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Combustion synthesis of AlN whiskers

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Long and coarse AlN whiskers comprising more than 80 vol% of the combustion product have been successfully produced through combustion synthesis. Addition of ammonia halides can accelerate the vaporization of Al, and retard the deposition rate of AlN, with the result that the growth of AlN whiskers is markedly promoted. A growth model for a spiral whisker by a helical screw dislocation mechanism, or a combination mechanism of a helical screw dislocation and the VLS process, is proposed. Periodic interactions of vacancies and the tip of a screw dislocation cause the growth of a spiral whisker in the model. Under an atmosphere of supersaturated "AlN vapor," the growth of whiskers along the axial direction slows down and gradually arrests, due to the limitation of the diffusion distance. A series of deposition sites are then produced at regular, isolated locations along the center line on the prismatic plane, and eventually cause the formation of dendritic whiskers.

1. Introduction

Aluminum nitride (AlN) ceramics have attracted much attention as a promising electrical substrate and packaging material, because of such properties as high thermal conductivity, excellent electrical insulation, low dielectric constant, and a thermal expansion coefficient closely matching that of silicon. AlN can also be used as an advanced refractory material, because of its non-wettability by molten aluminum and most of the nonferrous alloys. One example of the refractory use of AlN is as crucibles for the growth of single-crystal gallium arsenide. Another potential and very large market for AlN is as fillers to improve the thermal conductivity of epoxy [1, 2].

Powders comprised of larger particles, with a bimodal size distribution, are desirable for filler applications. Larger particles are less sensitive to high humidity, and a bimodal distribution results in higher packing density [3]. Whiskers are of interest for their small size, low defect content, and excellent mechanical and physical properties that are nearly equal to the theoretical values. AlN whiskers are preferred to powders for use as fillers. When polymers are reinforced with acicular AlN whiskers, their conductivity increases by a factor of 70 over that of the matrix [4]. Because heat flow occurs along conductive fillers, long and coarse whisker-type AlN is expected to significantly improve thermal conductivity.

Many fabrication methods for AlN whiskers had been developed, such as, the CVD method [4], vaporization and condensation of AlN powder [5–7], the direct nitridation of metallic aluminum [8] and the carbo-thermal reduction method [9–13].

Recently, self-propagating high-temperature synthesis (SHS), also known as combustion synthesis, of AlN whiskers has attracted considerable attention because it offers an energy- and time-saving process, as well as cost reductions. Bradshaw and Spicer found that different morphologies of AlN were associated with different sample regions and that AlN whiskers were especially predominant in the combustion product when 5 wt% of NH_3 is added to the atmosphere [14]. Lee *et al.* obtained high-aspect-ratio whiskers under low nitrogen pressure by adding 3 wt% $MgCl_2$ [15], and the volume ratio of whiskers to aloelike structures increased gradually as the distance from the sample surface increased. However, Shin *et al.* [16] found that AlN whiskers generally occurred in the outer-layer of the sample, a finding that

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agrees with the results of our earlier research, where the morphology of the product was strongly related to its oxygen content [17]. Several types of whisker structure, such as wavy structure, crossed structure, stack structure, bead-necklace structure, branch structure, dendritic crystal, have been found in the combustion product due to variations in the growth conditions [18, 19].

Shin *et al*. attributed the formation of AlN whiskers to the condensation of an AlN vapor phase formed during SHS under fairly low nitrogen pressure (<1 MPa) [16]. Because no whiskers showed characteristic VLS (vapor-liquid-solid) droplets on their tips, Bradshaw and Spicer concluded that AlN whiskers grow via the vapor-solid (VS) mechanism, although they did not exclude the VLS mechanism [14]. However, the intermediate morphologies of both AlN particles grown by the VS mechanism and AlN whiskers grown by the VLS mechanism have been observed in gas-release experiments [17]. In our opinion, AlN particles develop from the vapor by the way of platelet growth (VS mechanism) at low oxygen contents. The growth of AlN whiskers is mainly controlled by the VLS mechanism [17].

