Morphologies and growth mechanisms of aluminum nitride whiskers by SHS method—Part I

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AlN whiskers grown by combustion of Al powder under high nitrogen pressure were investigated. Several types of whiskers' structures, such as wavy structure, crossed structure, stack structure, bead-necklace structure, branch structure, dendritic crystal, were found due to the variation of growth conditions. The causes of some structures were explained.

1. Introduction

AlN is considered an ideal material for semiconductor substrate applications. It combines properties such as high thermal conductivity, low thermal expansion coefficient, high electrical resistivity, and good dielectric properties, which make it an effective heat sink or heat-dissipating medium. By considering the successful application of polymer-ceramic composite in transducers [1], it is thought that the composite can be used as substrate. For example, AlN in the form of powder or sintered grain, has been added as filler for polymer and glass compounds to increase the heat-transfer properties of these materials. Also, AlN fibres or whiskers have been used to optimize the thermal properties of electronic-packing application [2]. Now, the use of AlN whiskers in high density substrate [3, 4] and functional film [5] have attracted much interest.

Whiskers are minute, high purity, single crystal fibres which the proportion of length/diameter is 5–1000 [6]. In the early 1960s, AlN whiskers have been reported. AlN whiskers have been prepared by various methods, such as carbothermal nitridation of an alumina and carbon source [2, 7], VS method [8], CVD method [9], sublimation-recrystallization method [10]. To apply AlN whisker commercially, it is necessary to produce it by an economic means. The aluminum nitride whiskers used in this investigation have been produced by SHS technique. In SHS process, once initiated, highly exothermic reaction can become self-sustaining and will propagate through the reactant mixture in the form of a combustion wave. As the combustion wave (front) advances, the reactants are converted to the products. The use of such method to prepare materials has been commonly referred to as the self-propagating high temperature (combustion) synthesis (SHS) method. The potential advantages of the SHS process include low processing cost, energy efficiency, and high product purity, etc. [11].

In the present work, the microstructures of AlN whiskers are investigated in order to understand the growth mechanism and defect characteristics of the whiskers. Here, the morphology, chemistry, and growth mechanism of AlN whiskers have been investigated using optical microscopy, electron microscopy, and X-ray diffraction techniques.

2. Experimental procedure

2.1. Whisker synthesis

Al powder with an average particle size of 24.9 μm was used as starting material, its chemical composition was shown in Table I and its morphology was shown in Fig. 1a. The AlN powder used was synthesized in lab and with an average particle size of 6.03 μm, its morphology was shown in Fig. 1b. These two powders were AlN ball-mixed with a definite composition and then put into a graphite crucible drilled with many small pores. Al foil was used to separate the inner wall of crucible from reactants. The SHS experiments were conducted in a high-pressure, cold isostatic pressing vessel under nitrogen pressure from 1 to 10 MPa. The combustion reaction was initiated by burning a titanium powder compact placed on top of the packed reactant. The titanium powder compact was ignited by electric power.

2.2. Whisker characterization

Element amount of reactant was analyzed by using chemical analysis method. The distribution of particle size was analyzed on SICAS-4800 by light fluoroscopy method.

Secondary electron imagines were recorded in a EPMA-8705 QHII and KYKY-2000 SEM, typically operated at 13 KV to enhance the contrast of surface defects. Samples for SEM analyses were coated with a

