Structure characteristics of AlN whiskers fabricated by the carbo-thermal reduction method

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With Al_2O_3 and graphite as raw materials, CaF_2 and B_2O_3 as additives, AlN whiskers were fabricated by a carbo-thermal reduction method. The fabrication mechanism and growth characteristics of AlN whiskers were investigated. At the beginning of the high-temperature fabrication, AlN whiskers grew by the vapour/liquid/solid (VLS) mechanism, and defects existed on the surfaces of the whiskers. In later stages, the VLS mechanism possibly changed to a vapour/solid (VS) mechanism, and the defects disappeared. The orientation of most AlN whiskers was normal to $\{10\bar{1}n\}$ ($n=0, 1, 2, 3$), and normal to $\{\bar{1}2\bar{1}n\}$ ($n=0, 1, 2$). The growth processes of both two-dimensional nucleation and screw dislocations existed at the same time. © *1998 Kluwer Academic Publishers*

1. Introduction

Whisker materials are of interest for their small size, few defects, and excellent mechanical and physical properties that are nearly equal to the theoretical values. Whiskers are widely applied as reinforcements in composite materials. For example, Si_3N_4 composites with SiC whiskers as reinforcements have a higher heat-resistance and toughness than common Si_3N_4 ceramics [1]. Much of the previous literature has presented the fabrication process, crystallography, surface characteristics and relationship between microstructure and properties of such ceramic whiskers as mullite [2], Si_3N_4 [3, 4], SiC [5, 6], TiC [7], etc.

AlN belongs to the hexagonal crystal system, wurtzite structure, and P63*mc* space group. In its unit cell, each aluminium atom is encompassed by four nitrogen atoms, forming a distorted tetrahedron with three 0.1889 nm long Al–N(1) bonds and one 0.1905 nm long Al–N(2) bond along the [0 0 0 1] direction. Because of its structure characteristics, AlN has good physical and chemical properties, such as high theoretical thermal conductivity (319 W m^{-1} K^{-1}), perfect dielectric and sound-wave transmitting properties. So AlN whiskers may be used both as mechanical reinforcement materials in structural composites and as promising materials in functional composites. The studies on AlN whiskers started with Taylor's experiment [8] of treating aluminium powders under a high temperature. AlN whiskers were fabricated by the AlN powder vaporization method Evans and Davies [9], the CVD method of Iton *et al.* [10] and the carbo-thermal reduction method of Caceres and Schmid [11]. In this experiment, the carbo-thermal reduction method was adopted to fabricate AlN whiskers; CaF_2 and B_2O_3 were added as additives. The growth mechanism, structure characteristics and growth orientation of AlN whiskers were investigated.

2. Experiment and results

A source of a-Al_2O_3 and graphite in a ratio of $Al_2O_3:C = 2:1$ (wt %) with 2.5 wt % B_2O_3 and 2.5 wt % CaF_2 as additives, were mixed, ball-milled, dried, sifted and placed into a 200 mm diameter graphite reactor. In a graphite heater furnace, AlN whiskers were fabricated in a flowing nitrogen atmosphere at temperatures of 1600 and 800 °C for 3–5 h. The main parameters for fabrication are listed in Table I. Whiskers were treated at 600 °C for 4 h in a normal atmosphere to eliminate carbon. Thus pure transparent AlN whiskers were obtained.

The results showed that no AlN whiskers could be obtained by fabrication process 1, a few whiskers could be obtained by process 2, and many whiskers were easy to fabricate by process 3. Fluffy AlN whiskers homogeneously grew on white AlN powder, shown in Fig. 1, and a limited quantity of AlN whiskers grew in the AlN powder. Fig. 2 shows the XRD spectra, which indicate that the production was composed of AlN and a few second phases of Ca_3N_2, without Al_2O_3.

