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Morphological development and oxidation mechanisms of aluminum nitride whiskers

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ABSTRACT

Hexagonal aluminum nitride (AlN) whiskers have been synthesized at 1873 K under a flowing nitrogen atmosphere. The synthesized whiskers are long straight filaments with diameters between 1 and 5 μm and length in the cm range. In order to investigate its "oxidation resistance", a series of experiments have been performed. The oxidation behavior was quite different in the experimental temperature range assigned, which can be attributed to the kinetic factor and the morphological development during oxidation process. It was chemical controlled at lower temperature while both chemical reaction and diffusion controlled at medium temperature. Further accelerating of temperature to 1473 K, AlN whiskers was peeled into smaller parts, which increased the oxidation rate and hence showed powder-like oxidation behavior. Our new kinetic theory has been applied to study the oxidation behavior of AlN whiskers. The comparison of the experimental data with the theoretical ones validates the applicability of the new model.

1. Introduction

As whiskers are a kind of filamentary single crystal, they have been attracting much attention in their near-perfect crystalline nature, near theoretical value of the strength and their unique physical and chemical performances. Ceramic whiskers have become a subject of intense study in recent years because of their remarkable characteristics in mechanical and physical properties [1]. Aluminum nitride (AlN) has an excellent potential to be used as a substrate material for the high-density, high-power and high-speed integrated circuit [2]. In recent years, AlN whiskers have been suggested for use as filler in polymers to increase the thermal conductivity [3]. High thermal conductivity polymers have a wide variety of applications, from sealants and potting compounds for electronic applications to heat-dissipating structural, adhesive, or insulating materials [1,3].

AlN whiskers have been extensively studied ever since the earliest report about the growth of AlN whiskers by the Kohn's experiment [4]. While up to now, the research work mainly focuses on the synthesis, crystal growth and perfection [3,5–8]. The work on investigation of their properties is very limited.

In the present work, AlN whiskers have been synthesized using a mixture of alumina and aluminum under a flowing N_2 atmosphere. Considering the possible application of AlN whiskers as filler in polymers that are possibly applied under high temperature and oxygen containing atmosphere, the oxidation resistance of AlN whiskers is a very important issue and should be paid more attention. However, it has never been reported in the literature till now. In order to evaluate this new kind of materials as a candidate of filler agent in polymers, a series of questions should be clarified, they are: (i) What is the experimental result for the oxidation of AlN whiskers under an environment containing oxygen; (ii) Are there any theories that can be used to describe these experimental result satisfactorily; and (iii) Can we find a parameter that can be used as a general "index" to measure the "oxidation resistance". These questions will be answered in this article.

2. Material and methods

2.1. Synthesis of AlN whiskers

The synthesis experiment was carried out in a vertical controlled-atmosphere furnace. A mixture of alumina and aluminum in a molar ratio of 1:9 was used as raw materials. They were ball milled with ethanol as medium and then dried. The pellets of solid samples were made with a die and a hydraulic

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press. The samples were contained in a graphite crucible and placed into the furnace. The synthesis reaction took place at the temperature of 1873 K for 6 h under flowing nitrogen atmosphere with the flow rate of 0.6 l/min.

The phase was identified by X-ray diffraction (XRD; M21XVHF22, Japan) using Cu$K\alpha$ radiation. The microstructure was examined by thermal field emission scanning electron microscope (FE-SEM; ZEISS SUPRA^{TM} 55, Germany). Further characterizations were performed by energy dispersive spectroscopy (EDS) to analyze the chemical compositions of AlN whiskers.