The morphology, chemistry, and crystallography of the SHS of AlN were investigated by scanning electron microscopy (SEM) and X-ray diffractometry (XRD) in the present study. The effects of additives on the growth of whiskers, the growth mechanism of the spiral whisker, and the coarsening mechanism of AlN whiskers, are discussed in this paper.

2. Experimental procedures

Commercially available aluminum powders (Northeast Light-Alloy Co., Harbin, China), with an average particle size of ∼22 μm were used as the reactant. AlN powders, fabricated by ourselves using combustion synthesis, were used as the dilutant. NH_4Cl, NH_4F, were used as the additives.

The compositions of the starting mixtures are listed in Table I. After the mixtures of Al and AlN powders were first vacuum-dried, ammonia halides were added into them. They were ball-milled using twice alumina balls in a plastic container for 12 h. 1 kg of the mixtures was pressed into cylindrical compacts (10 cm in diameter and about 14 cm in length). The compact was placed in a graphite crucible. Some fine Ti powder as an igniter was put on the top of the compact. The crucible with the compact was put into a stainless steel combustion chamber. The air in the chamber was removed by purging twice with 0.5 MPa N_2. The chamber was then back-filled with commercial grade nitrogen at a pressure of 10 MPa. The compact was ignited by using a tungsten coil.

TABLE I Composition of the initial mixtures in samples A1, A2, and A3

Sample	Al (wt%)	AlN (wt%)	NH_4Cl (wt%)	NH_4F (wt%)
A1	50	50	–	–
A2	50	45	5	–
A3	50	42	5	3

The phase composition and interplanar distances of the product were investigated by X-ray diffraction (XRD) using a Phillips X-ray diffractometer with a proportional counter detection head. Graphite monochromated Cu Kα radiation at a voltage of 40 KV and a current of 20 mA, was used. The morphology of the product was examined by a JEOL scanning electron microscopy (SEM). The operation voltage was 20 KV.

3. Results and discussion

The combustion product in sample A1 (without additives) is a porous, sintered body. The AlN particles are mostly coarse and regular as shown in Fig. 1a. AlN whiskers can occasionally be observed. The combustion products in the sample A2 (containing 5 wt% NH_4Cl) were not densely packed. They mainly consisted of AlN particles and some fine AlN whiskers between the particles (Fig. 1b). This indicates that the formation of AlN whiskers can be promoted by adding NH_4Cl.

Addition of NH_4Cl has two effects on the growth of AlN whiskers. First, the growth of AlN whiskers is mainly controlled by a VLS mechanism. The formation of liquid required in the VLS mechanism depends on the presence of impurities, especially impurities containing oxygen. The addition of NH_4Cl significantly increases the oxygen content in the combustion product [17]. Thus, addition of NH_4Cl can promote the growth of AlN whiskers. Second, NH_4Cl sublimates at 350°C and decomposes into ammonia and HCl vapor at 520°C. HCl vapor is driven to the combustion front by the high temperature of the combustion zone and reacts with aluminum at the combustion front. The reactions between HCl vapor and aluminum are as follows:

$$2\mathrm{Al}(s,\ l,\ g) + 2\mathrm{HCl}(g) \rightarrow 2\mathrm{AlCl}(g) + \mathrm{H_2}(g) \tag{1}$$

$$\mathrm{Al}(s,\ l,\ g) + 2\mathrm{HCl}(g) \rightarrow \mathrm{AlCl_2}(g) + \mathrm{H_2}(g) \tag{2}$$

$$2\mathrm{Al}(s,\ l,\ g) + 6\mathrm{HCl}(g) \rightarrow 2\mathrm{AlCl_3}(g) + 3\mathrm{H_2}(g) \tag{3}$$

where s, l, g in brackets denote solid, liquid and gas states, respectively. Because of the surplus of Al and a deficiency of HCl vapor, Reaction (1) is the most favorable. Besides the above reactions, there is a vaporization reaction of Al.

$$\mathrm{Al}(s,\ l) \rightarrow \mathrm{Al}(g) \tag{4}$$

With respect to the amount of vaporized Al, Reaction (4) is the dominant mechanism. However, from the viewpoint of thermodynamics, Reaction (1) is more favorable than Reaction (4).

