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Self-propagating high-temperature synthesis of AlN in a graphite crucible in air by mechanical activation

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Powders of Al and C were mixed in a molar ratio of Al:C = 3:1 and were then ground in a planetary ball mill. When the thus mechanically activated mixtures were transferred into a graphite crucible and exposed to air, they spontaneously ignited and self-propagating high-temperature synthesis took place in two successive steps. The products were sliced along the depth direction and examined by X-ray diffraction. Depending on the depth of the crucible, aluminium nitride, aluminium carbide, aluminium oxynitride, aluminium oxycarbide and alpha alumina were detected. From measurements of the lattice constant, it was found that aluminium nitride with a 97% purity could be obtained at the bottom of the graphite crucible.

1. Introduction

Aluminium nitride (AlN) and AlN-based materials containing O, C, Si e.g., aluminium oxynitride (AlON) [1], aluminium oxycarbide (Al_2OC) [2–4], aluminium oxynitride carbide (AlONC) [2–4] and sialon (SiAlON) [1] have attracted a considerable amount of attention for use as advanced ceramics. Mechanical activation or mechanosynthesis is a promising process for the production of these AlN-based ceramics. Recently, we have proposed a novel method for producing aluminium nitride in air which is, in a strict sense, a solid solution between AlN and Al_2OC, designated as $(Al_2OC)_{1-x}(AlN)_x$ ($x \approx 0.8$) [5]. This technique is based on self-propagating high-temperature synthesis (SHS) induced by the energy stored during the mechanical activation of Al–C powder mixtures in a ball mill, rather than heating the powders to a high combustion temperature. The purpose of the present study is to produce purer AlN powders, i.e., x-values greater than 0.8, in air by using a graphite crucible as the reaction vessel.

2. Experimental procedures

The starting materials were aluminium metal (150–250 mesh, 99.9% Kojundo Chemical Laboratory) and natural graphite (mean flake size 5 μm, 97 wt% carbon, 2 wt% ash and 1 wt% volatile component, Nippon Kokuen Industry). These powders were mixed in a molar ratio of Al:C = 3:1 in an agate mortar, loaded in air in a p-7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) and then ground for 90 min. A 25 ml jar and four 12 mm diameter tungsten carbide balls were used in the grinding. The amount of powder mixture loaded was 8–9 g, and the weight ratio of powder to balls was about 1:6. The grinding was interrupted every 15 min, and the sample was scraped from the balls and the side walls of the jar and then reloaded and the grinding recommenced. The ground samples were transferred into either a porcelain saucer (inner diameter of 70 mm and depth of 10 mm) or a graphite crucible (inner diameter of 30 mm and depth of 40 mm) and allowed to react in air. The lump of product obtained in the graphite crucible was cut into the form of a rectangular parallelepiped (ca. 10 × 10 × 12 mm in size) and embedded into epoxy resin. Then, as shown in Fig. 1 it was sliced every 1 or 1.5 mm along the depth of the graphite crucible with a diamond cutter and then both surfaces of each slice were examined by X-ray diffraction (XRD) with a RAD-B diffractometer (Rigaku Denki) using Ni-filtered CuK_α radiation. The lattice constants of the aluminium nitrides were measured under the following conditions: Si as an internal standard, scanning speed of 0.25° min^{-1} and a time constant of 1 s.

3. Results

When the mechanically activated samples were transferred into a porcelain saucer and exposed to air, exothermic reactions spontaneously occurred in two successive steps [5]: just after the exposure to air a first exothermic reaction occurred at several spots, which evolved red heat (step 1), which then propagated towards neighbouring regions, and then a violent second exothermic reaction occurred, which evolved white heat (step 2). The temperatures attained in steps 1 and 2 were estimated to be about 800 and 1800 °C, respectively by use of an optical pyrometer. Similar reaction