2.2. Oxidation tests

The weight change in AlN whiskers during oxidation was monitored using a Netzsch STA449C thermal analysis system. The TG microbalance had the sensitivity of 1 μg. Before isothermal oxidation experiments were carried out, non-isothermal oxidation was investigated to have knowledge of the oxidation behavior of AlN whiskers. In the non-isothermal mode, the sample (about 7.1 mg) held in an alumina crucible was placed in the furnace (The alumina crucible has been stably treated and does not react with AlN whiskers.). The furnace was then heated from room temperature to the maximum temperature of 1773 K at a heating rate of 10 K/min. In the isothermal experiments, AlN whiskers (about 7.1 mg) were also placed in an alumina crucible and the temperature was rapidly raised to the required level in a flowing purified argon gas (<5 ppm O_2). After the thermal equilibrium was established, the argon gas was stopped and the air was then introduced. The mass increase due to oxidation was then monitored continuously for 2 h at the rate of 1 point/min. In all the experiments, the flow rate was kept constant, i.e. 20 ml/min.

SEM analysis was also applied to investigate and compare the morphological development of samples before and after oxidation.

3. Theory

In order to evaluate the oxidation resistance of materials, many criterions have been proposed by researchers in the literature, such as the oxidation rate etc. However, the oxidation rate cannot be taken as this index since there are many factors that affect the oxidation rate. For instance, at the very beginning of the oxidation reaction, the oxidation rate could be very fast, however this rate almost approaches to zero at the end of reaction. Therefore, it is certainly meaningless to compare the oxidation rate for two testing materials without assigning a reaction time. A new index, called the "characteristic oxidation time t_ϕ", has been proposed in our previous articles during the derivation of our oxidation model [9,10]. The physical meaning of the "characteristic oxidation time t_ϕ" is that, it is a required time that the test sample has been completely oxidized. Obviously, the longer the t_ϕ, the stronger is the oxidation resistance. According to the derivation, this "characteristic oxidation time" for a cylindrical sample under the condition of diffusion controlled can be calculated as following equation [10]:

$$t_{\phi Rd}=\frac{1}{\left(2D_O^0k_O^0(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})/v_mR_0^2\exp(\Delta E_d/RT)\right)} \tag{1}$$

where ΔE_d represents the apparent activation energy of diffusion; P_{O_2} is the oxygen partial pressure above the surface of sample, P_O^{eq} is the oxygen partial pressure in equilibrium with oxide in oxide/AlN interface, which is related to temperature T. Both $k_O{}^0$ and $D_O{}^0$ are constant, independent of temperature but relying on the materials; v_m is a coefficient that depends on the sample and reaction; and R_0 is the radius of the cylinder. From Eq. (1), it can be seen that, the "characteristic oxidation time" $t_{\phi_{Rd}}$ is closely related to a series of factors, such as the radius of the cylinder, the oxidation intensity of the environment, the character of medium where the oxygen pass through as well as the property of reactant and product materials. However, it has no relation with the oxidation time; that is why one can select this parameter to measure the oxidation resistance.

In general, the "characteristic oxidation time" can also be extracted from a set of experimental data fitting through our model, for instance, the diffusion controlled model for the cylinder can be expressed as following [10]

$$\xi=1-\left[1-\frac{1}{R_0}\sqrt{\frac{2D_O^0k_O^0(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})}{v_m\exp(\Delta E_d/RT)}t}\right]^2\left[1-\frac{2}{h_0}\sqrt{\frac{2D_O^0k_O^0(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})}{v_m\exp(\Delta E_d/RT)}t}\right] \tag{2}$$

Since the whiskers can be taken as a long cylinder with a very small radius, i.e. $h_0 \gg R_0$, therefore Eq. (2) can be simplified to the following approximate form

$$\xi\approx 1-\left[1-\frac{1}{R_0}\sqrt{\frac{2D_O^0k_O^0(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})}{v_m\exp(\Delta E_d/RT)}t}\right]^2 \tag{3}$$

Substituting Eq. (1) into Eq. (3) yields

$$\xi=1-\left[1-\sqrt{\frac{t}{t_{\phi_{Rd}}}}\right]^2 \tag{4}$$

In the case of the chemical reaction controlling the oxidation process, Chou et al. [9] and Chou and Hou [10] have also proposed a model under this condition. The relation of the reacted fraction ξ and time t for the whiskers is given by

$$\xi=1-\left[1-\frac{k_O(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})}{R_0v_m\exp(\Delta E_r/RT)}t\right]^2 \tag{5}$$