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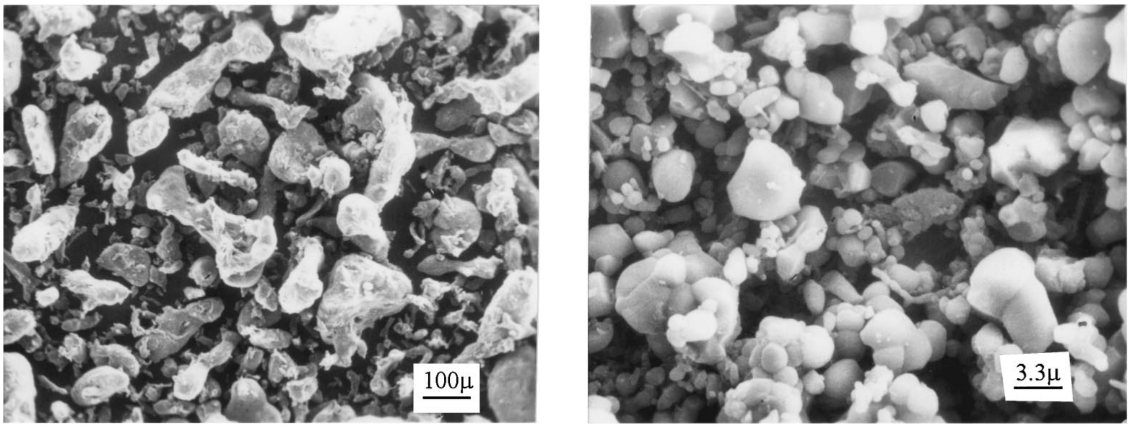


(a) (b)

Figure 1 SEM morphology of Aluminum powder and Aluminum nitride as diluent: (a) Aluminum powder; (b) Aluminum nitride as diluent.

thin film of sputtered gold to reduce the tendency for electrical charge buildup. The SEM was equipped with a LINKISIS windowless energy dispersive detector for light element detection.

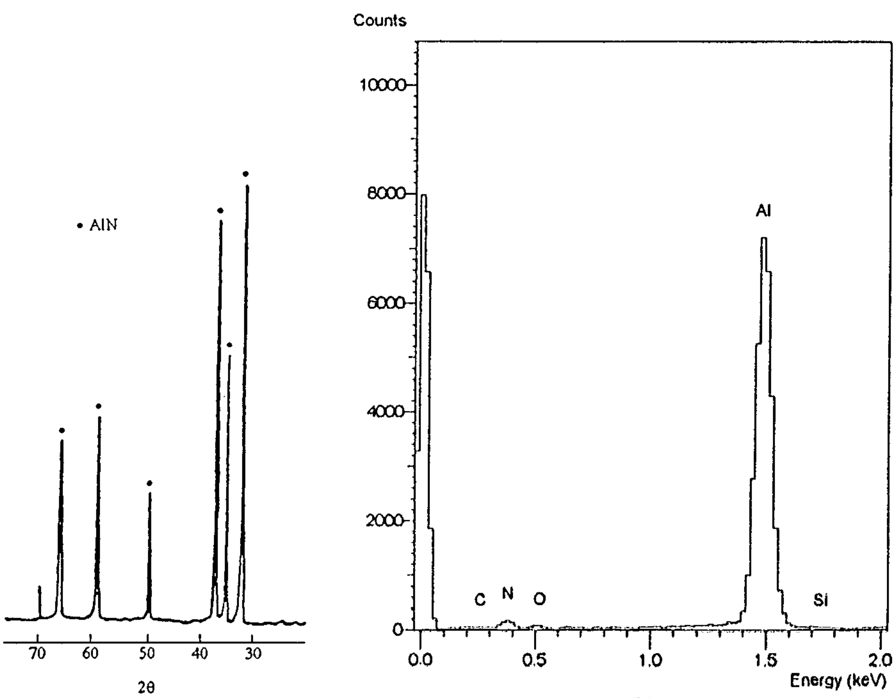
The crystalline phases of the products were identified by X-ray powder diffractometry. X-ray diffraction was carried out on a RAX-10 diffractometer made by Rigaku corporation using CuK_α radiation and a graphite monochromator. The working voltage was 40 KV. The working electric current is determined according to sample and concrete needs. A powdered sample for XRD was obtained by grinding the AlN whiskers to a suitable size.

