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Growth of aluminium nitride whiskers by sublimation-recrystallization method

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Aluminium nitride (AlN) with various morphologies was fabricated through a sublimation-recrystallization method. The influences of type of reactor and temperature gradient were explored, as well as the orientations and growth mechanism of the obtained AlN whiskers. In the early stage of preparation, a vapour-liquid-solid (VLS) mechanism dominated, producing AlN pillars, whiskers and noncrystalline fibres. In the later stage, as the catalyst liquid was removed by volatilization, the pillars and noncrystalline fibres stopped growing, but the growth of AlN whiskers continued through a vapour-solid (VS) mechanism. By Laue method and rotating-crystal method of x-ray diffraction, together with electron diffraction, most of the AlN whiskers were discovered to grow on planes $\{2\bar{1}\bar{1}0\}$, $\{0001\}$, or $\{10\bar{1}l\}$, where $l = 0, 1, 2, 3$, along crystal axes $[2\bar{1}\bar{1}0]$, $[0001]$, or $[10\bar{1}w]$, where $w = 0, 1, 2, 3$. Oblique grown whiskers also appeared, with a growth direction at an angle of about 54° to the growth plane, $(10\bar{1}2)$. © *2000 Kluwer Academic Publishers*

1. Introduction
Aluminium nitride (AlN) whiskers have been prepared by methods such as nitridation of aluminium powder [1], carbothermal-reduction of aluminium oxide at high temperature [2, 3], volatilization-condensation of AlN powder [4], and chemical vapour deposition (CVD) method [5]. Several mechanisms have been profused to explain the growth of whiskers, including the axial screw dislocation mechanism [6], the vapour-liquid-solid (VLS) mechanism [7], and others [8].

In the present study, a sublimation-recrystallization method was developed to prepare AlN whiskers of high purity and perfection. The orientations and growth mechanism of the achieved whiskers are discussed.

2. Experimental
Commercial AlN powder was used as raw material, to which 3 wt % of CaO and 2 wt % of B_2O_3 were added. After ball-milling, the mixed powders were placed in a reactor and then heated in a graphite furnace, with a flowing nitrogen atmosphere. It is of importance to control the air tightness of the reactor since the whisker growth depends on the supersaturation level of AlN vapour in it. To get comparison results, an AlN crucible and two graphite ones (one open, one close) were employed in the experiment. The preparation process was carried out at 1800 °C for 3 h.

The fabricated whiskers were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM) and energy dispersive spectrometer (EDS). Laue method, rotating-crystal method of x-ray diffraction as well as electron diffraction were used to analyze the orientation of the whiskers.

3. Results and discussion
3.1. Effects of reactors
In this experiment, three kinds of reactors were chose, including open graphite crucible, close graphite crucible, and close AlN crucible. When using the open graphite crucible, no whisker was produced. While the close graphite crucible was used, a lot of acerous and wool-like AlN whiskers were obtained (Fig. 1). When the reactor was changed to the AlN crucible, a large quantity of large AlN whiskers (Fig. 2), as well as some crystalline pillars and noncrystalline fibres, were obtained.

The differences of reactors caused different supersaturation level of AlN vapour in them, and consequently influenced the generation of whiskers. In the open graphite crucible, as insufficient supersaturation was achieved, hence whiskers could not grow. The AlN crucible was the tightest reactor, the high level of supersaturation resulted in the formation of coarse whiskers, as well as the change of growth direction from one dimension to polyandry. The close graphite crucible had a moderate level of supersaturation, which yielded whiskers with small sizes.

3.2. Effects of heating temperature
The sizes of reactors were all $\phi 120 \times 150$ mm. They were located in the furnace with the top part in the high

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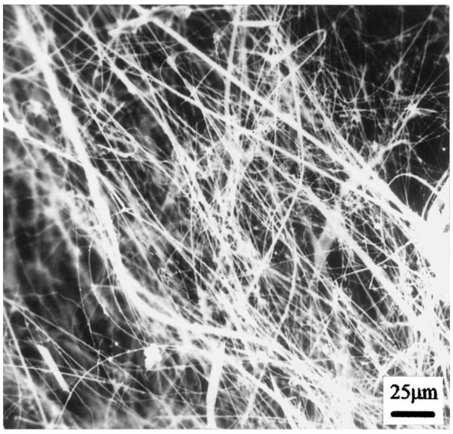

Figure 1 Wool-like AlN whiskers (SEM).