ΔE_r represents the apparent activation energy of chemical reaction, P_{O_2} is the oxygen partial pressure in equilibrium with oxide, k_O is a temperature-independent constant; $v_m$is a coefficient related to the density of reactant and product and R_0 is the radius of the cylinder. According to Eq. (5), the "characteristic oxidation time" for a cylindrical sample under the condition of chemical reaction controlled can be calculated as follows

$$t_{\phi Rc}=\frac{1}{\left(k_O(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})/v_mR_0\exp(\Delta E_r/RT)\right)} \tag{6}$$

Then Eq. (5) will become as follows

$$\xi=1-\left(1-\frac{t}{t_{\phi Rc}}\right)^2 \tag{7}$$

For other shapes of samples, a very similar formula can be obtained. The calculation formulae for the sample of a sphere ball under condition of the diffusion control are as follows [10]

$$t_{\phi Sd}=\frac{1}{\left(2D_O^0k_O^0(\sqrt{P_{O_2}}-\sqrt{P_{O_2}^{eq}})/v_mR_0^2\exp(\Delta E_d/RT)\right)} \tag{8}$$

And

$$\xi=1-\left(1-\sqrt{\frac{t}{t_{\phi Sd}}}\right)^3 \tag{9}$$

4. Results

4.1. Characterization of synthesized AlN whiskers

Fig. 1a shows the microstructure of synthesized AlN whiskers, among which the majority can be described as long and straight filaments with diameters between 1 and 5 μm and length in the cm range. The typical morphologies of AlN whiskers can be described as the cross-sectional views that were hexagonal in shape but with growth steps at its side as shown in Fig. 1b, which can be explained that AlN whiskers were nucleates by VS mechanism [3]. The XRD pattern and the EDS were employed to examine the synthesized material and the results were shown in Fig. 2a and b. The analyses confirmed that the AlN whiskers were in high purity.

4.2. Oxidation behavior of AlN whiskers

Fig. 3a shows the non-isothermal oxidation behavior of AlN whiskers. It can be found that the oxidation of AlN whiskers started at about 1200 K and the rate increased rapidly after 1400 K. While at about 1600 K, the oxidation rate slowed down. According to literatures, the stable crystalline form of Al_2O_3 is corundum (α-Al_2O_3) [11]. Other forms of alumina, such as δ-Al_2O_3 and κ-Al_2O_3 are in metastable state. The term γ-Al_2O_3 appears to be a "generic term for all low temperature forms." At temperature