Subsequently, Al and AlCl vapor react with nitrogen and generates "AlN vapor" in the approaching combustion zone.

$$\mathrm{Al}(g) + \mathrm{N_2}(g) \rightarrow \mathrm{AlN}(g) \tag{5}$$

$$2\mathrm{Al}(g) + 2\mathrm{NH_3}(g) \rightarrow 2\mathrm{AlN}(g) + 3\mathrm{H_2}(g) \tag{6}$$

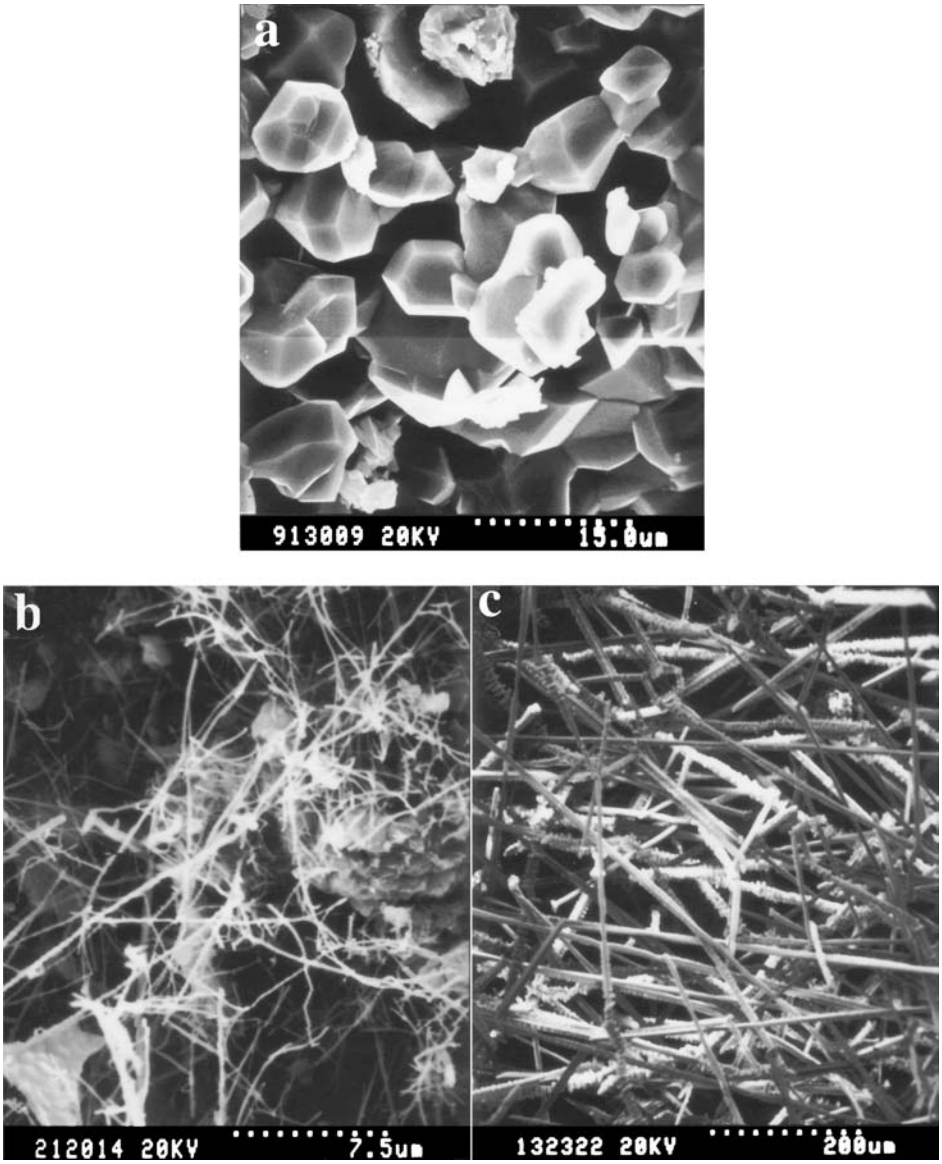

Figure 1 SEM micrographs of combustion products in samples (a) A1; (b)A2 and (c) A3.