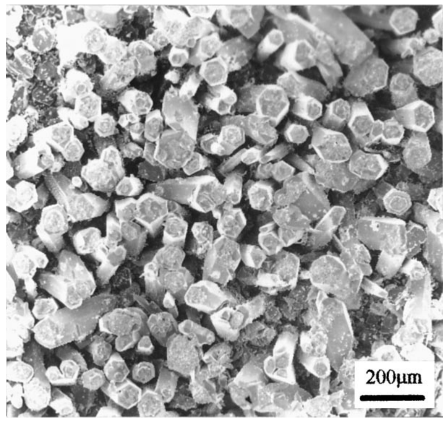

Figure 3 SEM micrograph of AlN pillars.

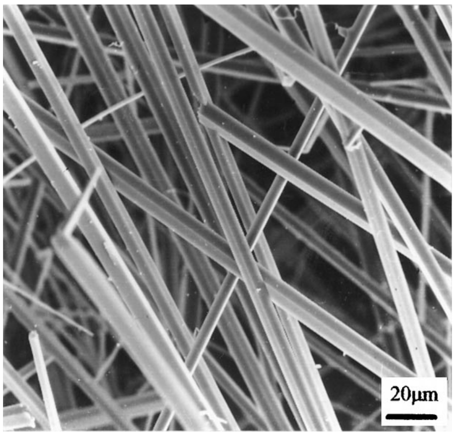

Figure 2 Coarse AlN whiskers (SEM).

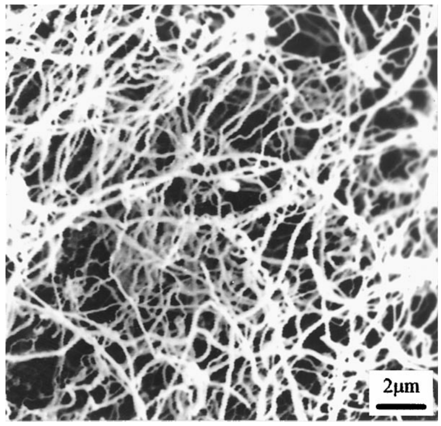

Figure 4 SEM micrograph of noncrystalline AlN fibres.

temperature region (1800 °C), the bottom in the low temperature region (1650 °C), and the middle in the region of about 1720 °C. The CaO-B_2O_3 doped AlN powders were placed as the sublimating sources in the upper region, under which several graphite (for graphite crucible) or AlN (for AlN crucible) substrates were set at different hights in the reactor.

During heating, AlN vapour was formed in the high temperature region and then diffused to the lower parts. In the regions with lower temperatures, the AlN partial pressure exceeded the saturation pressure. When the supersaturation got an enough level, AlN whiskers could be produced. Due to the existence of temperature gradient, different shapes of AlN were obtained, which were AlN pillars (Fig. 3) in the top region, whiskers in the middle, and noncrystalline fibres (Fig. 4) at the bottom. The whiskers had the largest amount, while the pillars and fibres were far less.

As shown in Fig. 3, AlN pillars grew on the substrates, with heights of 2–3 mm. The cross sections were equilateral hexagons with edges of 20–50 μm, inferring that the pillars grew along the *c* axis. Fig. 4 shows that the AlN fibres were garrulous and convolving, with diameters of 5–10 nm. Fig. 5c is the TEM micrograph of the fibres. Their electron diffraction patterns were halation rings. Only Al was detected by EDS. These results confirmed they were noncrystalline AlN fibres.

3.3. Growth mechanism

As catalysts, CaO-B_2O_3 melted at high temperature through the reaction with alumina which inevitably existed on the surface of raw AlN particles. The formed liquid vapourized in high temperature region and condensed to droplets on the substrates in lower parts. The existence of liquid was beneficial to the growth of AlN crystals with different morphologies through a vapour-liquid-solid (VLS) mechanism. Fig. 5 exhibits the observed droplets on the tips of AlN pillars (Fig. 5a), whiskers (Fig. 5b) and noncrystalline fibres (Fig. 5c). At different temperatures, the liquid had different viscosities and wetting angles with the substrates, which explains why various morphologies of AlN were formed.

At high temperature (1800 °C), the liquid had small viscosity. The AlN vapour, with high saturation pressure, could easily dissolve into the droplets. When the dissolved AlN reached a certain supersaturation level, the precipitation process began. Due to the strong wetting power of the liquid at high temperature, the droplets spread on the substrates, with small angle and large area of contact, which led to the AlN pillars. However, it was of small probability that the droplets were condensed on the substrates at high temperature, so only a small amount of pillars were produced.