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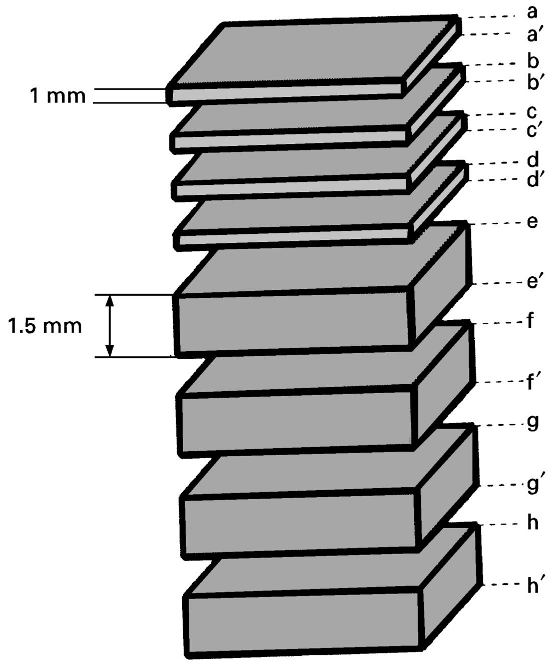

Figure 1 The products sliced every 1 to 1.5 mm. The products were sliced along the depth of the graphite crucible and examined by XRD techniques.

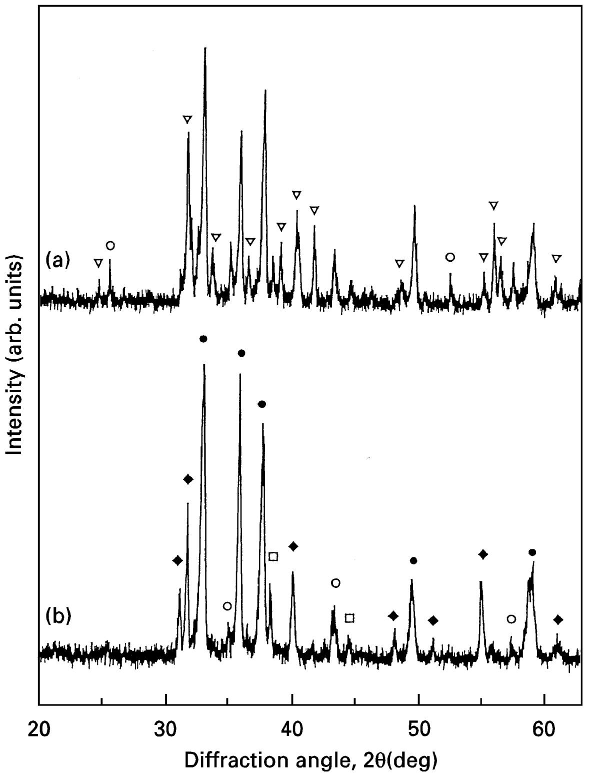

Figure 2 XRD patterns of the products obtained in (a) the porcelain saucer and (b) the graphite crucible. (●) AlN; (◆) Al_4C_3; (▽) AlONs; (○) α-Al_2O_3 and (□) Al.

behaviours were observed in the graphite crucible, however the product phases were different depending on the reaction vessel used.

Fig. 2(a and b) show the XRD patterns of the products obtained in the porcelain saucer and the graphite crucible respectively. The main products were aluminium nitride and aluminium oxynitrides in the former case, and aluminium nitride and aluminium carbide in the latter case. The difference in the product phases seemed to be dependent on the extent to which oxygen in the air penetrated into the reactant mixtures, i.e., there was less oxygen in the graphite crucible than in the porcelain saucer. A small amount of α-Al_2O_3 was observed in both cases, which exclusively formed at the surface of the product as a white thin layer.

