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Formation of aluminium nitride whiskers by direct nitridation

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Abstract

This work describes novel results on the growth of aluminium nitride (AlN) whiskers by direct nitridation of Al–NH_4Cl starting mixtures. The nitridation experiments were carried out in a horizontal tube furnace at 1000 °C for 1 h in 1 l/min N_2 gas flow. It is found that the growth of AlN whiskers was principally promoted by NH_4Cl which provided a different reaction pathway depends on vapor-phase reactions mechanism instead of normal liquid–gas mechanism. The thermodynamic analysis of possible intermediate reactions in the operating temperatures range confirmed that the AlN whiskers could be grown through spontaneous vapor-phase chlorination–nitridation sequences. The SEM observation revealed that depending on NH_4Cl concentration homogeneous AlN nanowhiskers of <150 nm in diameters can be obtained as well as composites of particles-whiskers of AlN which may be potential for preparing useful sintered AlN materials.

Keywords: AlN; Nitrides; Whiskers

1. Introduction

Aluminium nitride (AlN) is important technical ceramic being currently an ideal substrate material for advanced electronic and optoelectronic devices. AlN is a III–V nitride-based semiconductor with unique physical properties such as wide bandgap (6.2 eV),[1] high thermal conductivity (0.823–2.0 W/cm K),[1] high volume resistivity (>10^{11} Ωm),[2] low dielectric constant (8.5)[1,3] and a thermal expansion coefficient (≈4×10^{-6}/K) similar to silicon.[2,4,5] It has also good chemical stability and high hardness and is used in various structural and refractory composites applications.[6]

The direct nitridation is a primary process used for the commercial production of AlN powders from metallic Al powder. It is a low cost technique utilizes simple nitridation system. The complete nitridation is usually achieved at temperatures up to 1500 °C under flowing nitrogen-based gases and results in agglomerated AlN powders due to the low melting point of Al which is less than the temperature required for nitridation.[7–9] It has been published previously that the addition of NH_4Cl to the starting Al powder enhances the nitridation rate and can promote the formation of nanocrystalline AlN powders with good output.[10,11] The evolved gases from sublimation or decomposition of NH_4Cl produces many pores which prevents the Al particles coalescing after melting and allows better nitrogen access into the burden. But it has not been reported before to promote the growth of whiskers.

In the present study, we discovered that during the direct nitridation reaction of Al presence of NH_4Cl greatly assists the growth of AlN whiskers. The following sections describe the nitridation of various Al–NH_4Cl starting mixtures in nitrogen gas stream and the characteristics of produced AlN powders. A proposed reaction mechanism supported by a thermodynamic analysis will be reported.

2. Experimental procedure

The direct nitridation experiments were carried out in a porcelain boat (8-cm long) set in the center of an alumina tube (3-cm inner diameter and 100-cm long) mounted in a horizontal electric-resistance furnace. A schematic diagram of the overall nitridation system is shown in Fig. 1. The starting materials were commercially available aluminium

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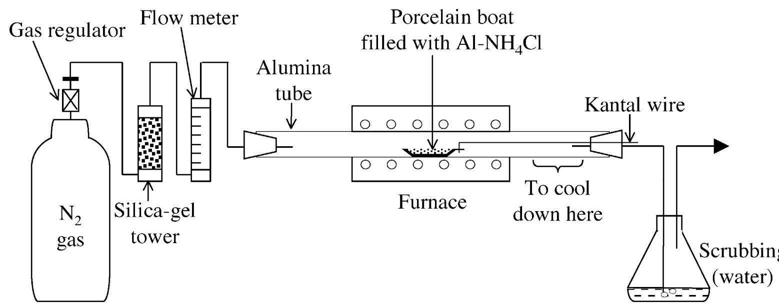

Fig. 1. Schematic diagram of the nitridation apparatus used.

