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High-pressure direct synthesis of aluminium nitride

M Boćkowski, B Łucznik, I Grzegory, S Krukowski, M Wróblewski and S Porowski

High Pressure Research Centre 'Unipress', Polish Academy of Sciences, 01-142, Warsaw, 29/37 Sokolowska, Poland

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Abstract
We report the results of direct synthesis of aluminium nitride (AlN) under high nitrogen pressure up to 1 GPa and temperatures up to 2000 K. At pressure from 10 to 650 MPa we observe the combustion synthesis of AlN. As the result of the combustion process one can obtain the AlN sintered powder or AlN/Al metal matrix composites. For N_2 pressure higher than 650 MPa the crystal growth of AlN from the solution of atomic nitrogen in aluminium is possible. Both needle-like and bulk AlN single crystals, up to 1 cm and 1 mm, respectively, have been obtained.

1. Introduction

Aluminium nitride (AlN) is a material with excellent thermal conductivity, high electrical resistivity and low thermal expansion coefficient, similar to those of silicon. These properties make this material suitable for electronic applications, especially as microcircuit substrates [1]. On the other hand, due to good thermal stability and good electrical and optical properties, AlN is applied as a wide-band-gap semiconductor and in surface acoustic wave (SAW) devices [2].

AlN powder has been industrially synthesized by direct nitridation of metallic aluminium powder or by carbothermic reaction of alumina, carbon and nitrogen at atmospheric N_2 pressure. Dense-sintered AlN is fabricated either by hot pressing or by pressureless sintering [3]. The main method used to grow bulk AlN crystals is the sublimation technique [4]. It should be recalled that AlN cannot be crystallized by the standard growth method, from a stoichiometric melt, because of its very high melting temperature—3500 K [5].

In this paper we report the results of direct synthesis of AlN, from aluminium bulk as a starting material, under high nitrogen pressure up to 1 GPa and temperatures up to 2000 K.

At low pressure, below 10 MPa we observe that the synthesis or crystal growth of AlN is difficult due to strong evaporation of aluminium. This leads to destruction of the furnace elements; thus it leads to stopping of the synthesis (crystallization) process.

For pressure higher than 10 MPa the self-propagating high-temperature synthesis—SHS (combustion synthesis)—of AlN takes place [6]. As the result of the combustion process one can obtain very pure, low-oxygen-content AlN sintered powder or AlN/Al metal matrix composites (MMCs). It depends only on the nitrogen pressure applied.

The crystallization of large and high-quality AlN crystals by combustion synthesis is almost impossible. The combustion is a strongly non-equilibrium process. Only AlN whiskers can be obtained according to Guojian *et al* [7]. However, for nitrogen pressures above 500 MPa, the combustion of aluminium in N_2 starts to slow down. At pressure higher than 650 MPa we do not observe the SHS reaction. Additionally, high density of N_2 at high pressures reduces the evaporation and diffusion of aluminium. Therefore, high-pressure growth of AlN single crystals from atomic nitrogen solution in liquid aluminium becomes possible. Such a growth method, also called high-nitrogen-pressure solution growth (HNPSG), is very useful for gallium nitride and allows one to obtain excellent, dislocation-free GaN substrates, over 1 cm^2 in size [8]. Up to now, for AlN this method has allowed crystallization of needle-shaped and bulk crystals. These crystals were grown at temperatures of the order of 2000 K and at nitrogen pressure of 1 GPa.

2. Experimental details

The high-pressure–high-temperature experiments on AlN synthesis were performed in special equipment constructed at the High Pressure Research Centre 'Unipress'. The vertically positioned high-pressure chamber of internal diameter 40 mm was connected by a capillary to the gas–oil compressor. In such a system one can obtain a gas pressure of 1.5 GPa. Inside the chamber the multi-zone graphite furnace, capable of reaching 2000 K, was placed. The temperature in the furnace was measured by a set of PtRh6%–PtRh30% thermocouples. They were positioned along the axis of the crucible with the aluminium sample. The nitrogen pressure in the system was detected by a manganin gauge located in the cold zone of the high-pressure chamber. The signals from the thermocouples and manganin gauge were transmitted to the Keithley DMS 199 Scanner multimeter and then to an IBM-PC-compatible computer.

In a typical experiment the bulk aluminium, contained in the BN crucible, located in the furnace inside the high-pressure chamber, was heated at a constant rate of 10 K h^{-1} to the given temperature. For the SHS process the aluminium was heated only to the temperature at which the combustion reaction started. After that the system was cooled down. In the case of AlN crystallization the metal sample was annealed at high temperature (i.e. 1800–2000 K) for many hours (typically 120). The supersaturation, which is the driving force for the crystal growth process, was created by application of a temperature gradient of the order of 5–25 K cm^{-1}, during annealing, along the axis of the Al sample.

The AlN crystals and also combusted samples were characterized by the x-ray diffraction (XRD) method, a scanning electron microscope (SEM) and an energy-dispersive x-ray analyser (EDS) attached to the SEM.

