AlN even if ALON was a stable phase at this temperature [3]. Nevertheless, the ALON phase was, indeed, less stable at 1550 °C than at 1650 °C and above, which can be seen in Fig. 1b. In Fig. 1a, the content of ALON phase in the product powder is plotted against soaking time and always increases at 1650 °C; at 1550 °C the amount of ALON phase first increased, but then it decomposed into AlN and Al_2O_3.

The XRD results of Al_2O_3/C mixtures heated in coke powder at 1650 °C are shown in Fig. 2. ALON and Al_2O_3 coexisted in the powder product and no AlN phase appeared. Only corundum phase was found in the same mixture heated at 1600 °C.

3.2. The Al_2O_3–AlN reaction system

Reaction sintering of Al_2O_3/AlN mixtures has frequently been used to synthesize ALON materials. In the present work, in order to compare with the carbothermal reduction method, the temperature of formation of ALON in reaction sintering was studied. Al_2O_3/AlN mixtures were treated in a flowing nitrogen stream and also in a coke powder bed.

The XRD patterns of all the heated samples are shown in Figs 3 and 4. It was found that no ALON phase was detected in the powder product below 1650 °C, either in flowing nitrogen or in the coke powder bed, but above this temperature, ALON phase considerably appeared in the products in both experiments mentioned above.

When small amounts of additives, e.g. MgO, $MgAl_2O_3$ were included in the AlN–Al_2O_3 mixtures, samples heated at 1600 °C in flowing nitrogen showed ALON phase in the products (Fig. 5).

3.3. Annealing experiments

In order to confirm the instability of ALON phase below 1650 °C, but that ALON nevertheless occurred as an intermediate compound in these reactions, two annealing experiments were carried out.

Powders with a high content of ALON were reheated in flowing nitrogen gas at 1550 °C. The ALON powders used were produced previously at 1800 °C and were mainly ALON with a little AlN (Fig. 6a), the lattice parameter of the ALON phase was 0.7951 nm. After annealing for 3 h at 1550 °C, Al_2O_3 together with AlN and ALON was found in the powder (Fig. 6b) and the lattice parameter of ALON had changed to 0.7952 nm.

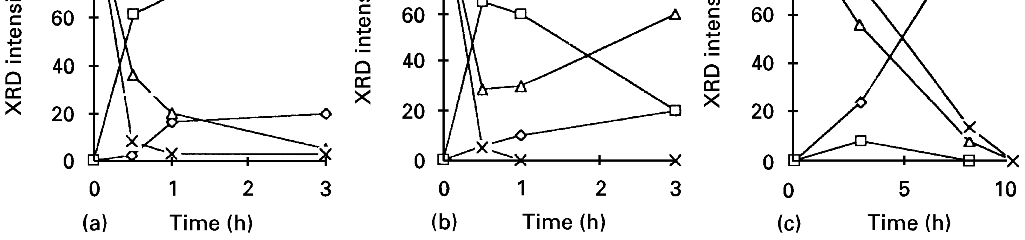

Figure 1 The phase changes in different mixtures with soaking time. (a) 1650 °C, 0.4 $m^3 h^{-1}$, C/Al_2O_3 = 23/15; (b) 1550 °C, 0.4 $m^3 h^{-1}$, C/Al_2O_3 = 23/15; (c) 1650 °C, 0.05 $m^3 h^{-1}$, C/Al_2O_3 = 3/1. (◇) AlN, (□) ALON, (△) Al_2O_3, (×) residual carbon.

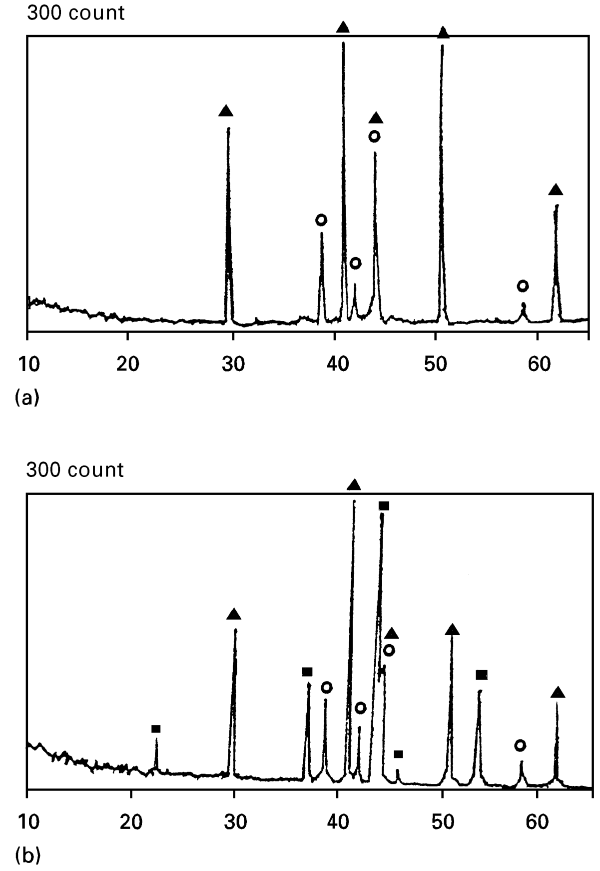

Figure 3 XRD patterns of product powders, at (a) 1550 °C and (b) 1650 °C, in a flowing nitrogen atmosphere. (○) AlN, (▲) corundum, (■) ALON.