$$2AlCl(g)+N_2(g)+H_2(g)\rightarrow 2AlN(g)+2HCl(g) \tag{7}$$

$$AlCl(g)+NH_3(g)\rightarrow AlN(g)+HCl(g)+H_2(g) \tag{8}$$

Compared with reactions (6) and (8), Reactions (5) and (7) are the dominant mechanisms because the amount of NH_3 is much less than that of nitrogen. From the viewpoint of thermodynamics and kinetics, Reaction (5) is more favorable than Reaction (7), which means that the deposition rate of AlCl(*g*) is lower than that of Al(*g*). According to the above reactions, HCl vapor is not consumed and just acts as a catalyst (or a transportation agent) for Al vaporization. It can be transported to the combustion front and takes part in the reaction again. Thus, an addition of NH_4Cl can accelerate the vaporization of Al.

Some ammonia is consumed by Reaction (8), the remaining ammonia will react with the HCl vapor and form NH_4Cl after combustion. This is why a layer of white NH_4Cl powder could be seen on both the product and the chamber wall.

High deposition rates generally result in a growth of particles. The vaporization rate of Al is relatively low and the deposition rate is high in the sample without additives. The Al vapor cannot be transported very far. Thus, AlN particles grow from the vapor by the way of platelet growth (VS mechanism) at low oxygen contents.

Different supersaturation levels of the AlN vapour cause the generation of different whiskers. In an atmosphere of low supersaturation of AlN vapor, whiskers can not grow. A high level of supersaturation results in the formation of coarse whiskers. A moderate level of supersaturation yields fine whiskers [5]. When NH_4Cl is added into sample, the vaporization rate of Al is improved, a relatively high supersaturation of AlN vapor will be easily achieved, and the Al (AlCl) vapor can be transported further, which aids in the growth of whiskers.

If NH_4F is used instead of NH_4Cl, the reactions for the vaporization and deposition change and are shown as Reactions (9) and (10).

$$2\mathrm{Al}(s,\ l,\ g) + 2\mathrm{HF}(g) \rightarrow 2\mathrm{AlF}(g) + \mathrm{H_2}(g) \quad (9)$$

$$2\mathrm{AlF}(g) + \mathrm{N_2}(g) + \mathrm{H_2}(g) \rightarrow 2\mathrm{AlN}(g) + 2\mathrm{HF}(g) \quad (10)$$

Reaction (9) is more thermodynamically favorable than Reaction (1), and Reaction (10) is less thermodynamically favorable than Reaction (7). In other words, the vaporization rate of Al is greatly improved (a highly supersaturated vapor will be easily achieved), the deposition rate of AlF(g) is much lower than that of Al(g), and the Al (AlF) vapor can be transported greater distances. If the contents of NH_4Cl and NH_4F in the initial materials are high enough, the Al(g) content will be significantly reduced during combustion due to Reactions (1) and (9). The deposition of AlN will be determined by Reactions (7) and (10) and will be significantly retarded, with the result that the growth of Al whiskers is highly promoted.

In order to produce long, coarse AlN whiskers, 3 wt% NH_4F and 5 wt% NH_4Cl was added to sample A3. AlN whiskers constituted more than 80 vol% of the combustion product in sample A3. The AlN whiskers were on average more than 1 mm in length and about 5 μm in diameter (see Fig. 1c). Of the AlN whiskers in sample A3, about 60% were long, coarse, round whiskers with few surface defects, about 20% were spiral, about 10% were dendritic, and the remainder were irregular in shape. Helical AlN whiskers have been observed previously in whiskers prepared by combustion synthesis [18] or by vaporization and condensation of AlN powder [5]. There