3. The morphology and growth orientation of AlN whiskers

3.1. AlN whisker crystal morphology

AlN whiskers were investigated by optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). AlN whiskers have different crystal morphologies, as

TABLE 1 High temperature fabrication process and quantity of AlN whiskers

	First temperature retaining stage		Second temperature retaining stage	
	Temperature (°C)	Time (hrs.)	Temperature (°C)	Time (hrs.)
1	1600	5	—	—
2	1600	0	1800	5
3	1600	2	1800	5

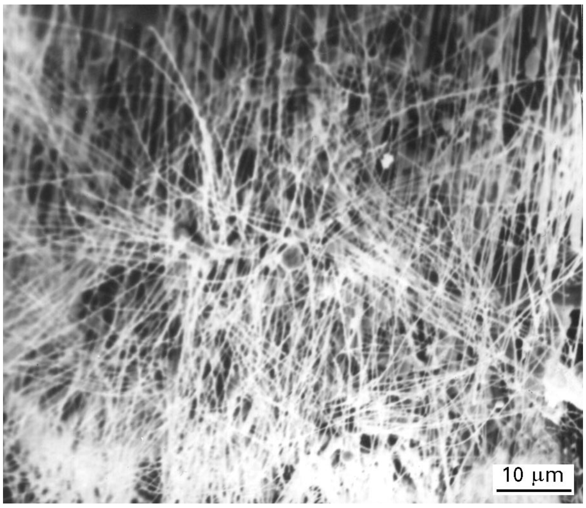

Figure 1 The growth of AlN whiskers.

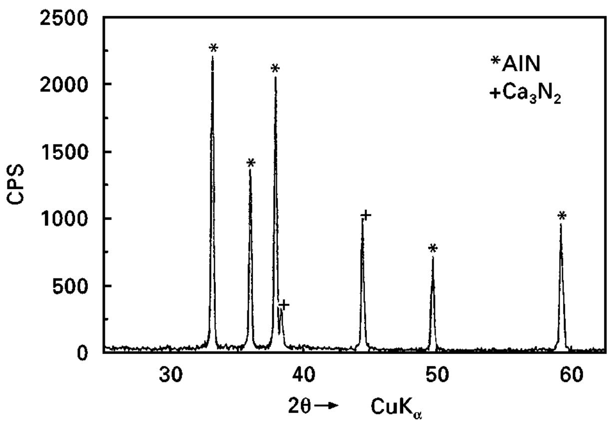

Figure 2 XRD analysis of whiskers.

shown in Fig. 3. The whiskers are 0.1–10 mm long and are 1–10 μm in diameter. Many of the AlN whiskers obtained are long-columnar and plate crystals with clear edges, and they have few surface defects. Other whiskers are cylindrical crystals with many surface defects. Wave-like whiskers formed by growth diversion, cross-like whiskers and secondary whiskers growing on the surface of rough whiskers, are also observed. A screw-dislocation growth stripe can be seen in the indented crystals. Fig. 4 shows a whisker with a liquid droplet on its tip.

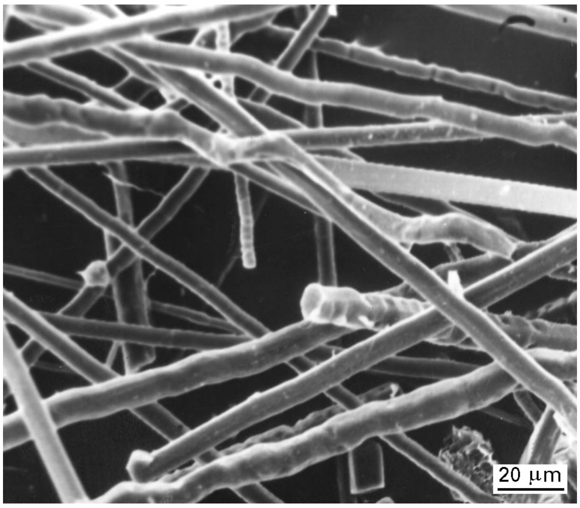

Figure 3 Morphology of AlN whiskers (SEM).