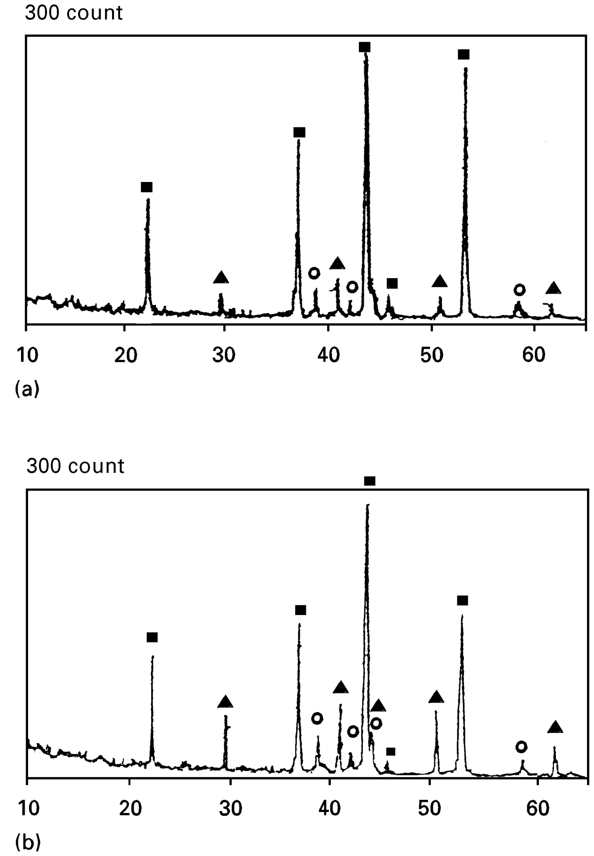

Figure 5 XRD patterns of product powders: (a) MgO, (b) $MgAl_2O_4$, in flowing nitrogen gas at 1600 °C. (○) AlN, (▲) corundum, (■) ALON.

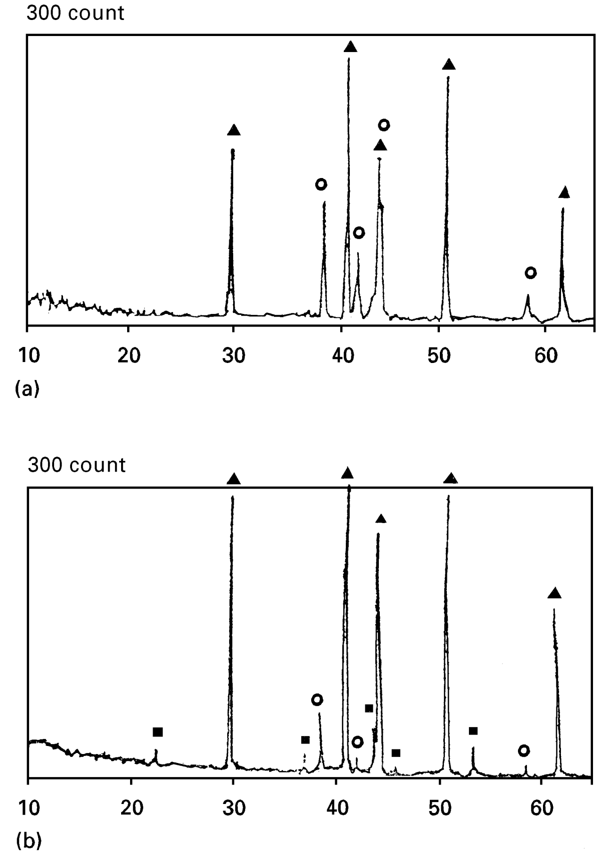

Figure 4 XRD patterns of product powders at (a) 1600 °C, and (b) 1650 °C, in a coke powder bed. (○) AlN, (▲) corundum, (■) ALON.

Secondly, the same ALON powder used in the above experiments was mixed with excess carbon, and then retreated in flowing nitrogen at 1550 or 1800 °C. The results showed that ALON phase was completely reduced to AlN (Fig. 6c).

