Morphology of AlN whiskers grown by reacting N₂ gas and Al vapor

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Abstract

We have investigated the morphology of AlN whiskers on a polycrystalline AlN substrate by using Fe-Al alloy melts under the different synthesis conditions. Formation density of the AlN whiskers increases and the diameter of the whisker decreases with increasing Al content of the Fe-Al alloy melt. Most of the AlN whiskers were zigzag shape with the hexagonal cross section. The longitudinal direction was the [0001] direction. The facet with the zigzag shape was the {1-101} or {1-10-1} pyramidal plane and the period of the zigzag facet was almost constant. The average diameter of the whiskers and the period of the zigzag facet decrease with increasing Al content. At the initial stage of the whisker formation, the island of AlN formed on the AlN substrate and the pyramidal facet grows via step-flow growth. From the observation, we discussed the possible mechanism for the formation of the zigzag-shape AlN whiskers.

Keywords

B1. Aluminium nitride; B1. Whisker; A2. Growth from vapor phase; A1. Morphology

1. Introduction

As the importance of heat-management of various devices such as LEDs, power devices, electrical devices, batteries, motors, actuators and others, heat-dissipation capability of resin materials used between heat-generation components and heatsink has been a matter of importance [1-4]. In order to increase the thermal conductivity of resin materials, ceramic fillers with high thermal conductivity are often used [5-7]. AlN is a candidate for filler materials because of its high thermal conductivity and high electrical insulation. One method to increase the thermal conductivity of composite materials is to increase the volume fraction of fillers [8]. However, the increase in the volume fraction of fillers is reported to lead the poor mechanical properties and formability [9]. The volume fraction of fillers is usually limited to 70 vol% to keep the strength and formability. The other method to increase thermal conductivity is to load high aspect ratio whiskers to the composite materials. Yamada and Ota reported that loading the fillers with high aspect ratio effectively increase the thermal conductivity of composite materials [10]. They formulated the thermal conductivity of composite materials with the aspect ratio of fillers. Figure 1 shows the thermal conductivity of the epoxy/AlN composites as a function of volume fraction of the filler with the different aspect ratio calculated by Yamada-Ota model. The reported thermal conductivity of AlN ($319 \text{ Wm}^{-1}\text{K}^{-1}$) and epoxy ($0.2 \text{ Wm}^{-1}\text{K}^{-1}$) was used in the calculation [11, 12]. The thermal conductivity of the composite increases with the increase of the aspect ratio. Surprisingly, the value of thermal conductivity for the composite with the aspect ratio of 100 with the addition of 70 % of the fillers is expected to be as high as that for iron ($74 \text{ Wm}^{-1}\text{K}^{-1}$) [13]. Therefore, AlN whiskers having high-aspect-ratio are excellent candidate for the filler materials for polymer-ceramic composites.

AlN whiskers have been synthesized various methods, such as sublimation method [14, 15], carbothermal method [16-18] and physical combustion method [19, 20]. Two typical growth mechanisms of the whiskers, vapor-liquid-solid (VLS) mechanism and vapor-solid (VS)

mechanism have been proposed for the growth of the AlN whiskers. In the VLS mechanism, a catalytic liquid droplet rapidly dissolves vapor to the supersaturation level, and then a whisker subsequently grows at liquid-solid interface [21-23]. In the VS mechanism, the growth of whiskers proceeded by the reaction in vapor phase [19, 24].

Recently, we proposed the synthesis of AlN whiskers by the reaction of N₂ gas and Al vapor from melt alloy. Among the various kinds of the Al containing melts, we found that Fe-Al and Si-Al melts efficiently synthesize the large amount of AlN whiskers with high aspect ratio. In the present study, we chose Fe-Al alloy melt as the source of Al vapor for the synthesis of AlN whiskers because Fe has relatively low vapor pressure and the contamination in the furnace by the Fe vapor can be suppressed. In addition to the aspect ratio of the fillers, recently, the morphology of the fillers was reported to affect the thermal conductivity of the composites because of the thermal resistance at the interface between the fillers and the polymer [25]. Therefore, in the present study, we have investigated the morphology of AlN whiskers by using Fe-Al alloy melts under the different synthesis conditions.