Fig. 3(a–h) shows the XRD patterns of the product obtained in the graphite crucible which was sliced every 1 or 1.5 mm in the manner shown in Fig. 1. Pattern (a) which corresponds to the top surface of the product contains reflections that can be associated with α-Al_2O_3 and aluminium oxycarbide (Al_2OC). In contrast, aluminium nitride was always observed to form as the main product in all the other patterns which correspond to a distance 1 mm below the sample surface to the bottom of the crucible. In pattern (b), i.e., position b, the intensity of the aluminium nitride peaks increased, whilst those of α-Al_2O_3 drastically decreased and traces of aluminium oxynitrides (AlONs) appeared. Further into the sample, pattern (c), the intensity of the AlON peaks further increased while those of α-Al_2O_3 disappeared. In the deeper positions, represented by patterns (d–h), aluminium nitride and carbide are mainly observed. Unreacted aluminium metal was also detected at the positions represented by patterns (f–h).

The peak positions of the aluminium nitrides obtained from patterns (a′ to h) were observed to shift. Therefore, the respective slices of a–a′, b–b′, … and h–h′ were finely ground and used to measure the lattice constants. The precise lattice constants a and c of the aluminium nitrides were calculated using the 105, 213, 302 and 205 diffraction peaks that occur in the diffraction angle (2θ) in the range of 100–150° and are plotted in Fig. 4, where they are compared with those reported for AlN [6], $(Al_2OC)_{1-x}(AlN)_x$ [7, 8] and Al_2OC [2, 8, 9]. All these compounds have a wurtzite structure. It can be seen from Fig. 4 that the lattice constants of the aluminium nitrides obtained from the slices a–a′ to h–h′ lie between the values for AlN and Al_2OC, indicating that the aluminium nitrides obtained in the present study are solid solutions with the composition $(Al_2OC)_{1-x}(AlN)_x$. The x-value for the aluminium nitride solid solution obtained at the bottom of the graphite crucible, i.e., for h–h′, was estimated using Vegards' law to be about 0.97.

4. Discussion

The mechanical grinding of powder mixture of Al and C was found to lead to an activated state accompanied by a decrease in the particle size and the coating of the Al particles with disordered carbon [5]. When these mechanically activated samples were exposed to air, exothermic reactions spontaneously occurred in two successive steps, evolving red heat in step 1 and then white heat in step 2. On the basis of these experimental results, a possible reaction process has been proposed [5] that consists of: in step 1 the reaction being initiated by the ignition reaction between the disordered