All TEM imagines were recorded in a JEM-200CX made by JEOX corporation, operated at 200 KV. The TEM equipped with an EDAX 9900 energy dispersive system (EDS) attachment for chemical analysis. Sample for TEM examination were prepared by the following procedure: dispersing the whiskers in a ethyl alcohol absolute with the aid of ultrasonic stirring (about 15 min), and then placing the whiskers on a carbon-filmed (50–60 nm thickness) copper grid (Φ2.3 mm) for TEM analysis. Defects in the whiskers were identified utilizing diffraction, phase-contrast image (bright-field imagine and dark-field imagine) and high-magnification techniques.

The morphology of the crystal was also established by means of optical microscopy techniques using normal transmitted light and side light.

TABLE I Chemical composition of aluminum powder

Element	Al	O	C	Fe	Si	Ca	Mg	Others
Content (wt %)	99.1	0.7	0.05	0.0375	0.089	0.009	0.008	Trace



(a) (b)

Figure 2 (a) Typical energy dispersive X-ray spectrum of the AlN whiskers observed under the SEM; (b) X-ray diffraction spectrum of the AlN whiskers.

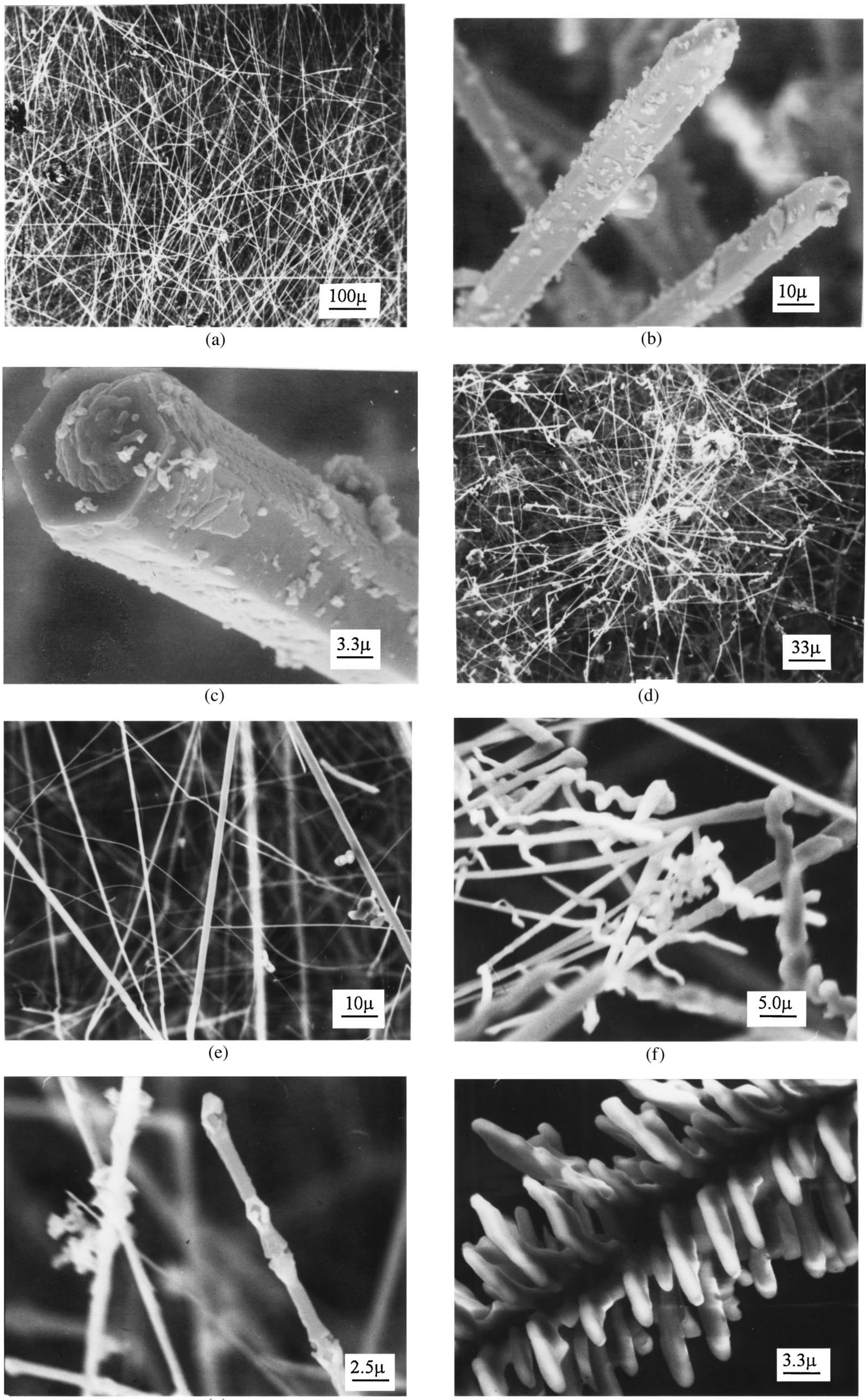
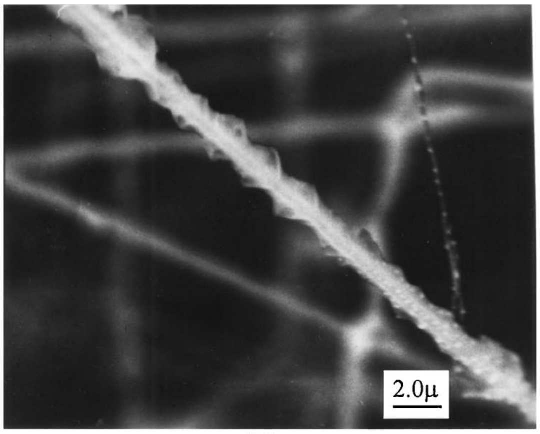
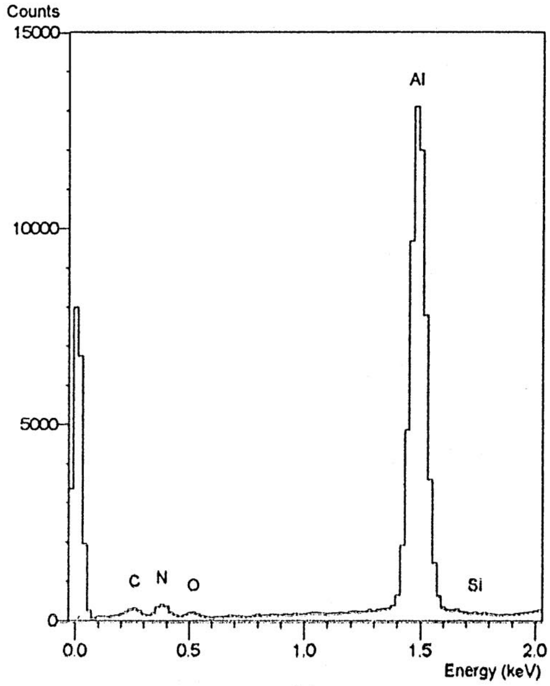