In the middle region, as the temperature was lower (1720 °C), liquid not only got a suitable viscosity, but also could easily be condensed on the substrates. Plenty

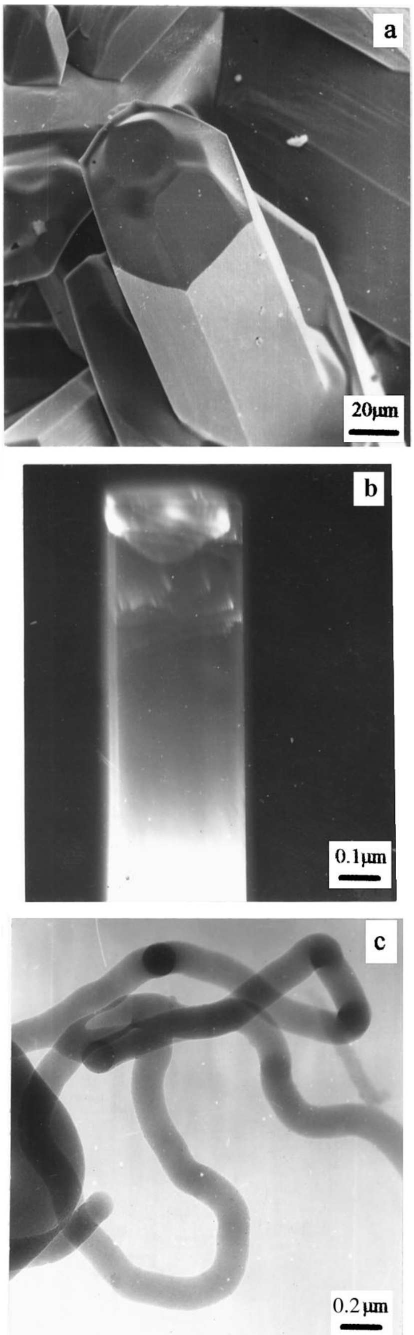

Figure 5 Droplets on the tips of (a) AlN pillar (SEM), (b) AlN whiskers (TEM), and (c) noncrystalline AlN fibres (TEM).

of droplets were yielded, with moderate contact angle to the substrates. When crystallization occurred because of the supersaturation of AlN in the droplets, large quantity of whiskers were generated.

The liquid in the low temperature region (1650 °C) had high viscosity and weak wettability for the substrates. As a result, spherical droplets were formed. Moreover, the dissolution of AlN into the liquid needed longer time under such conditions. During the procedure, the fluctuation of temperature resulted in the formation of noncrystalline AlN fibres.

As the heating went on, the catalyst liquid was gradually removed by volatilization. In the later stage of heating, the growth of AlN pillars and fibres was retarded and finally ended due to the lack of liquid, while the AlN whiskers kept growing through vapour-solid

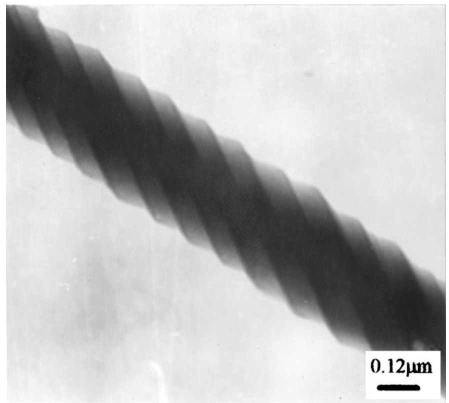

Figure 6 Screw growth of AlN whisker (TEM).

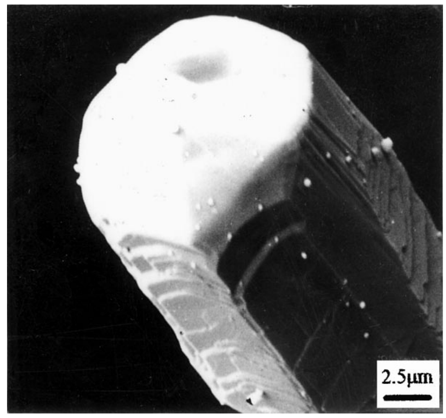

Figure 7 Growth benches on the tip and side faces of AlN whisker (TEM).

(VS) mechanism. By SEM, screw growth (Fig. 6) and the growth benches on the tips of the whiskers (Fig. 7) were observed.

3.4. Morphologies and orientations of AlN whiskers

3.4.1. Morphologies

The prepared AlN whiskers in this experiment had lengths of 2–8 mm and widths of 3–8 μm. It can be seen in Fig. 2 that the whiskers were smooth and straight, with few surface defects. The cross sections were hexagon, tetragon, square, or circle. When the heating was prolonged or the supersaturation got a level too high, lateral growth would happen in some whiskers, which brought about branches as Fig. 8 shows. Besides this, turning process was also found in whisker growing (Fig. 9). As equivalent planes have the same possibilities of growth at equivalent directions, the turning process could be realized with the aid of droplets [3].