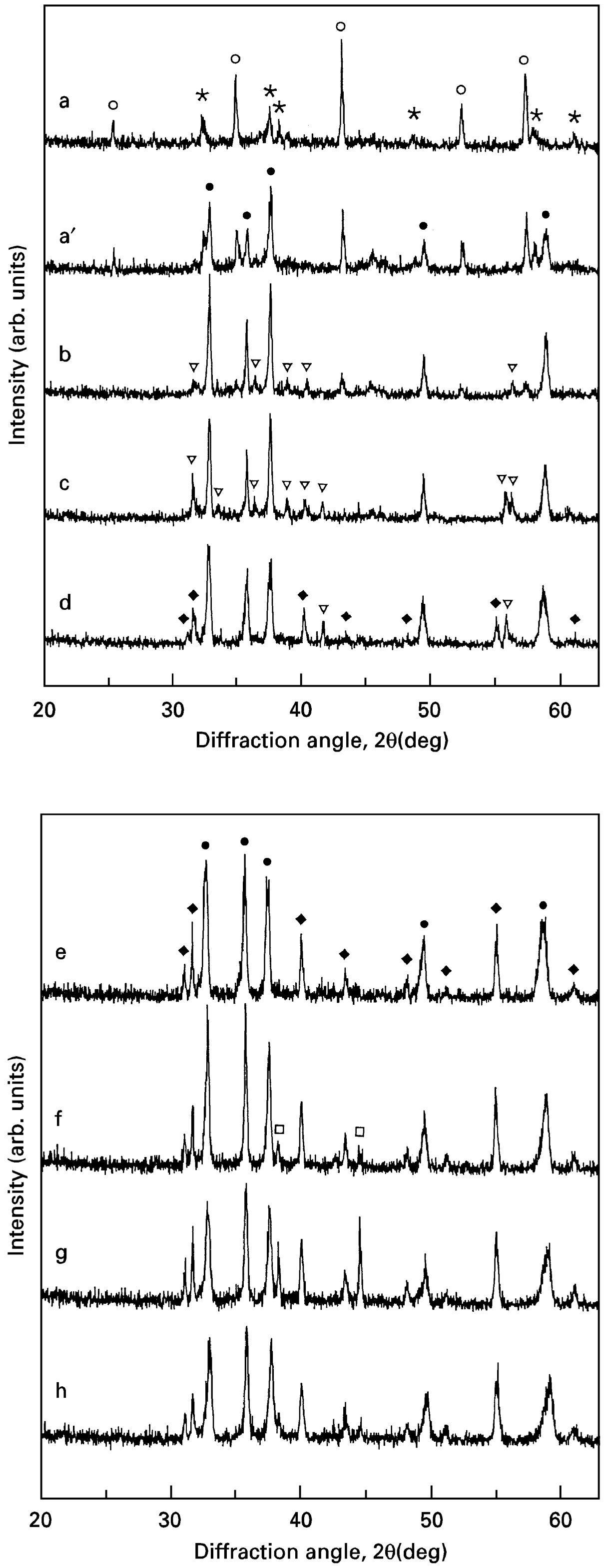

Figure 3 XRD patterns of the surfaces of the products sliced as shown in Fig. 1. (●) AlN; (◆) Al_4C_3; (*) Al_2OC; (▽) AlONs; (○) α-Al_2O_3 and (□) Al.

carbon formed on the surface of the Al metal particles by the mechanical grinding and the oxygen in air.

$$C + O_2 = CO_2 + \Delta H_1 \tag{1}$$

At the expense of the enthalpy ΔH_1, the Al metal reacts with C to form Al_4C_3 evolving ΔH_2.

$$4Al + 3C = Al_4C_3 + \Delta H_2 \tag{2}$$

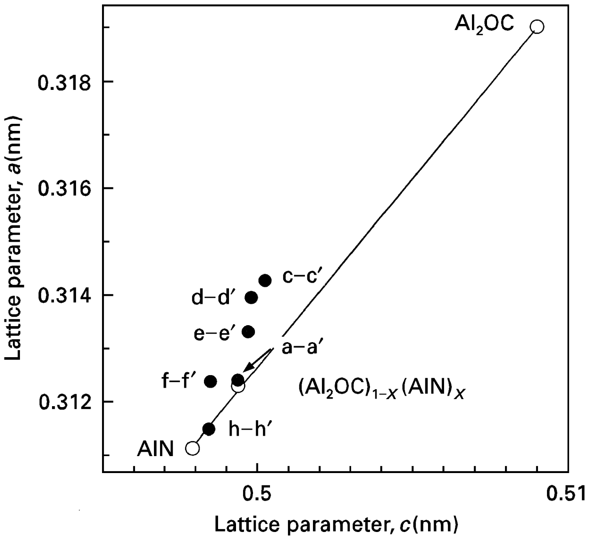

Figure 4 Variation of the *a* and *c* lattice constants of the aluminium nitrides obtained for the slices from a–a′ to h–h′ positions shown in Fig. 1.

In step 2, the Al metal reacts with the nitrogen in the air by using the heat evolved in step 1, i.e., ΔH_1 and ΔH_2.

$$2Al + N_2 = 2AlN + \Delta H_3 \tag{3}$$

The reaction shown in Equation 3 is also an exothermic reaction with an enthalpy ΔH_3 and evolves white heat. On the other hand, as is evident from Fig. 3(a–h), the oxygen-contained compounds, α-Al_2O_3 and Al_2OC are exclusively observed near the surface of the product. This result shows that the oxidation of Al metal, which was uncovered by the reaction shown in Equation 1, took place only at the surface of the reactants, and consequently a nitrogen rich atmosphere is achieved just underneath the α-Al_2O_3 and Al_2OC product layer. Then, in the inner part of the reactant sample, the Al metal particles are surrounded by fine particles of disordered carbon whose oxidation is inhibited, and thus the carbonization reaction of aluminium metal occurs. The heat released by the exothermic reactions in step 1, i.e., ΔH_1 and ΔH_2, become a trigger for the reaction of Al metal with nitrogen in step 2. Furthermore, since it is impossible for the surface layer of α-Al_2O_3 and Al_2OC formed to inhibit the penetration of oxygen into the sample, the Al_4C_3 formed reacts with this oxygen to form aluminium oxycarbide, Al_2OC.