Figure 3 Secondary electron images of AlN whiskers: (a) Low-magnification image; (b) high-magnification image showing a whisker with hexagonal in shape; (c) whisker showing rectangular cross section; (d) whiskers with a "starlike" morphology; (e) straight whiskers and whiskers with arc structure; (f) layer structure; (g) branch structure; (h) dendritic crystal structure.



(a)



(b)

Figure 4 (a) Scan electron micrograph of whiskers with secondary thickening structure; (b) Energy dispersive X-ray spectrum of the thickening structure observed under the SEM.

3. Results and discussion

In this work, we will conventionally refer to single-crystal fibers or filaments with a high aspect ratio as whiskers.

The whiskers investigated in the present work were AlN whiskers prepared by SHS method. The as-received whiskers were white or light gray in color, wool-like, with dimensions of 0.01–20 μm diameter and 0.1–50 mm length. Typical EDS and XRD analyses of the whiskers were shown in Fig. 2a and b respectively. The chemical analysis shown strong aluminum and nitrogen peaks, while their structure was identified as hexagonal wurtzite-type AlN, PDF No. 25-1133 with lattice parameters $a = 0.3111$ nm and $n = 0.498$ nm.

A series of electron micrographs of whiskers at different magnifications were shown in Fig. 3a–h. The whiskers can be described as long and straight filaments with diameters between 2 and 13 μm and 2–20 mm length in the centimeter range (Fig. 3a). The cross-sectional views were either rectangular or hexagonal in shape (Fig. 3b and c, respectively). In equilibrium condition, the cross section is hexagonal (the structure of AlN); on the contrary, in unequilibrium condition, the structure with other cross section will occur.) AlN whiskers growing in a "star-like" pattern are shown in Fig. 3d. Two different explanations are possible for this type of growth. Either they are the result of nondirectional growth from an active nucleation site, or they can form by a change in the mechanism of whisker growth, allowing other crystallographic planes to become active during growth.

The majority of whiskers are sensibly straight, but others are not. Thick whiskers are straight, but the thin exhibit an arc with a big diameter. The surfaces of some whiskers are smooth, but others are not. AlN or impurity stick on the whiskers to form rough face (Fig. 3d and Fig. 3e).

The structure of two whiskers crossing each other is shown in Fig. 3f. These two whiskers encounter at the growth stage, but they do not influence each other. Thus this crossed structure was formed.

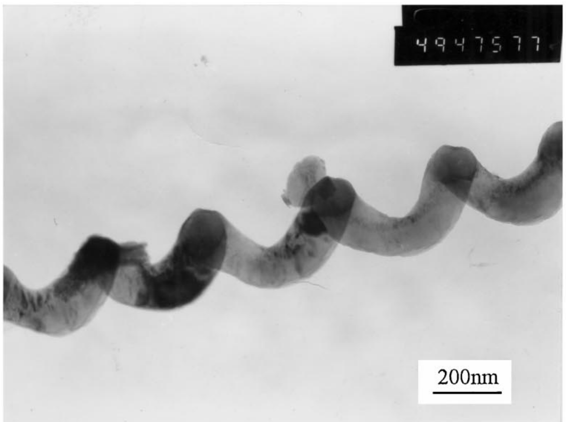
Some whiskers are formed by stacking of the AlN single crystals. This stack structure can be also clearly observed in Fig. 3f. Single crystals of AlN were joined face-to-face and grew without especial direction.

AlN whiskers with branch structure are shown in Fig. 3g. The structure may be result from the fluctuation of supersaturation. When the supersaturation is small, the whisker will pause growth; when the supersaturation is high, the whisker will grow again and form branch structure.

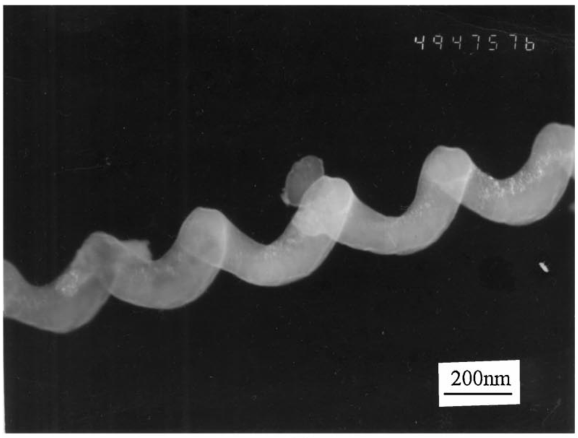
AlN whiskers with the dendritic crystal structure are shown in Fig. 3h. It is also associated with the fluctuation of supersaturation. Its production mechanism is proposed in Paper 2.

The secondary thickening structure may result from the secondary nucleation caused by impurities or change of the growth conditions, as shown in Fig. 4a. Some impurities are observed on secondary structure by EDS analysis. The phenomenon is associated with the growth mechanism [12].