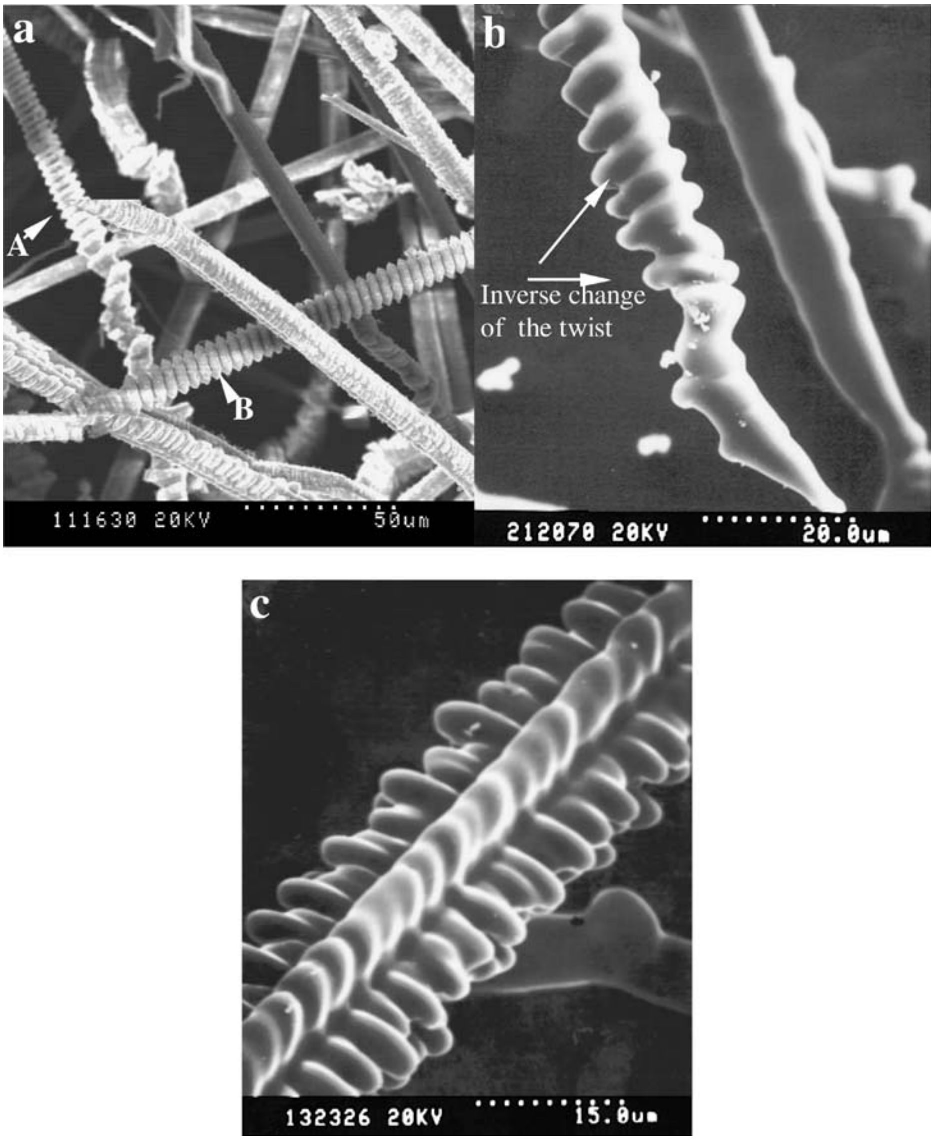

Figure 2 SEM micrographs of (a) spiral whiskers, (b) the tip of the spiral whiskers and (c) dendritic whisker.

were so many helical AlN whiskers in the product in this study that the presence of helical whiskers cannot be thought of as an isolated phenomenon, but there must be some intrinsic reason for their formation.

Both right- and left-handed helices are observed (see whiskers A and B in Fig. 2a). The pitch of the twist along the length is fairly even and the whiskers' diameter is unchanged along the stem of the whisker. The pitch of the twist for the different spiral whiskers is different. Sometimes, abrupt changes from straight to helical form occur and there are switches between right- and left-handed twist (see in Fig. 2b). The secondary branches are distributed fairly evenly on the prism planes along the dendritic whiskers as can be seen in Fig. 2c.