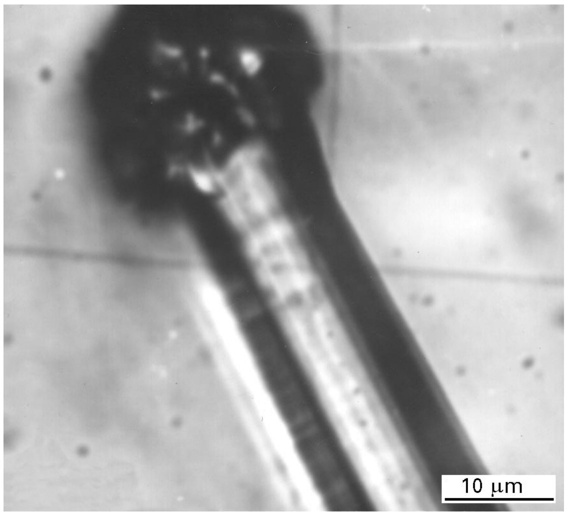

Figure 4 Droplet at the tip of a whisker (OM).

3.2. AlN whisker growth orientation

3.2.1. The measurement of AlN whisker growth orientation by the Laue method

Using the XRD Laue method (geometric disposition of transmission method), the integrity of AlN whiskers was analysed, and the growth orientation was measured. The distance between the sample and the film was 20 mm, and the sample was irradiated for 5 h. Most Laue spots were not distorted or split in the Laue photos of AlN whiskers with different morphologies. This shows that the AlN whiskers are single crystals and have an integral structure. The Laue method measurement of many AlN whiskers show that several growth orientations exist. The growth orientation has two chief systems. One is normal to $\{10\bar{1}\,n\}$ $(n = 0, 1, 2, 3)$, and the other is normal to $\{\bar{1}2\bar{1}\,n\}$ $(n = 0, 1, 2)$. Fig. 5 shows a (1 1 0) standard 0.7 : 1 projection of AlN crystal. The Laue photo of an AlN whisker with its growth orientation normal to $(2\bar{1}\bar{1}1)$ is shown in Fig. 6; the arrow indicates the growth orientation. $\{10\bar{1}0\}$ and $\{\bar{1}2\bar{1}0\}$ are densely packed crystal planes in the AlN crystal [12]. AlN

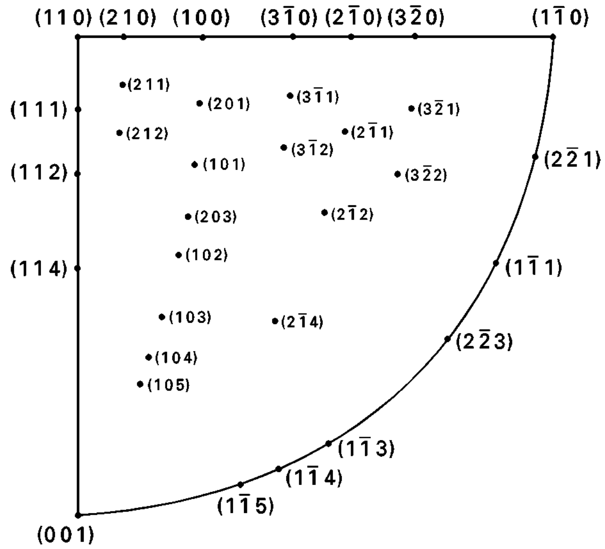

Figure 5 (1 1 0) projection of the AlN crystal.