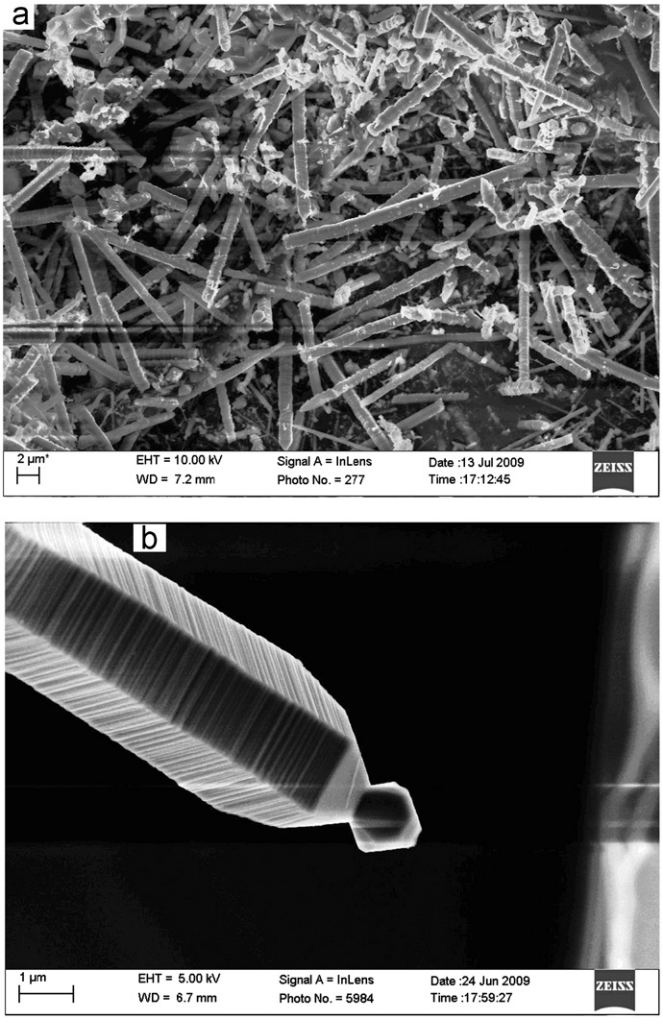

Fig. 1. Microstructure characterization of synthesized AlN whiskers.

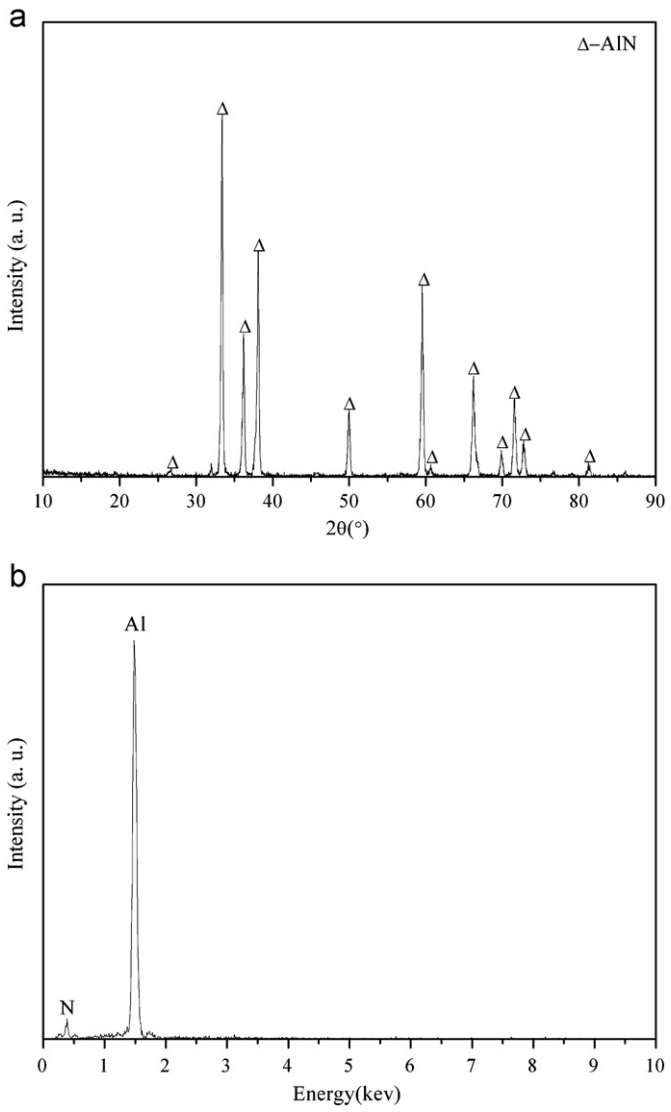

Fig. 2. (a) The XRD pattern of the synthesis AlN whiskers and (b) EDS spectrum of the AlN whiskers.

above 1600 K, γ-Al_2O_3 transforms to the stable corundum form [11]. Therefore, in our experiment, the oxide should be in the form of α-Al_2O_3 at the temperature higher than 1543 K, while at lower temperatures, the formation of one of the metastable form is possible. When the form of product changes, an accompanying volume change can cause the crack formation. This, in turn, can lead to the change in the kinetics of the reaction.