XRD patterns of the combustion product in sample A1 and the whiskers in sample A3 are shown in Fig. 3a and b, respectively. Compared with the pattern for AlN particles, the (0002) diffraction peak for AlN whiskers in sample A3 is absent. A similar XRD pattern for AlN whiskers prepared by carbothermal reduction was observed by Fu *et al.* [12]. AlN whiskers were randomly spread on the substrate for the XRD test. The absence of the (0002) diffraction peak means the $\{0002\}$ planes in all AlN whiskers are parallel to the incident beam resulting in no diffraction from the (0002) planes. In other words, the axial orientation of the AlN whiskers is $\langle 0002\rangle$. Some whiskers with $[2\bar{1}\bar{1}0]$, $[1\bar{2}10]$ or $[10\bar{1}0]$ as the growth direction have been observed by means of TEM by other researchers [5–8, 11]. The XRD pattern reflects a statistical result. Although we cannot exclude the existence of these other growth directions because AlN whiskers with these growth directions are maybe too few to produce sufficient intensity in the XRD pattern, we can at least draw the conclusion that an overwhelming majority of AlN whiskers grow along the $\langle 0002\rangle$ direction. Also, the combustion synthesized AlN whiskers were not contaminated with AlN particles, otherwise there would have been a measurable (0002) diffraction peak.

In our previous work, we have shown that the growth of most AlN whiskers is mainly controlled by the VLS mechanism [17]. We suggest that the long and coarse whiskers with few surface defects, and the dendritic whiskers, grow by a VLS mechanism. We will now discuss the growth mechanism of the spiral whiskers.

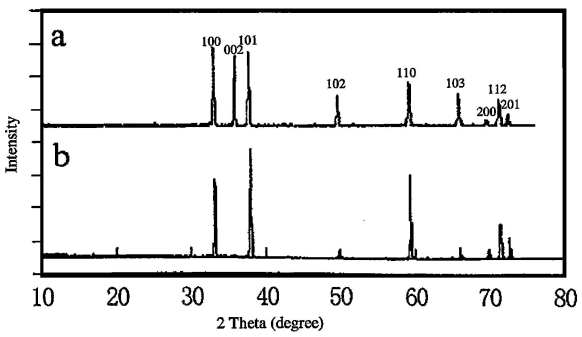

Figure 3 XRD patterns of (a) the combustion products in sample A1 and (b) whiskers in sample A3.

Spiral whiskers are rarely observed. Their growth mechanism is complex and has seldom been examined. Spiral whiskers were first observed in palladium whiskers by Webb and co-workers [20, 21]. They conjectured that the contortions of these whiskers are due to climb of the dislocation inside the tip of the whiskers during growth due to condensation of the $<0.1\%$ vacancies that are trapped in the lattice at the tip of the whisker during growth. This forces the point of intersection of the dislocation with the surface to prescribe a helical path which successively crosses the several facets comprising the growing whisker tip, thus periodically changing the effective grow direction [21]. However, this mechanism cannot explain many details of the spiral dislocation growth [22].

Spiral whiskers most likely grow by a helical screw dislocation mechanism or a combination mechanism involving a helical screw dislocation and the VLS process. A screw dislocation emerging from a crystal face provides a permanent growth step, which results in extreme crystal elongation in the direction of rapid growth (whisker) [23]. If the screw dislocation is helical, a helical whisker will develop.