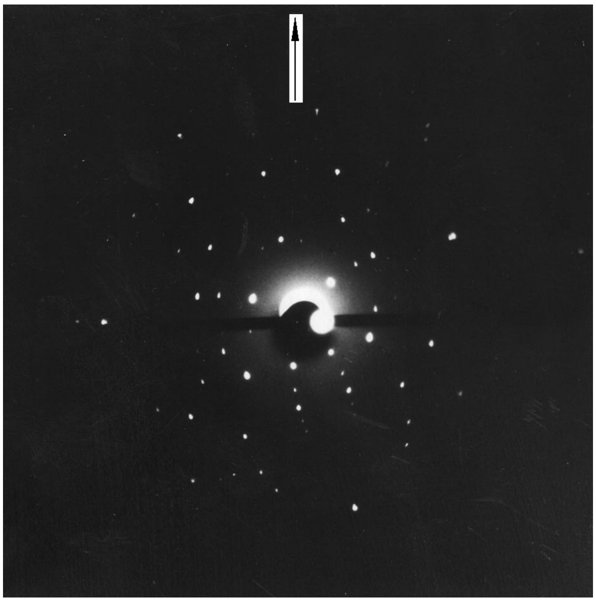

Figure 6 Laue photo of an AlN whisker normal to $(2\,\bar{1}\,\bar{1}\,1)$.

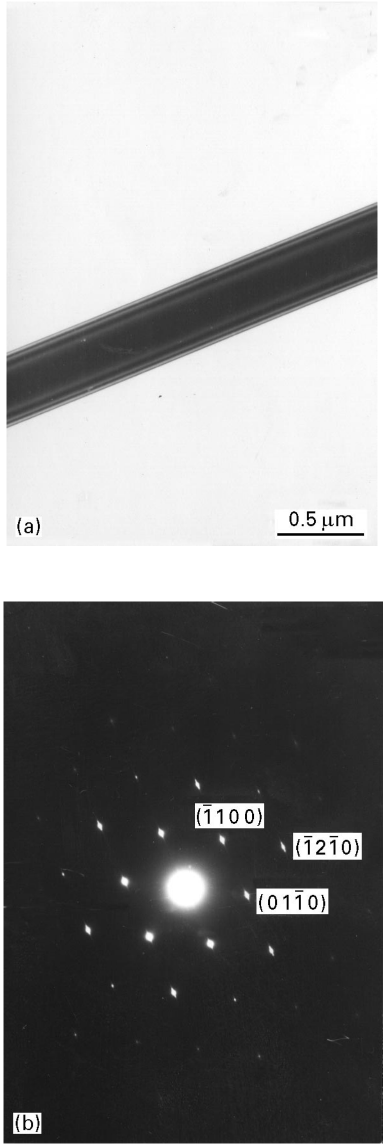

Figure 7 TEM analysis of a long plate-like AlN whisker: (a) morphology of AlN whiskers, (b) diffraction pattern of AlN whiskers.

whiskers with $\{10\bar{1}0\}$, $\{\bar{1}2\bar{1}0\}$ and $\{10\bar{1}1\}$ growth planes have already been reported [11, 13]. In this experiment, further growth orientations of AlN whiskers were found. The main reasons are the change in the degree of supersaturation in the gas phase and the effect of the distorted tetrahedron structure.

3.2.2. Measurement of AlN whisker growth orientation with TEM

Different morphologies of AlN whiskers can be observed by TEM. The electron diffraction shows different growth orientation of the AlN whiskers. Fig. 7a shows the TEM morphology of long plate-shaped AlN whiskers, and Fig. 7b shows the diffraction pattern. The analysis shows that the growth plane is $(\bar{1}2\bar{1}0)$ and the growth direction is $[\bar{1}2\bar{1}0]$. Fig. 8a shows the morphology of indented AlN whiskers with a screw growth stripe. Fig. 8b shows the diffraction pattern of part 1 of the whisker, and the screw growth plane is $\{10\bar{1}2\}$. The angle between the growth plane and the axis of part 1 was measured as 42°. It is known that the angle between (0 0 0 1) and $(10\bar{1}2)$ in AlN crystal is 42.7°, so it can be stated that the macro-growth direction of part 1 is normal to (0 0 0 1). The diffraction pattern of part 2 of the AlN whisker is the same as in Fig. 8b, and the screw growth plane is also $\{10\bar{1}2\}$. The screw growth plane is supposed to be $(01\bar{1}\bar{2})$, and the angle between the growth plane and the axis of part 2 was measured as 36°. It is known that the angle between $(\bar{1}10\bar{3})$ and $(01\bar{1}\bar{2})$ is 36.5°, so the growth direction of part 2 is normal to $(\bar{1}10\bar{3})$. The theoretic angle between (0 0 0 1) and $(\bar{1}10\bar{3})$ is 148.4°, approximately equal to the measured result, 149.8°. The geometric relationship of crystal planes is shown in Fig. 8c. The phenomenon whereby the whisker macro-growth direction disagrees with the growth plane and forms an angle, can be observed in many whiskers with a screw growth stripe. The existence of a macro-growth direction can be confirmed by the Laue method. This phenomenon is attributed to the vapour/liquid/solid (VLS) growth mechanism and