3. Results and discussion

From the thermodynamic point of view the high nitrogen pressure is not necessary for AlN synthesis. The AlN is stable at N_2 atmospheric pressure up to 2800 K [4]. However, we observed that if we heated the Al bulk to high temperatures (1800–2000 K) at a few (1–10) MPa of nitrogen, the evaporation of aluminium was so strong that the experiment was stopped. The vapour of Al attacks the furnace elements and the synthesis process cannot be realized. As was

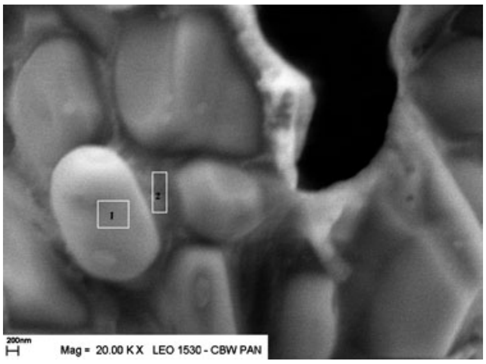


Figure 1. An SEM micrograph of an AlN sample combusted in pure nitrogen at a pressure of 20 MPa (fracture).

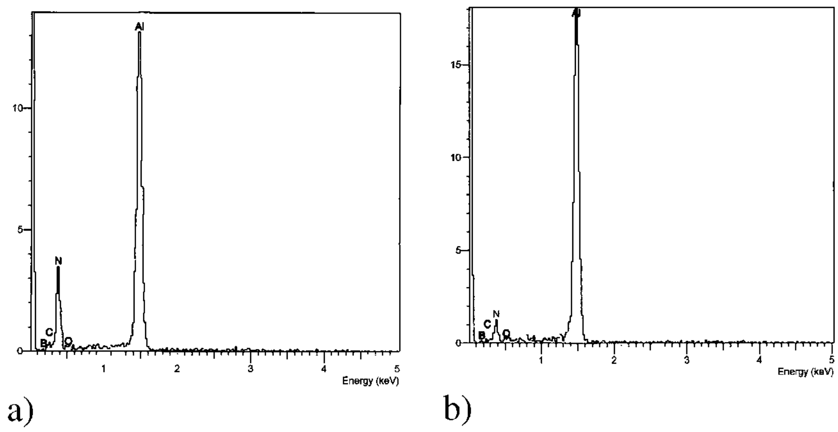
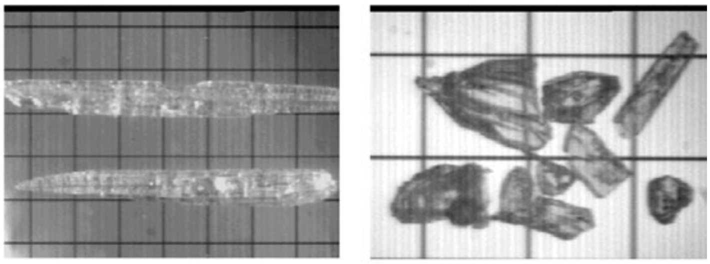


Figure 2. EDS spectra (a) for AlN grains, (b) for the Al matrix (see the text).

mentioned in the introduction, the high density of N_2 at high pressure can reduce the evaporation and diffusion of aluminium. However, the use of N_2 pressure higher than 10 MPa leads to a combustion reaction between liquid aluminium and nitrogen gas. The liquid aluminium burns in nitrogen at temperatures of 1300–1400 K. The fraction of aluminium converted to AlN during the combustion reaction is a function of the nitrogen pressure. Increasing the nitrogen pressure leads to increase in the conversion to AlN, with almost complete conversion (99% of AlN) at 100 MPa. Then, the degree of conversion decreases and, after combustion in 500 MPa, the sample contains only 70% AlN. Figure 1 presents a typical structure of an AlN/Al sample combusted in 20 MPa. Grains of AlN of about 1 μm in size immersed in an aluminium matrix are visible. This situation can be shown better by EDS analysis. Figures 2(a) and (b) show respectively, the EDS spectrum for an AlN grain (point 1 in figure 2) and the Al matrix (point 2 in figure 1). In the first case one can see two strong peaks, from aluminium and nitrogen, whereas in the second case only the signal from aluminium is well detected.

At pressure higher than 650 MPa we never observed the SHS process. The extinction of the combustion flame is associated with the increase in the thermal conductivity and thermal capacity of nitrogen gas at high pressure. The heat losses during combustion reaction under high pressure increase and, finally, the reaction can be totally stopped [6]. At pressure higher



a b

Figure 3. Some typical AlN crystals grown from a liquid solution of nitrogen in aluminium: (a) needle-like crystals; (b) irregular bulk (grid spacing: 1 mm).