Fig. 5a, b, c respectively show the bright-field, the dark-field and the electron diffraction image of AlN whiskers with wavy structures. From the view of energy, it is easy to change the direction of growth by the aid of droplet. At the same time, from the image (Fig. 5) of wavy structure, some spots on the whiskers are observed, and the contrast of bright-field and dark field is contrary. From the knowledge of electron



(a)



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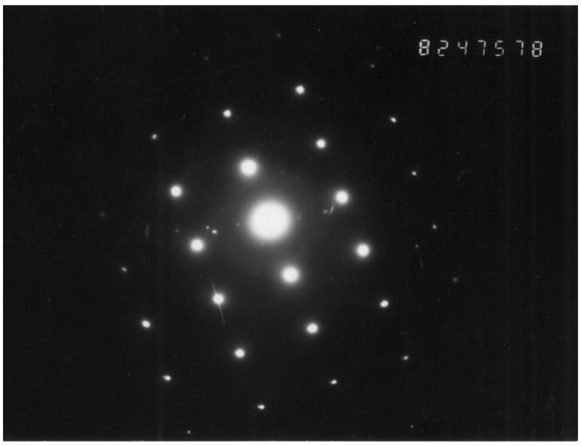
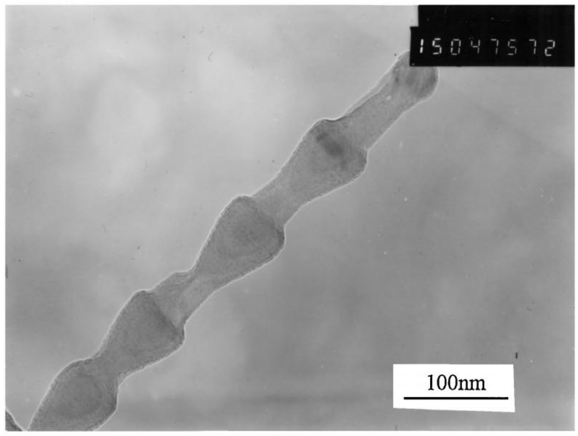


(c)

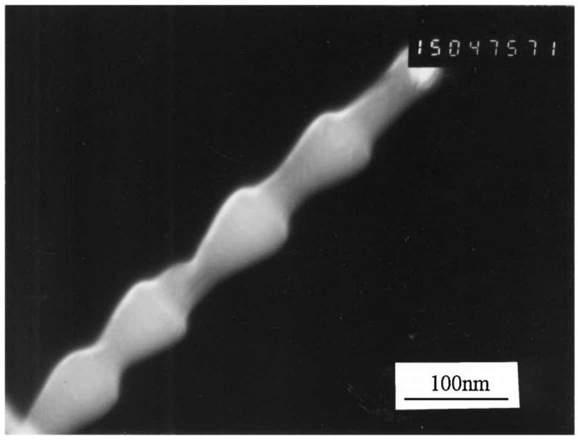
Figure 5 Transmission electron micrograph of AlN whiskers with wavy structure: (a) Bright-field image; (b) dark-field image; (c) electron diffraction image.

micrography, there are some dislocations or stack faults in the whiskers.

Fig. 6a, b, c respectively show the bright-field, the dark-field and the electron diffraction image of AlN whiskers with "bead-necklace structures." Corresponding to Fig. 4a, this is also secondary thickening structures. The structure is so ordered that it may be formed after the completion of the whiskers' growth. Unlike this condition, some knuckles were found in the secondary thickening structure, as shown in Fig. 7. It is interesting to see that the knuckles are homogeneously distributed along the whisker, which may indicate that some secondary thickening structures are



(a)



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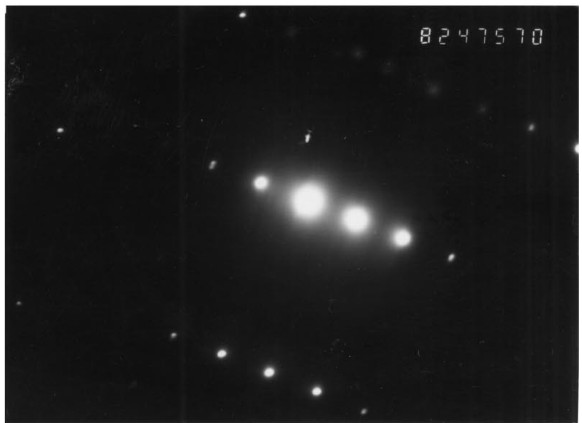

(c)

Figure 6 Transmission electron micrograph of AlN whiskers with "bead-necklace" structure: (a) Bright-field image; (b) dark-field image; (c) electron diffraction image.