According to the non-isothermal oxidation result, the isothermal experiment was carried out in the temperature range from 1323 to 1473 K with an interval of 50 K and the result was shown in Fig. 3b. It can be easily observed from the curves that the oxidation fraction increased considerably with increase in temperature along with the change in the nature of the curves, indicating change in the mechanism of oxidation. The reaction rate at temperature ranging from 1323 to 1373 K increased linearly with time, indicating it was controlled by chemical reaction. With increase in temperature, the oxidation behavior became a little complicated, i.e. it increased linearly at initial stage while became slower with increase in time, indicating both chemical reaction and diffusion controlled the reaction. Further increase in the temperature to 1473 K, the oxidation rate increased linearly at first then parabolically in the later stage

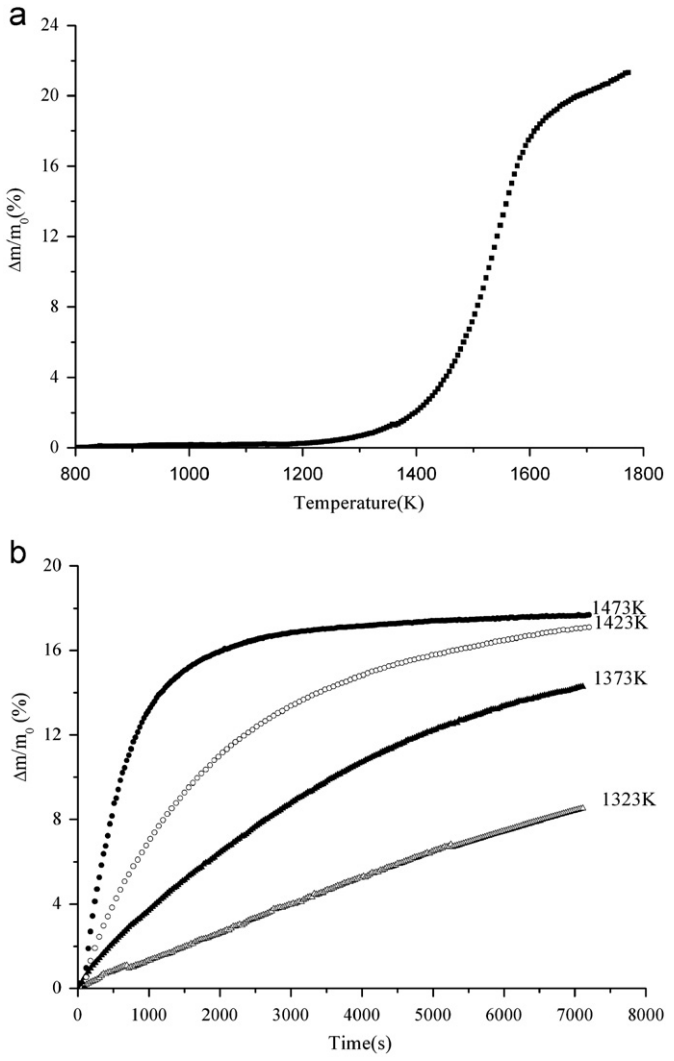

Fig. 3. Oxidation behavior of AlN whiskers: (a) Non-isothermal oxidation and (b) isothermal oxidation.

that represent the oxidation mechanism change from chemical reaction controlled to the diffusion controlled.

4.3. Morphological development of AlN whiskers during oxidation

Fig. 4 shows the surface morphological development of AlN whiskers after oxidation. Fig. 4a and b shows the SEM images of AlN whiskers oxidized at 1323 and 1373 K. It can be seen that the shape of AlN whiskers after oxidation was well kept comparing with that of AlN whiskers before oxidation (Fig. 1), indicating their good oxidation resistance at this temperature range. According to the oxidation curves at this temperature range (Fig. 3b), the reaction mainly occurred at the surface of AlN whiskers, i.e. it was controlled by chemical reaction.