$$Al_4C_3 + 2O_2 = 2Al_2OC + CO_2 + \Delta H_4 \tag{4}$$

Then, Al_2OC reacts with the AlN formed in the reaction shown as Equation 3 to form the solid solutions.

$$(1 - x)Al_2OC + xAlN = (Al_2OC)_{1-x}(AlN)_x + \Delta H_5 \tag{5}$$

The reactions shown as Equations 3–5 occur continuously during the self-propagating high-temperature synthesis (SHS) process.

In the case of the graphite crucible, it is assumed that a concentration gradient of oxygen exists from top to bottom of the crucible, and depending on this gradient, products with different oxygen contents are formed. At the sample positions of (a and a′), α-Al_2O_3 and Al_2OC were formed due to a sufficient supply of oxygen. At the deeper position of (c), where the concentration of oxygen decreases abruptly aluminium nitride solid solutions, $(Al_2OC)_{1-x}(AlN)_x$, and aluminium oxynitrides, AlONs, were formed. Many aluminium oxynitrides are known to form in the AlN–Al_2O_3 system [10, 11]. The AlN rich compositions i.e., oxynitrides such as $Al_{10}N_8O_3$ and $Al_9N_7O_3$ have superstructures based on the AlN wurtzite structure while the Al_2O_3 rich compositions are non-stoichiometric spinel structures. The XRD diffraction peaks of these phases often overlap each other and hence the phase obtained at the b and c positions could not be clearly determined. Various aluminium oxynitride phases seem to have formed depending on the oxygen concentration gradient along the depth of the crucible. At the a–c positions, no diffraction peaks of Al_4C_3 were observed. It is thought that most of the Al_4C_3 formed at the a–c positions immediately changed to Al_2OC according to reaction shown in Equation 4 and subsequently this Al_2OC reacted with AlN to form $(Al_2OC)_{1-x}(AlN)_x$ with different contents of Al_2OC. At the d–h positions, oxygen was markedly deficient and unreacted Al_4C_3 and Al metal was detected.

On the other hand, as is shown in Fig. 4, the variation of the lattice constants of the solid solutions, $(Al_2OC)_{1-x}(AlN)_x$, formed at the positions from c–c′ to h–h′ almost depends on the amount of Al_2OC dissolved into the AlN, which in turn is determined by the oxygen concentration gradient from the top to bottom of the graphite crucible. In contrast, a considerable amount of Al_2OC existed at the a–a′ positions as is shown in Fig. 3(a and a′) and a solid solution with a small content of Al_2OC (i.e., $x \approx 0.8$) was formed. This is thought to be a result of a lower reaction temperature at the a–a′ positions, due to significant heat losses from the surface. At the bottom of the graphite crucible, i.e., the h–h′ positions, purer aluminium nitride, i.e., $(Al_2OC)_{1-x}(AlN)_x$ ($x \approx 0.97$) was obtained.

5. Conclusions

Powders of aluminium metal and natural graphite were mixed in a molar ratio of $Al:C = 3:1$ and ground in a planetary ball mill. When the thus mechanically activated mixtures were transferred into a graphite crucible and exposed to air, exothermic reactions spontaneously occurred in two successive steps, initially evolving red heat and then white heat. The main product was an aluminium nitride solid solution with a composition of $(Al_2OC)_{1-x}(AlN)_x$, in which the value of x changed with the depth of the crucible achieving a value of 0.97 at the bottom of the crucible. A possible reaction mechanism has been discussed.

Acknowledgements

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