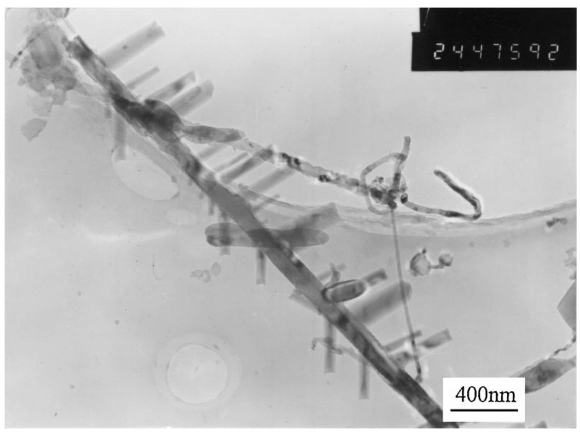

Figure 7 Transmission electron micrograph of AlN whiskers with many uneven-distribution branches.

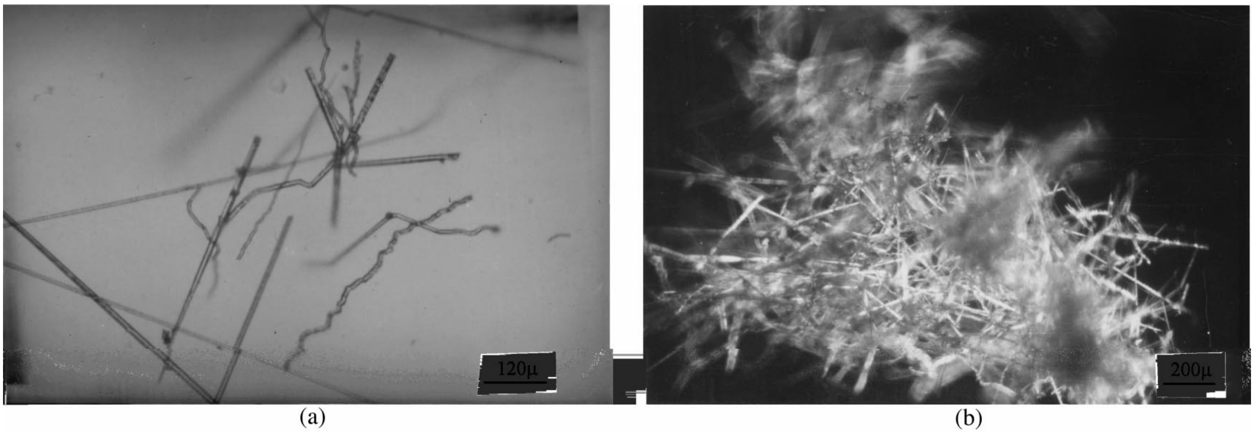

Figure 8 Optical microscopy of AlN whiskers: (a) Transmitted normal light; (b) side light.

formed during the whisker growth process, not in the later stage.

Highly pure and highly dense AlN is known to be optically transparent or translucent. Fig. 8 shows optically micrographs using normal transmitted light and side light. Finally, these whiskers are expected to be optically transparent or translucent and therefore suitable for some electrooptic applications.

4. Conclusions

1. AlN whiskers were synthesized by using SHS method. Many analysis methods, such as XRD, SEM, TEM, OM, EDS, are used to study the morphologies of AlN whiskers.

2. The AlN whiskers whose the cross section is hexagonal was formed in the equilibrium condition, while other shapes were formed in unequilibrium condition.

3. Independent growth of whiskers forms crossed structure. The fluctuation of supersaturation caused the branch structure and dendritic crystal structure.

4. The "star-like" were also observed in whiskers.

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