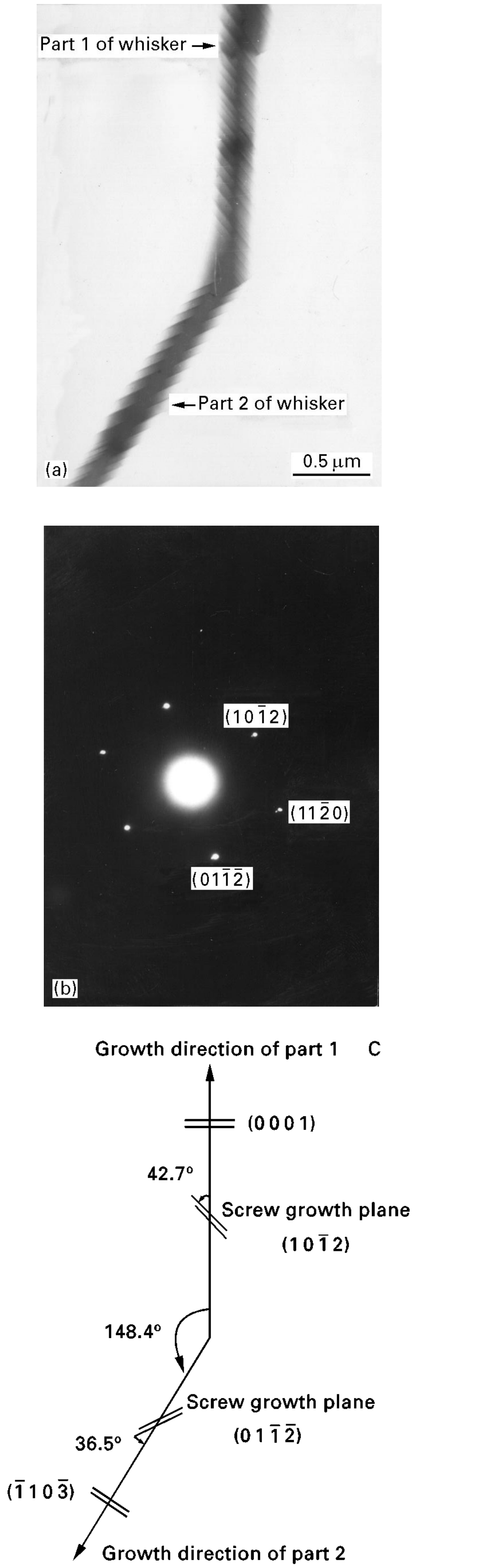

Figure 8 TEM analysis of AlN whisker with screw growth layers: (a) morphology, (b) diffraction pattern from area 1, (c) relation between plane and orientation.

the change of interfacial tension, which was induced by the fluctuation of the degree of gas supersaturation.