With temperature increase to 1423 K, some cracks appeared on the surfaces of whiskers, although the shape of whisker was still kept well (Fig. 4c). Thus oxygen can directly reacted with AlN through the diffusion in crack gaps. Therefore the oxidation was controlled both by chemical reaction and diffusion. At 1473 K, AlN whiskers were peeled off into small fragment because of more cracks appearing on the surface (as shown in Fig. 4d). The oxidation behavior became more complicate: at the beginning chemical reaction controlled and at later stage diffusion controlled due to a longer diffusion path.

4.4. Oxidation kinetics of AlN whiskers

4.4.1. Application of the new model

From the above analysis, the oxidation behavior of AlN whiskers belongs to gas–solid reaction [12]. In our previous work, a series of formulae have been developed explicitly expressing the reacted fraction ξ as a function of time "t", cylinder diameter "R_0" and other related physical parameters. This new model was established using the rate limited-step method. Until now, this new model has been successfully applied to the hydrogen absorption/desorption processes and the oxidation of non-oxide materials [10,12,13]. At present, this model will be extended to treat the oxidation of AlN whiskers, expecting this method being able to predict the service life of AlN whiskers and provide some other useful information for its future applications.

Since the oxidation mechanism changes during the whole experimental temperature range, different equations should be applied in different stages. In view of the oxidation curves at the temperatures of 1323 and 1373 K, the process is controlled by chemical reaction. Thus Eq. (5) should be used.

If defining

$$B = \frac{1}{\left(k_O(\sqrt{P_{O_2}} - \sqrt{P_{O_2}^{eq}})/v_m R_0\right)} \tag{10}$$

Eq. (5) becomes

$$\xi = 1 - \left[1 - \frac{\exp(-(\Delta E_r/RT))t}{B}\right]^2 \tag{11}$$

Note that the y-axis in the experimental plots (Fig. 3b) is not the reacted fraction ξ but the dimensionless mass change $\Delta m/m_0$ (m_0 denotes the sample original weight and Δm the increment of sample weight after oxidation at time t). A transformation is required according to the following equation

$$\xi = \frac{\Delta m/m_0}{\Delta m_{\max}/m_0} \tag{12}$$

where $\Delta m_{\max}$ is the theoretical maximum increment after a complete oxidation. By regression of the experimental data, these two parameters, B and ΔE_r are extracted to be 1.98×10^{-7} and 278.5 kJ/mol. Substituting these two parameters into Eq. (11), the oxidation kinetic model is obtained. For comparison, the theoretical predicted lines are also plotted in the same plot (Fig. 5). It can be seen that at relatively low temperature range, i.e. 1323–1373 K, the curves of the mass change percentage of oxidation versus time can fit the experimental data very well.

With temperature increasing to 1423 K, the oxidation behavior is a mixed controlling process at this temperature. Eqs. (4) and (7) are combined to treat the oxidation, i.e., when time $t \le 3000\,s$, Eq. (7) is applied to treat the oxidation behavior while time $t \ge 3000\,s$, Eq. (4) is used. The obtained result is shown in Fig. 6 and can be seen that it fit data very well.

In the case of the oxidation behavior of AlN whiskers at 1473 K, at initial time ($t \le 600\,s$), the oxidation rate increased linearly indicating chemical reaction controlled. With increase in time, more cracks appeared on the surface of AlN whiskers as shown in Fig. 5d and led AlN whiskers to peel off into small fragments resulting in the increase in surface area. Hence in this case, AlN whiskers behaved as powder and this validated the use of powder model at higher temperature. In addition, the steep increase in the oxidation rate (Fig. 3b) also supported the application of powder model (Eq. (9)) when time $t \ge 600\,s$. The curve obtained from Eqs. (4) and (9) is shown in Fig. 7 and it can fit the experimental data very well.