2. Experimental

AlN whiskers were synthesized by the reaction of Al vapor from the Fe-Al alloy melt and flowing N₂ gas. Figure 2 shows the schematic illustration of experimental setup. The synthesis system is composed of functions for supplying Al vapor, supplying N₂ gas and reacting and growing AlN whiskers as shown in Fig. 2. Al vapor is supplied from the Fe-Al alloy melt in an alumina boat heated indirectly by induction heating furnace (Nisshin-Giken Co. Ltd, NEV-AlN40). The detailed configuration is shown in Fig. 2(d). By supplying N₂ gas, the Al vapor reacts with N₂ gas and the AlN whiskers grow on the AlN polycrystalline substrate (Furukawa-Denshi, FAN-230) bridging above the alumina boat which was located on the carbon blocks put on both sides of the alumina boat. The AlN whiskers were formed mainly on

the substrate. A few whiskers on the surface of the melts was also observed. As the raw materials, Fe and Al grains were used. The raw materials were weighed to be Fe-20at%Al, Fe-30at%Al, Fe-50at%Al and Fe-70at%Al. The total amount of raw materials is 0.25 mol. The furnace was filled with high-purity Ar gas after evacuated to 1 Pa. The furnace was heated to 1660°C for 1 h and kept at 1660°C for 30 min under a high-purity Ar gas flow in order to prevent the nitridation of the surface of the Fe-Al alloy melts. Then, AlN whiskers were synthesized under a high purity N₂ flow in a moment with the flow rate of only 1 L/min for 1 min. After the synthesis, the furnace was cooling to the room temperature for 5 h.

The morphology of AlN whiskers were investigated by scanning electron microscopy (SEM, Hitachi S-4800). In order to avoid charge up in SEM observation, AlN whiskers were coated Pt by ion sputtering (Hitachi E-1045) for 120 s.

Oxygen and carbon may be incorporated in the whiskers because alumina boat and carbon blocks are used in the synthesis. It was reported that high density of the impurities incorporation of oxygen and carbon would lead to the decrease in the thermal conductivity of AlN crystal [26, 27]. Now we are evaluating the thermal conductivity. The detail of the influence of the impurities on the thermal conductivity of the AlN whiskers will be published elsewhere.

3. Results

3.1 Formation density

Fig. 3 shows the AlN polycrystalline substrates after the synthesis. AlN whiskers colored with white were formed and covered the substrates. It seems that the formation density of AlN whiskers increases with increasing Al content in the melts. Note that the substrate synthesized by using the Fe-70at%Al melt was taken a photograph after the sputtering of Pt, which result in black color. However, we confirmed larger amount of AlN whiskers was also formed on the substrate by using the Fe-70at%Al melt than the other melt.

Fig. 4 shows the low-magnification SEM images of the center of the substrate. The AlN whiskers were formed and covered the polycrystalline AlN substrate by using the Fe-30at%Al, Fe-40at%Al and Fe-70at%Al melts (Fig. 4(b), 4(c), 4(d)). On the other hand, the formation density of AlN whiskers by using the Fe-20at%Al melt were much lower than the other melts. The AlN whiskers were sparsely grown from the rough surface of the AlN substrate. The length of the whiskers grown by using the Fe-20at%Al melt was as short as 100 μm at most, which was much shorter than the other melt compositions.

3.2 Morphology

Fig. 5 shows the SEM images of the AlN whiskers using the Fe-20at%Al, Fe-30at%Al, Fe-50at%Al and Fe-70at%Al melts. By using the Fe-20at%Al melt, the flat columnar AlN whiskers were grown from the AlN polycrystalline substrate (Fig. 5(a)). Most of the AlN whiskers grown by using the Fe-30at%Al melt was zigzag shape having hexagonal cross section as shown in Fig. 5(b), which indicates that the longitudinal direction is the [0001] direction. Considering the angle between the (0001) plane and the smooth facet of the pyramidal plan, the facet plane was expected to be $\{1-101\}$ or $\{1-10-1\}$ (the angle between (0001) and (1-101) is 61.6° [28]). The larger diameter (d_1) and the smaller diameter (d_2) of the whisker was 250 and 350 nm, respectively, and the period of the zigzag facet was almost constant and the interval was 200 nm. The AlN whiskers grown by using the Fe-50at%Al melt was also zigzag shape having hexagonal cross section as shown in Fig. 5(c). The interval of zigzag facet and the difference in the value of d_1 and d_2 for the Fe-50at%Al melt was smaller than the Fe-70at%Al melt. The AlN whiskers grown by using the Fe-70at%Al melt was fine zigzag shape. Fig. 6 shows the composition dependence of the average diameter of the AlN whiskers. The average of the larger diameters for the zigzag whiskers are shown. The average diameter of the whiskers decreases with increasing Al content.

Fig. 7 shows SEM images of the polycrystalline AlN substrate after the synthesis. AlN islands before growing to the whisker shape were observed on the substrate (Fig. 7(a)). The island has hexagonal shape with the flat {0001} plane at the top. At the top of the whiskers, any metal droplet has never been observed as shown in Fig. 7(b). This indicates that the AlN whiskers were grown via VS mechanism. Furthermore, steps on the facet of the pyramidal plane was observed and it seems that the step source was the top of the whisker (Fig. 7(c)).