3.4.2. Orientation determination by x-ray diffraction

The x-ray Laue method was used to analyze the orientations and the perfection of crystal structure, using a tungsten target, arranging the apparatus in a transmission style, and spending 5 h taking photograph.

The Laue diffraction patterns were composed of fine spots with no distortion nor cleavage, which indicated the investigated whiskers to be perfect single crystals.

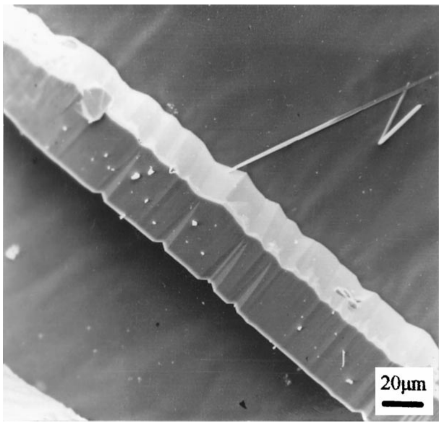

Figure 8 AlN whisker with a branch (SEM).

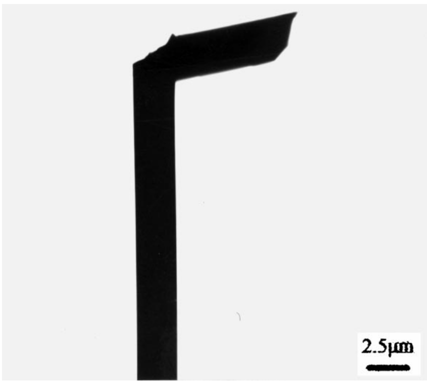

Figure 9 AlN whisker with a turn (TEM).

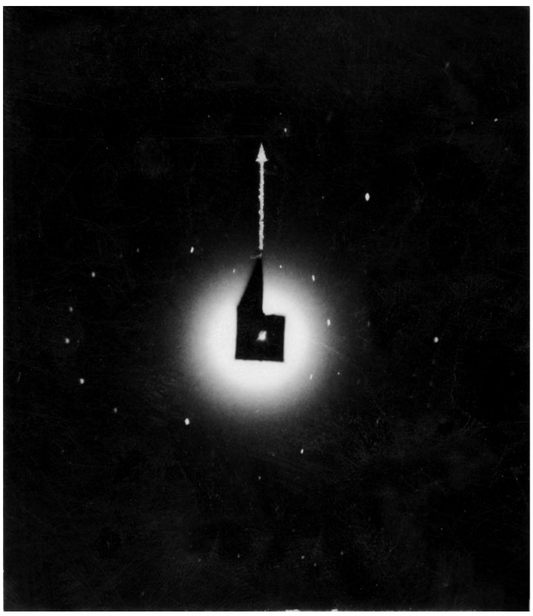

Figure 10 Laue photograph of a [0001] oriented AlN whisker.

Many kinds of orientations were discovered, e.g. [2110] for the cuboid flat whiskers with wide side faces of {0001} and narrow ones of {0110}, [1010] for the tetragonal elongated whiskers with side faces of {0001} and {1210}, [0001] for the hexagonal prism whiskers with side faces of {1010}. Fig. 10 displays the Laue photo of a [0001] oriented whisker.

Laue method seems bothering in determining orientations of whiskers. Actually, the rotating-crystal

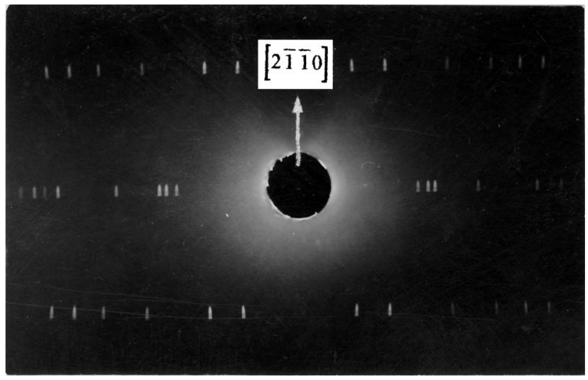

Figure 11 Rotating-crystal x-ray photograph of a $[\bar{1}2\bar{1}0]$ oriented AlN whisker.

method is more available for whiskers with a known structure. Fig. 11 gives the low angle part of a rotating-crystal x-ray photograph taken of a cuboid flat whisker. The diameter of the camera was 57.3 mm. Cu K_α was used. The growth axis of the whisker was precisely located on the rotating axis of the camera. The measurement told that the distance between reciprocal planes ordered 0 and 1 was 3.1065 Å, only 0.0049 Å less than the lattice parameter a(3.1114 Å) of AlN, which indicated that the growth direction was [2110]. On the other hand, the zeroth order diffraction spots, from center to outside, were (0110), (0002), (0114), (0112), and (0113), etc. They all belong to crystal zone [2110], which proved the growth direction to be [2110].