Helical dislocations have been observed in the AlN whiskers by Drum [6]. Thomas and Whelan [24] proposed a formation mechanism for helical dislocations whereby an initially straight dislocation with a screw component undergoes climb, or combined glide and climb, which is associated with the condensation of vacancies onto the dislocations [25]. A prismatic, circular dislocation loop can react with a straight screw dislocation to form a helix [26]. In this mechanism, the growth of the helical screw dislocation should occur spontaneously with the growth of the helical whisker. Obviously, a helical dislocation cannot result from the climb of a straight one. Every step of the helical dislocation growth requires a twist and a small displacement, which is perpendicular to the axis (the screw dislocation). Mann and Eshelby (cited in reference [7]) pointed out that a small filamentary crystal with an axial screw dislocation should be twisted. The twist is due to the fact that the stress field $\sigma_{z\theta}$ about the dislocation effectively exerts a torque on the free surfaces at the tip of the crystal. But where does the small displacement come from? In general, point defects can equilibrate at dislocations because the latter can act as sources or sinks for point defects. A charged vacancy can decompose into four charged jogs and kinks along a screw dislocation. In dissociating in this way, the coulombic energy is greatly reduced. Thus, with a supersaturation of vacancies, a screw dislocation should acquire a net charge in the same way as an edge dislocation, via the formation of a preponderance of kinks and jogs of one sign [25]. A screw dislocation would try to attract vacancies to reduce its energy. Since there is no line tension force at the dislocation tip, the interaction of a screw dislocation tip and a vacancy could form a jog and a kink (a small displacement) as shown in Fig. 4a. The jog and kink further form an incipient spiral

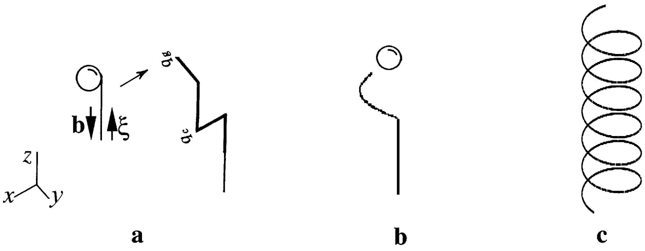

Figure 4 Scheme of a growth model of a spiral whisker through interaction of the tip of a screw dislocation and vacancies (a) Interaction of the tip of a screw dislocation (left-handed) and a vacancy (formation of a jog and a kink); (b) The jog and kink form an incipient helix the stress field of the screw dislocation and (c) Formation of a larger helix (left-handed) through the periodical interaction of the tip of the screw dislocation and vacancies due to the existence of supersaturated vacancies.

under the stress field of a screw dislocation (see Fig. 4b. The periodic interaction of the tip of the screw dislocation and vacancies causes a formation of a larger spiral due to the existence of supersaturated vacancies (see Fig. 4c). Thus, the direction of the helix of the whisker morphology should be the same as the direction of the lattice twist, which had been observed by Webb [27]. In the particular case of palladium whiskers, screw dislocations were sometimes found in the helical whiskers after completion of growth [28]. The pitch of the helix is determined by the composition of vacancy and the vector of the screw dislocation.

The vacancies may be thermally activated or result from defect reactions in AlN nitride crystal lattice ($Al_2O_3 \rightarrow 2Al_{Al} + 3O_N + V_{Al}$), where O_N means that the oxygen takes on a nitrogen site; V_{Al} denotes a vacant aluminum site [29, 30]. The oxygen content of AlN in sample A2 was about 5.90 wt%, and the oxygen content in sample A3 should be higher than for sample A2 since more salts (halides) were added. According to the above reaction, the vacancy content could be as high as 2.8%. Although, some the vacancies are annihilated due to two adjacent ones combining to form a single octahedral defect, or a number of adjacent ones condensing into oxygen containing stacking faults, the vacancy content resulting from impurity reactions should still be much higher than that of thermally activated vacancies. Thus, these oxygen-related vacancies are the dominant ones that interact with the tip of the screw dislocation.

The reaction of a left-handed screw into a left-handed helix involves vacancy absorption (or matter rejection); the reaction of a left-handed screw into a right-handed helix or of a right-handed screw into a left-handed helix involves vacancy emission [25]. Therefore, the existence of both right- and left-handed helical whiskers is not difficult to understand. Helices can be in a constrained equilibrium with respect to a change in pitch, but not with respect to a change in radius, except in very unusual distributions of internal stress [31]. Thus, the diameter of the whiskers is unchanged along the stem of the AlN whiskers.