4. Discussion

Based on the above results, it may be concluded that ALON phase is, indeed, an intermediate compound in the carbothermal reduction process. Samples with a high content of ALON phase can be manufactured below 1550 °C if processing parameters, e.g. C/Al_2O_3 ratio, heating rate, nitrogen flowrate, etc., are carefully controlled. These conclusions are in good agreement with Ish-Shalom [5] and may be explained by the Ellingham diagram drawn with data set from Willems *et al.* [3]

From Kaufman's diagram it is expected that ALON is formed as an intermediate phase at all temperatures and that the ALON phase is stable at all temperatures. However, other researchers have reported that ALON is stable above 1873 K only [3]. This diversity of opinion may come from the fact that the stability region of ALON is fairly small in the diagram, so it is difficult to observe it as an intermediate compound in the reduction process when alumina/carbon mixtures with surplus carbon are used. In this case, when the oxygen pressure is low, the stable phase will be AlN. Especially at lower temperatures, for example below

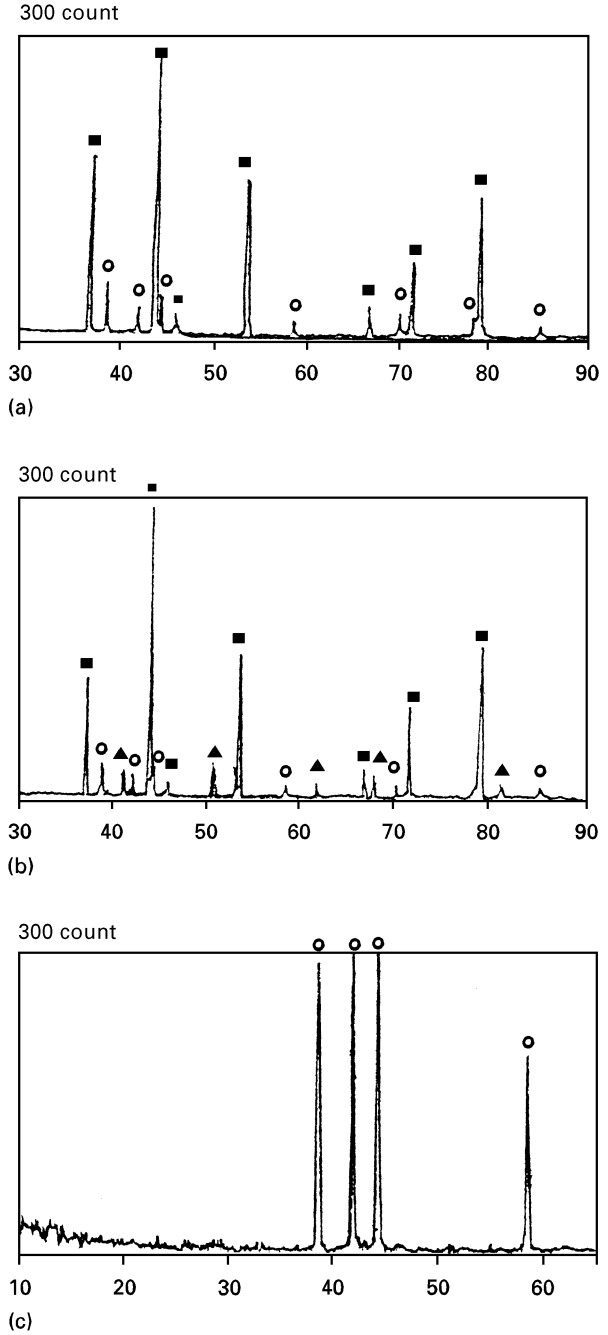

Figure 6 The XRD patterns of product powders. (○) AlN, (■) ALON, (▲) corundum.

1650 °C, ALON is much more difficult to detect than above 1650 °C because the reaction rate is slow and the little ALON produced is subsequently rapidly nitrided into AlN. This is the reason why Willems *et al.* did not observe ALON phase in their experiments until 1650 °C [3].

The relatively small stability region for the ALON phase indicates that ALON phase is strongly influenced by the local P_{O_2} and P_{N_2}. From the activity diagram drawn by Dörner *et al.* [8], it can be seen that it easily decomposes into AlN and Al_2O_3 below 1650 °C. In this case, it is impossible for AlN to react with Al_2O_3 and form ALON unless MgO, $MgAl_2O_4$, etc. are added. However, such a reaction may occur above 1650 °C because of the wider region of stability.

For the Al_2O_3–C–N_2 and AlN–Al_2O_3 systems, the mechanisms of formation of ALON are different; the former involves a solid–gas reaction mechanism and the latter a solid–solid reaction mechanism, although ALON phases were detected at 1650 °C in both processes in Willems *et al.*'s experiments [3]. Also, Lefort *et al.* [4], found the appearance of ALON phase in carbothermal reduction experiments above 1600 °C.

5. Conclusions

1. In the carbothermal reduction process, ALON phase occurs as an intermediate compound. Powders with high ALON content can be produced below 1650 °C in flowing nitrogen gas if process parameters are carefully controlled; also, ALON forms when Al_2O_3/C mixtures are treated in a coke powder bed above 1650 °C.
2. The additives, MgO, $MgAl_2O_4$, etc., affect the formation and stability of ALON in the reaction between AlN and Al_2O_3 at temperatures below 1650 °C.
3. The reaction mechanisms are different in the Al_2O_3–C–N_2 and AlN–Al_2O_3 systems.

Acknowledgements

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