Other researchers reported whiskers with [2110], [1010] or [0001] as growth directions, i.e. {2110}, {1010} or {0001} as growth planes [2, 9, 10]. These are close-packed planes of AlN. Furthermore, this study found whiskers with growth planes of (1011), (1012) or (1013), i.e. (101l), where $l = 0, 1, 2, 3$, which are secondary close-packed planes of AlN. The relative orientations should be [101w], where $w = 0, 1, 2, 3$. What's interesting is that whiskers were also discovered with growth axes perpendicular to (101l), where $l = 7, 8, 9$. This will be further discussed in Section 3.4.3.

3.4.3. TEM analysis

TEM observation got results agreeable to the above discussion. Fig. 12 shows the TEM micrograph and electron diffraction pattern of an AlN whisker oriented

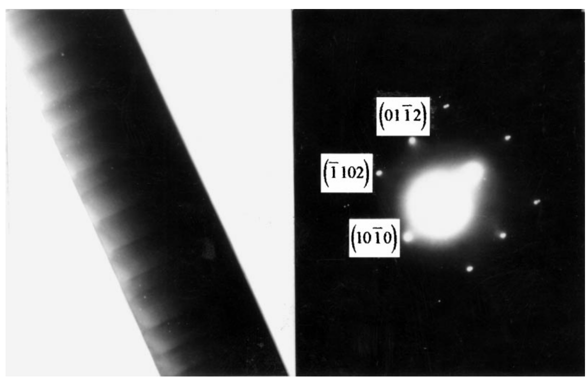

Figure 12 TEM analysis of an AlN whisker with a growth axis $[10\bar{1}2]$.

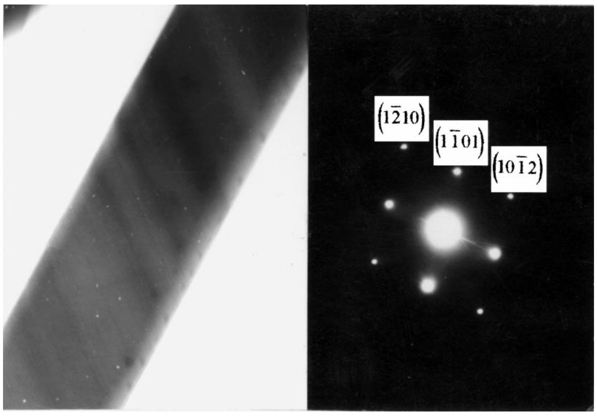

Figure 13 TEM analysis of oblique grown AlN whisker.

[10$\bar{1}$2], which is perpendicular to the growth plane (10$\bar{1}$2).

Moreover, oblique grown whiskers were observed (Fig. 13). The whisker in Fig. 13 grew along an axis at an angle of about 54° to the growth plane, (10$\bar{1}$2). As we know, for AlN, the angle included between (10$\bar{1}$9) and (10$\bar{1}$2) is 54.3°. This explains why the macroscopical growth axis was normal to (10$\bar{1}l$), where $l = 9$, which was observed in Laue method experiment. The oblique growth mechanism has been reported in the films due to the size effect [11], but has not been found in whiskers. The droplet's surface tension might be one of the causes of this effect [3].

4. Conclusion

AlN pillars, whiskers and noncrystalline fibres were fabricated through a sublimation-recrystallization method, with AlN powder as raw material and a CaO-B_2O_3 as catalysts, in a closed graphite or AlN crucible reactor.

In the early stage of preparation, VLS was the dominant mechanism, producing various morphologies of AlN. When the heating went on, liquid phase was removed by volatilization, therefore the pillars and noncrystalline fibres stopped growing, but the growth of AlN whiskers continued through VS mechanisms.

Most of the AlN whiskers exposed orientations of [2$\bar{1}\bar{1}$0], [0001], or [10$\bar{1}w$], where $w = 0$, 1, 2, 3, the growth planes being{2$\bar{1}\bar{1}$0}, {0001}, or {10$\bar{1}l$}, where $l = 0$, 1, 2, 3. Oblique growth also happened.

Acknowledgements

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