4. Problems and discussion

4.1. The effect of additives and the growth mechanism

The additives play an important role in the fabrication process of AlN whiskers. The CaF_2–B_2O_3 low-melting point additives were changed into liquid droplets at high temperature, and AlN dissolved in the droplet to form whiskers. Fig. 4 indicates that a liquid droplet existed at the tip of the whisker, verifying that whiskers grew via the VLS mechanism. The change of the degree of AlN supersaturation in the liquid droplet and the deflection of the center of gravity of the liquid droplet, resulting from the slanted growth of the whiskers, explain the change in the interfacial tension between the two phases. Thus the diversion of the whisker growth direction, as well as the wave-shaped, crossed and twin crystal whiskers, can be observed.

CaF_2 addition is helpful in the fabrication of AlN whiskers, but excess of CaF_2 results in a rough surface of the AlN whiskers. The fused mass of CaF_2 and Al_2O_3 may erode AlN whiskers [14]. The reaction takes place as follows

$$6CaF_2 + 2AlN + 2Al_3O_2 \rightarrow 4AlF_3\uparrow + Ca_3Al_2O_6 + Ca_3N_2 \quad (1)$$

This result has been testified by XRD analysis. So the quantity of CaF_2 should be controlled.

Although a screw dislocation is not necessary for the formation of whiskers via VLS mechanism, the existence of a screw dislocation is helpful to the growth of whiskers. This accounts for the existence of both screw growth and non-screw growth.

Many observations exhibit that few AlN whiskers had liquid droplets, while most whiskers had no droplets on their tips. As the temperature was raised and soaking time was prolonged, the liquid phase was constantly vaporized, and the VLS mechanism becomes a vapour/solid (VS) mechanism. The gas phase is deposited directly on the surface of AlN whiskers and AlN powders. In later stages of fabrication, Al_2O_3 has almost completely changed into AlN, and the AlN vapour supersaturation in the gas phase is high enough to fabricate whiskers via a two-dimension nucleation process. At the same time, CaF_2 and B_2O_3 also vaporized quickly, so the AlN whiskers obtained have few surface defects and clean edges.

4.2. Fabrication temperature control

In the Al_2O_3 carbon thermal reduction method, the gas-phase reaction mechanism, controlled by Al_2O_3 vaporization, coexists with the solid-phase reaction mechanism, controlled by diffusion [15]. The series of reactions is represented as follows

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

$$Al_2O_3(s) + C(s) \rightarrow Al_2O_2(g) + CO(g) \quad (3)$$

$$Al_2O_2(g) + C(s) \rightarrow Al_2O(g) + CO(g) \quad (4)$$

$$Al_2O(g) + N_2 \rightarrow 2AlN(s) + \tfrac{1}{2}O_2(g) \quad (5)$$

$$Al_2O(g) + N_2 + 3CO(g) \rightarrow 2AlN(s) + 3CO_2(g) \quad (6)$$

At a high reduction temperature, Al_2O_3 vaporizes quickly and decomposes much of the aluminium, Al_2O and AlO vapour. These substances can quickly combine with nitrogen to produce AlN. So the nitridation is carried on via gas Reactions 5 and 6. At a low reduction temperature, Al_2O_3 vaporizes slowly, and a solid-phase reaction takes place quickly because the size of the powder is very small. So the reaction is chiefly based on solid phase Reactions.

If the heat retaining process at 1600 °C for 5 h (group 1) is adopted, Al_2O_3 nitridation is chiefly based on a solid-phase reaction. However, normal whisker growth requires the existence of a gas phase. So only AlN powders, and not AlN whiskers, can be obtained. If the temperature rises to 1800 °C directly (group 2) the nitridation is chiefly based on gas-phase reaction. The AlN vapour, produced in gas phases is deposited on the surface of Al_2O_3. The inner Al_2O_3 cannot vaporize completely. So the Al_2O_3 nitridation degree is low and the AlN vapour pressure is low in the gas phases. The dissolved AlN in the liquid droplets is too little to support the growth of whiskers. In this process, only a few AlN whiskers can be fabricated. The process of heat retention at both 1600 and 800 °C for several hours can ensure that the solid-phase and gas-phase reactions proceed to completion. The nitridation degree and AlN supersaturation are high enough to fabricate many AlN whiskers.

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