4. Discussion

The formation density of AlN whiskers increases with increasing Al composition of the melt. Fig. 7(a) indicates that the AlN formation is originated from the islands on the polycrystalline AlN substrate. Thus, the formation density of the AlN would be determined by the nucleation rate of the AlN islands at the initial stage. Therefore, here we focus on the supersaturation (σ). The supersaturation for the formation of AlN from the Al vapor and the atmospheric pressure of N₂ gas was described by the following expression:

$$\sigma = \frac{P_{\text{Al}} - P_{\text{Al}}^e}{P_{\text{Al}}^e}, \quad (1)$$

where P_{Al} is the partial pressure of Al and P_{Al}^e is the partial pressure of Al under the equilibrium condition for the formation of AlN. The value of P_{Al}^e at 1660°C is calculated to be 0.812 Pa [29]. The value of P_{Al} is equal to the equilibrium vapor pressure of Al for the melts, which is calculated by using the reported thermodynamic parameters [30, 31]. Fig. 8 shows the calculated values of σ depending on the Al content of the Fe-Al melt. When the Al content is larger than 4 at%, the vapor phase is supersaturated, and the supersaturation increases with increasing Al content. The value of σ is very high under the current experimental condition and reaches as high as 350 by using the Fe-70at%Al melt. The increase in the formation density of the AlN whiskers would be caused by the increase in the supersaturation resulting from the

promotion of the formation of AlN islands on the substrate at the initial stage of the AlN whisker growth.

Here we discuss about the possible formation mechanism of the zigzag shape AlN whiskers. It is reported that the zigzag facet on the whiskers has been formed by twinned domains [32, 33]. However, the twinned domains were not observed by TEM images in our AlN whiskers synthesized by the other conditions. Fig. 9 shows schematic illustration of formation mechanism of the zigzag shape AlN whisker. Firstly, the island of AlN would be formed on the AlN substrate as shown in Fig. 9(a). The polynucleation on the (0001) or (000-1) basal plane would occur by the high supersaturation. The facet of the {1-101} or {1-10-1} pyramidal plane is formed because these pyramidal planes are one of the densely packed plane in wurzite-type structure. Secondly, the two dimensional (2D) nucleation on the top of the basal plane would occur and the pyramidal plane grows via step-flow growth as shown in Fig. 9(b). By the occurrence of step bunching the other facet of pyramidal plane would be formed. As the growth proceeds, finally the zigzag facets of AlN whiskers would formed.

5. Conclusion

The morphology of AlN whiskers grown on the polycrystalline AlN substrate by the direct nitridation method using the Fe-Al alloy melts were investigated by SEM. Formation density of the AlN whiskers increases and the diameter of the whisker decreases with increasing Al content of the Fe-Al alloy melt. Most of the AlN whiskers were zigzag shape with the hexagonal cross section. The facet with the zigzag shape was the {1-101} or {1-10-1} pyramidal plane and the period of the zigzag facet was almost constant. The average diameter of the whiskers and the period of the zigzag facet decrease with increasing Al content. At the initial stage of the whisker formation, the island of AlN formed on the AlN substrate and the pyramidal facet grows via step-flow growth. From the observation, we discussed the possible mechanism for the formation of the zigzag-shape AlN whiskers.

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Figure caption

Fig. 1. The thermal conductivity of epoxy/AlN composites as a function of the volume fraction of the fillers with the different aspect ratio calculated by Yamada-Ota model. The values of thermal conductivity for epoxy resin ($0.2 \text{ Wm}^{-1}\text{K}^{-1}$) and AlN ($319 \text{ Wm}^{-1}\text{K}^{-1}$) were used in the calculation.

Fig. 2. The schematic illustrations of (a) a side view, (b) a front view for the experimental setup and (c) an upper view (d) the detailed configuration of reaction area for the experimental setup.

Fig. 3. The pictures of the polycrystalline AlN substrate after the synthesis by using (a) the Fe-20at% Al, (b) Fe-30at% Al, (c) Fe-50at% Al and (d) Fe-70at% Al melts.

Fig. 4. The low-magnification SEM images of the AlN whiskers using (a) the Fe-20at% Al, (b) Fe-30at% Al, (c) Fe-50at% Al and (d) Fe-70at% Al melt.

Fig. 5. The SEM images of AlN whiskers grown at the center of the substrate using (a) the Fe-20at% Al, (b) Fe-30at% Al, (c) Fe-50at% Al and (d) Fe-70at% Al melt.

Fig. 6. The composition dependence of the average diameter of the AlN whiskers.

Fig. 7. The SEM image of polycrystalline AlN substrate after the synthesis AlN whiskers using (a)(b) the Fe-30at% Al melt and (c) the Fe-20at% Al melt.

Fig. 8. The calculation result of supersaturation of AlN at 1660°C. This result is calculated by considering the equilibrium between Fe-Al melt and Al vapor based on regular solution model.

Fig. 9. Formation mechanism of the zigzag shape AlN whiskers. (a) The island of AlN formed on the AlN substrate and the pyramidal facet is formed by the polynucleation. (b) 2D

nucleation on the top of the whisker supply the steps to the pyramidal plane and zigzag shape facet is formed by step bunching.

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(a) First step

(b) Second step

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