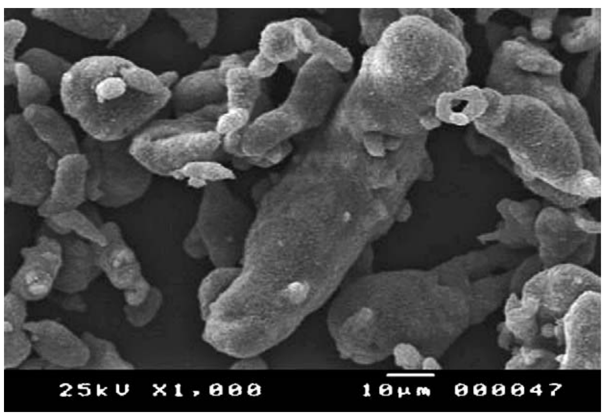

Fig. 2. SEM micrograph of starting Al powder.

powder with about 99% purity and an average particle size of 180 µm, and a chemical-grade ammonium chloride powder with minimum assay of 99%. SEM micrograph of starting Al powder is shown in Fig. 2. They were mixed for different ratios (NH_4Cl concentration = 10, 20, 30, 40 and 50 wt%) manually in agate mortar. About 1 g of loose powder mixture was put into the boat and placed in the alumina tube. The system was flushed with nitrogen gas for several minutes to remove any oxygen and moisture. The nitrogen gas used was purified from moisture by passing it through a silica gel tower. The furnace was heated to 1000 °C with a rate of 15 °C/min under nitrogen gas flow of 1 l/min and maintained at 1000 °C for 1 h. Finally, the boat was drawn to the end of the tube outside the heating zone and kept for cooling down to room temperature under the nitrogen atmosphere. The nitride products were observed visually and analyzed by X-ray diffraction (XRD, BRUKER axc – D8 Advance) using Cu Kα radiation (40 kV/40 mA). The morphology of as-synthesized AlN powders was examined with scanning electron microscope (SEM, JEOL-JSM-5410).

3. Results and discussion

In preliminary experiments, the direct nitridation of only Al powder was performed at different temperatures (600–1000 °C) for 1 h in 1 l/min nitrogen gas. The maximum nitridation yield (73.3%) was achieved at 1000 °C and the resultant nitride powder at this temperature was relatively sintered. Fig. 3 shows the microstructure of this product. It had a complicated dense microstructure, like connected half-broken egg-shells structure. It was explained that above the melting point of Al (660 °C) the Al particles tend to coagulate and form molten Al spheres. The nitridation occurs at the surfaces of these molten spheres forming nitride shells surrounding the melted Al.[11,12] Due to the thermal stress of large volume of Al melt, the Al melt breaks the nitride shells (layers), penetrates among them by a capillary-like phenomena and reacts with nitrogen gas.[11,12] The formed consolidated microstructure (Fig. 3) inhibits the further nitrogen gas access to unreacted Al particles and retards the development of nitridation to completion.

The nitridation of various Al–NH_4Cl starting mixtures, containing 10, 20, 30, 40 and 50 wt% ammonium chloride, was carried out at optimum condition of above preliminary experiments. The XRD patterns of resultant nitride powders are given in Fig. 4. The amounts of AlN phase (hexagonal structure) obtained were 71.1, 89.8, 95.1, 94.3 and 95.6%, respectively. The resultant AlN products were loose white powders (see Fig. 5) indicating the high AlN purity. The nitridation was enhanced as predicted.

The SEM observation of as-synthesized nitride powders showed unique AlN whiskers growth results. Fig. 6 gives the morphology of as-synthesized AlN powders obtained from nitridation of Al–20 wt% NH_4Cl and Al–40 wt% NH_4Cl mix-

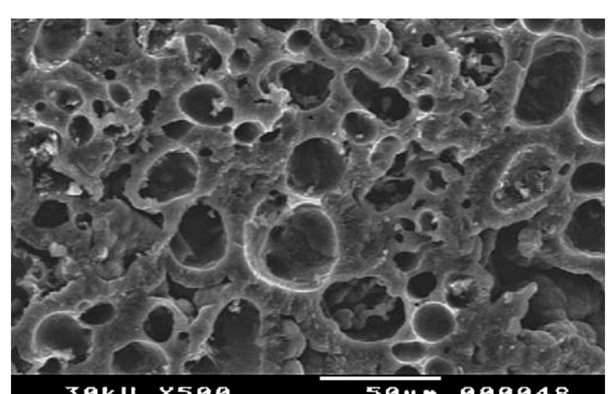

Fig. 3. SEM micrograph of AlN powder obtained from direct nitridation of pure Al powder.