Low energy stacking faults occur only in the basal plane in hcp crystals. At a high oxygen concentration, the vacancies just beneath the top atomic layer aggregate together, and collapse into an oxygen containing stacking fault and a dislocation loop. Sometimes, the tip of the growing helical screw dislocation could directly inpact the stacking fault. The loop should be perpendicular to the axis of the helix. After interaction with the stacking fault, the magnitude, and even the sign, of the vector of the screw dislocation growing through it could be changed since the structure of the oxygen containing stacking fault is greatly different from the AlN. This will cause a change in pitch. If the signs of the vectors of the two dislocations are opposite, this will result in an abrupt change in twist direction as can be seen in Fig. 2b.

All whisker growth consists of a number of distinct stages: (1) An induction period resulting in nucleation; (2) A primary growth stage known as leader growth; (3) A secondary thickening or overgrowth stage (this stage is sometimes not present and one goes directly into the fourth stage); (4) slowing down or cessation of growth [32].

High aspect ratio whiskers with a hexagonal cross section were often observed in sample A2. Comparing the diameter of the growing whiskers to those in a gas-release sample [17], AlN whiskers in sample A2 did not undergo the third stage; whereas the whiskers in sample A3 obviously experienced a secondary thickening or overgrowth stage.

The branches of the AlN whiskers with obvious preferred-growth directions are homogeneously distributed along the AlN whiskers, suggesting that the growth of the branches doesn't start from impurities, since the impurities are usually distributed randomly on the surfaces of the whiskers. According to XRD analysis, the preferred growth orientation of the AlN whiskers was $\langle 0002 \rangle$. Based on the orientation relation between the axes of the branches and the whiskers, the growth directions of the arms on the prism planes $\{10\bar{1}0\}$ would be $\langle 12\bar{3}0 \rangle$.

Aluminium nitride has a hexagonal wurtzite structure ($c/a = 1.60$, $c = 0.4982$ nm and $a = 0.3113$ nm). In addition to the (0002) plane, the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes of this structure are also closely packed [7]. Whiskers with these planes as growth layers have been reported [16]. Low deposition rates controlled by Reactions (7) and (10) cause a significant after-burn, which prolongs the period of the whisker growth. When the liquid at the tip of the whiskers evaporates or disappears due to the impurities the liquid depends on being consumed by the growth whiskers, the growth of whiskers has to change from the VLS mechanism to the VS mechanism and slows down. However, the whiskers are still immersed under an atmosphere of the supersaturated "AlN vapor." Since the surface area of the prism planes is much larger than that of the whiskers' tips, thickening will take a dominant role in the growth of whiskers instead of the axial growth at the initial stage. If there is no kink and edge on the prismatic plane, the center of the prismatic plane is the preferred site for deposition. If AlN molecules are deposited on the prismatic plane, HCl and HF can diffuse far enough, and long, coarse, round whiskers with few surface defects develop. Under the limitations of the diffusion distance due to the decrease in temperature during the afterburn, a series of deposition sites are then produced at regular, isolated locations along the center line on the prismatic plane, and eventually cause the formation of dendritic whiskers.

4. Conclusions

The main conclusions from this study are as follows:

1. Addition of ammonia halides can accelerate the vaporization of Al, and retard the deposition rate of AlN, which results in a significant enhancement of the growth of AlN whiskers.
2. The spiral whiskers could grow either by a helical screw dislocation mechanism or by a combination mechanism involving a helical screw dislocation and the VLS process.
3. A model is presented whereby periodic interactions of vacancies and the tip of a screw dislocation cause the growth of a spiral whisker.
4. Interaction between a stacking fault and the tip of a screw dislocation causes the magnitude, and even the sign of the vector, of the screw dislocation growing through the stacking fault to be different from the original one, which results in a change in pitch of the helix or an abrupt change in twist of a spiral whisker.
5. Under an atmosphere of supersaturated "AlN vapor," the growth of whiskers along the axial direction slows down and gradually arrests, due to the limitation of the diffusion distance, and a series of deposition sites are the produced at the regular, isolated location along the center line on the prismatic plane, and eventually cause the formation of dendritic whiskers.

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