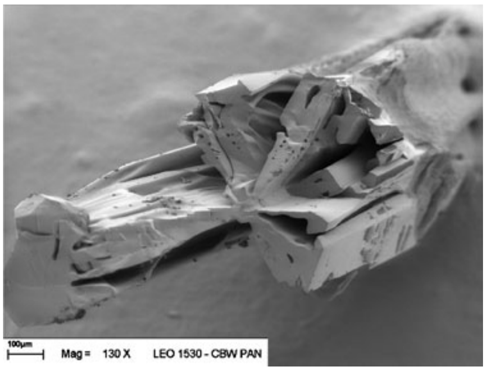


Figure 4. Typical fracture of the AlN needle.

than 700 MPa crystal growth of AlN becomes possible. Figure 3 shows typical AlN crystals obtained in our experiments. They are needle shaped, elongated in the *c*-direction, with diameters of about 1 mm and up to 10 mm in length (see figure 3(a)) or in the form of irregular bulks of maximal dimension equal to 1 mm (see figure 3(b)). These crystals are white in colour, and they have the wurtzite structure. They have grown spontaneously at the cooler end of the crucible from the polycrystalline AlN layer created on the surface of liquid aluminium. The AlN needle-shaped crystals have been grown in a large temperature gradient, greater than $10\ \mathrm{K\ cm^{-1}}$. For temperature gradients lower than $10\ \mathrm{K\ cm^{-1}}$ we have observed only the growth of bulk AlN.

The AlN needles obtained in our experiments generally have hollow-cored forms, consisting of a few crystals arranged in a hexagonal skeleton (see figure 4). The AlN bulks are generally irregular. They grow from the polycrystalline nitride layer. Due to the small distances between various crystals they join together. As a result, one can obtain polycrystalline sets of small, bulk AlN single crystals, like those shown in figure 5. In some cases the final result of the nitride growth is an irregular bulk form, as presented in figure 6.

It seems that the AlN crystal growth process from liquid solution consists of a few stages:

(i) formation of an AlN polycrystalline layer on the surface of liquid aluminium;
(ii) dissolution of the AlN film in liquid metal at high temperature;
(iii) transport of dissolved atomic nitrogen from the hot part of the sample to the cooler end;
(iv) crystallization in the cooler part of the solution.

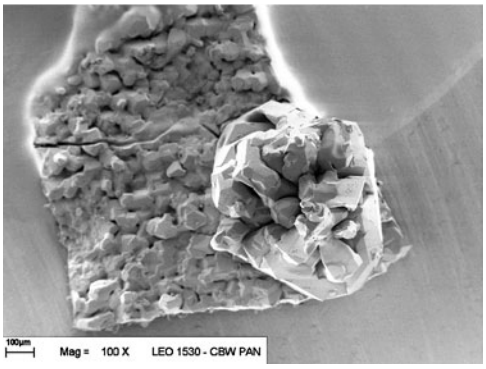


Figure 5. A polycrystalline set of joined, small, bulk AlN single crystals.

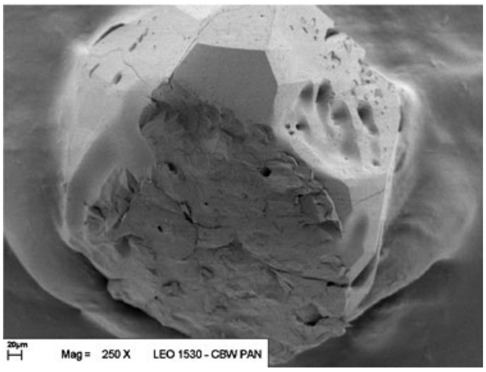


Figure 6. An irregular AlN bulk.

The first stage, formation of an AlN layer on the surface of liquid aluminium, was observed earlier and also for lower pressures and temperatures than 1 GPa and 2000 K [4, 6]. The contact of nitrogen molecules and aluminium was also analysed by means of quantum mechanical calculations [9]. It was shown that when an N_2 molecule approaches the metal surface, the dissociation of the molecule and the formation of bonds between nitrogen and aluminium atoms take place. At high temperature the AlN layer dissolves in liquid aluminium and in this way one can obtain a solution of atomic nitrogen in liquid Al.

The next step of AlN crystal growth is transport of atomic nitrogen in liquid metal. Due to the application of a temperature gradient along the aluminium, nitrogen atoms are transported by diffusion and/or convection from the hot end of the sample to the cooler part. Probably, the relatively high temperature gradient (>10 K cm^{-1}) creates strong convection in the solution. In effect, unstable needle-like crystals have been grown in the cooler part of liquid aluminium. A decrease in temperature gradient leads to a change in the mass transport mechanism in liquid metal: the convection weakens and the diffusion transport starts to play an important role. Then, one can observe a change of the AlN crystal habit from needle-like to bulk. The bulk crystals are, however, small and unstable, having irregular shape, which is not well understood at present.

4. Conclusions

We have shown that nitrogen pressure allows one to control the mechanism of synthesis of AlN. At pressures from 10 to 650 MPa we have observed the combustion synthesis of AlN. As a result of the combustion process one can obtain high-purity AlN sintered powder or AlN/Al metal MMCs. For N_2 pressure higher than 650 MPa the crystal growth of AlN from a liquid solution of atomic nitrogen in aluminium can take place. Needle-like and bulk AlN single crystals have been obtained at temperatures up to 2000 K and N_2 pressure up to 1 GPa.

Acknowledgment

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