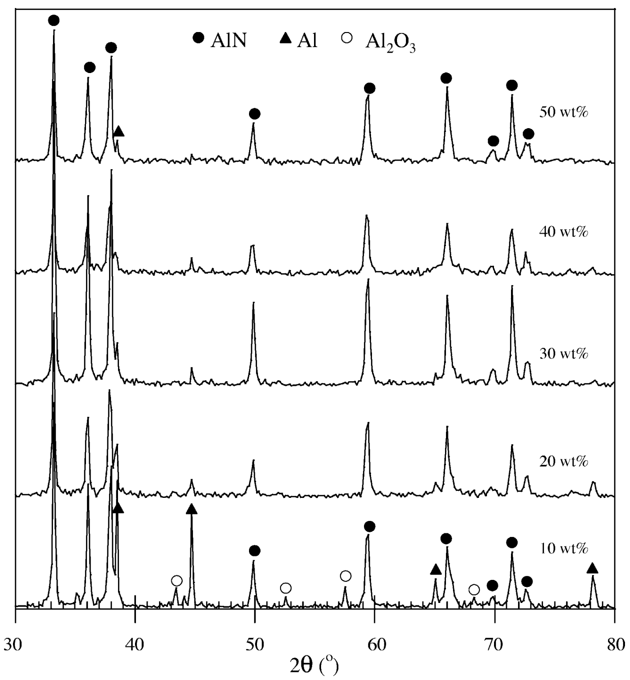

Fig. 4. X-ray diffraction patterns of nitrided powders in presence of different NH_4Cl concentrations (10, 20, 30, 40 and 50 wt%).

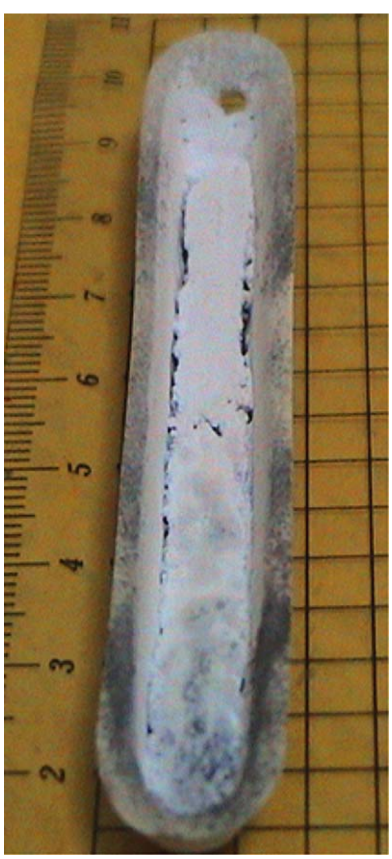

Fig. 5. Visual appearance of as-synthesized AlN powder (with 30 wt% NH_4Cl in starting Al).

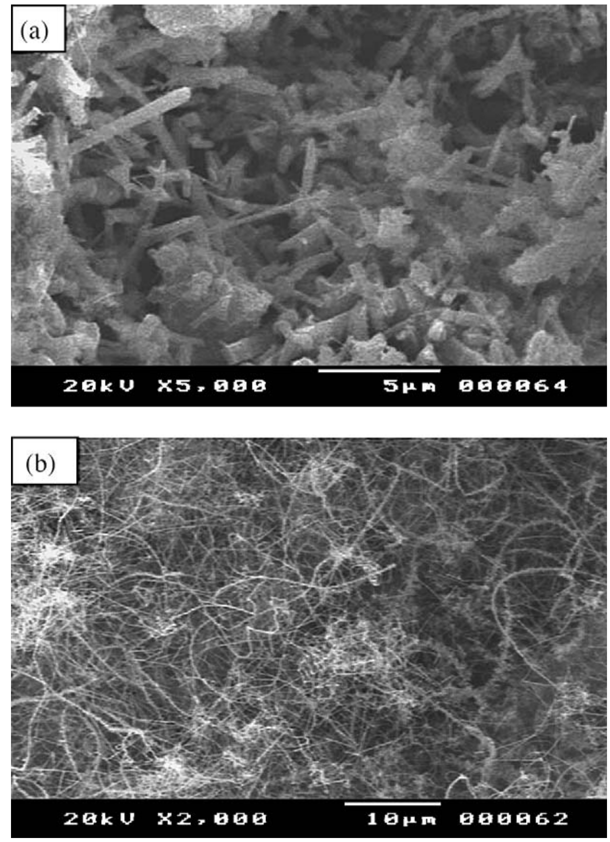

Fig. 6. SEM micrographs of produced AlN powders at: (a) 20 wt% NH_4Cl and (b) 40 wt% NH_4Cl.

tures. It is obvious that the NH_4Cl promoted the growth of AlN whiskers and it is found possible to synthesize homogeneous nano-AlN whiskers (40–150 nm diameters) with the 40 wt% addition as shown in Fig. 6(b).

The fundamental reaction of direct nitridation of aluminium by nitrogen can be described according to the following equation:

$$Al_{(l)} + N_{2(g)} = AlN_{(s)} \quad (1)$$

where the nitridation proceeds by a liquid–gas mechanism. The addition of NH_4Cl to starting Al powders offers however a different reaction pathway than this liquid–gas nitridation mechanism. Since the tips of all observed AlN whiskers did not have droplets, this may suggest that these whiskers were grown probably by a vapor-phase mechanism which can be summarized as follows:

$$NH_4Cl_{(s)} = NH_{3(g)} + HCl_{(g)} \quad (2)$$

$$Al_{(s,l)} + 3HCl_{(g)} = AlCl_{3(g)} + \tfrac{3}{2}H_{2(g)} \quad (3)$$

$$AlCl_{3(g)} + \tfrac{1}{2}N_{2(g)} + \tfrac{3}{2}H_{2(g)} = AlN_{(s)} + 3HCl_{(g)} \quad (4)$$

The values of Gibbs energy change of encountered intermediate reactions in the operating temperatures range, calculated from JANAF thermochemical data,[13] are given in Fig. 7. The thermodynamic calculations confirm the postu-

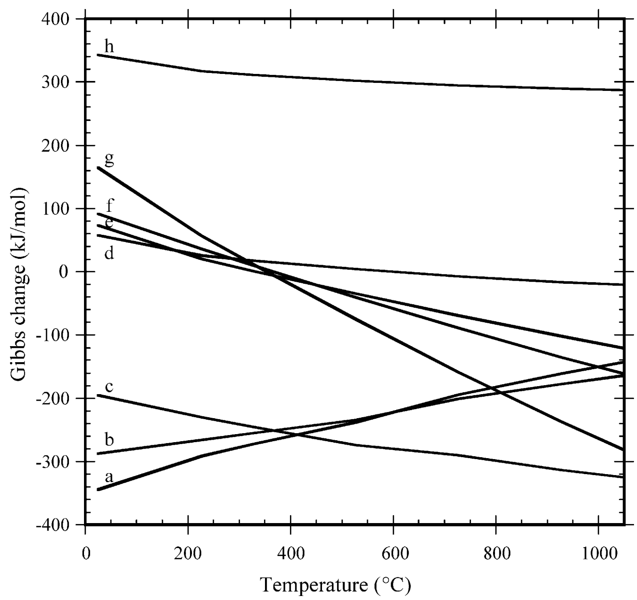

Fig. 7. Gibbs energy change of possible intermediate reactions: (a) $Al + 3HCl = AlCl_3 + \frac{3}{2}H_2$; (b) $Al + \frac{1}{2}N_2 = AlN$; (c) $Al + NH_4Cl + \frac{1}{2}N_2 = AlN + NH_3 + HCl$; (d) $AlCl_3 + \frac{1}{2}N_2 + \frac{3}{2}H_2 = AlN + 3HCl$; (e) $AlCl_3 + NH_3 = AlN + 3HCl$; (f) $NH_4Cl = NH_3 + HCl$; (g) $AlCl_3 + NH_4Cl = AlN + 4HCl$; (h) $AlCl_3 + \frac{1}{2}N_2 = AlN + \frac{3}{2}Cl_2$.

lated growth mechanism through spontaneous vapor-phase chlorination–nitridation sequences.

4. Conclusions

In the direct nitridation of Al–NH_4Cl starting mixtures at 1000 °C for 1 h in 1 l/min nitrogen gas flow, it is found that ammonium chloride not only enhances the nitridation to near completion but also promotes the growth of AlN whiskers through spontaneous intermediate chlorination–nitridation reactions in the vapor phase.

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