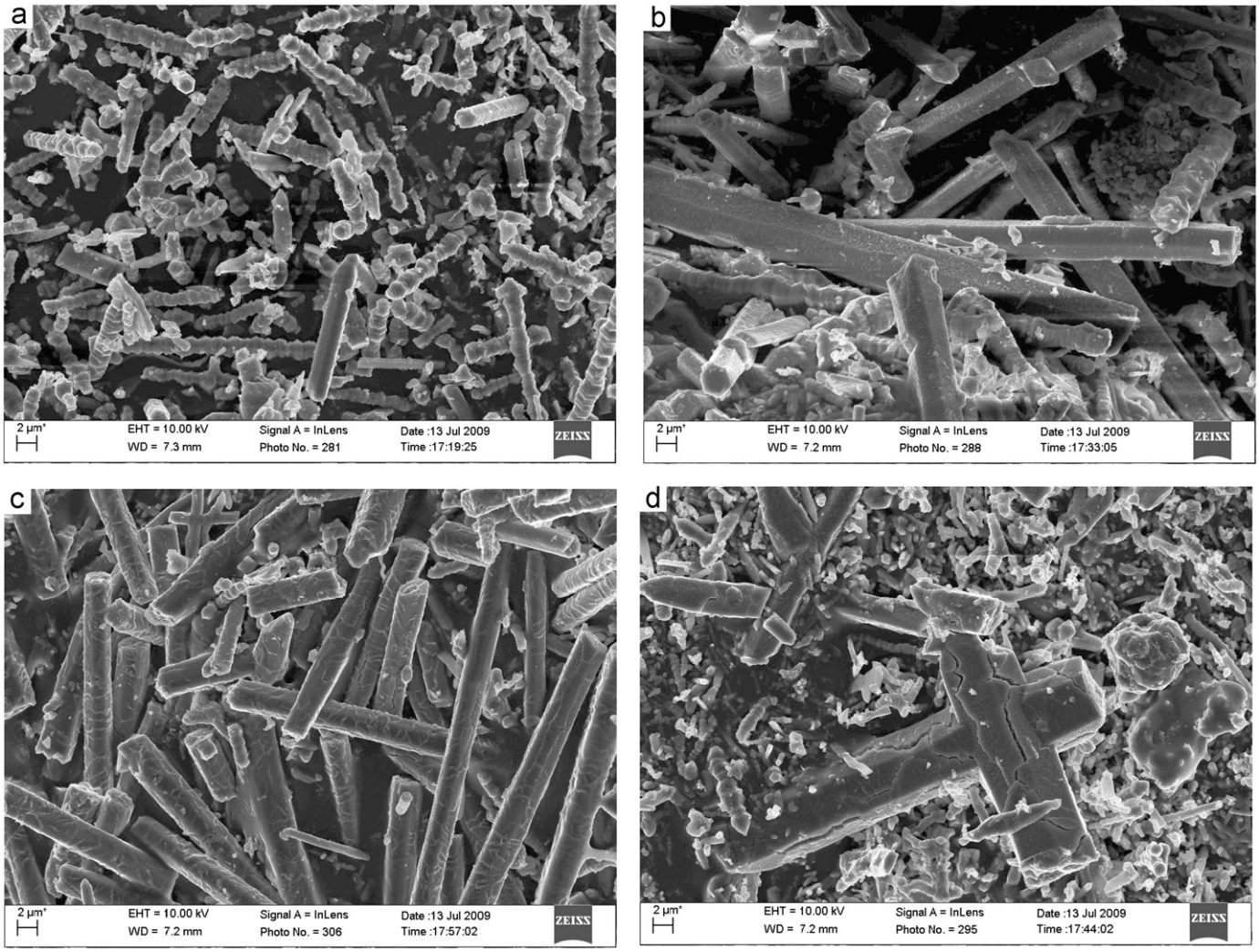

Fig. 4. Surface morphological development of AlN whiskers after oxidation at different temperatures: (a) oxidized at 1323 K; (b) oxidized at 1373 K; (c) oxidized at 1423 K and (d) oxidized at 1473 K.

4.4.2. Comparison with the traditional models used in the literature

There are many theoretical kinetic models used in the literature to treat the oxidation kinetics, such as Jander's model, the Carter's formula, the parabolic rate law, the linear rate law etc. The major difference between our model and theirs' is that, we have revealed the physical meaning of the parameter "k" of their models that can be expressed as a function of temperature T, diffusion coefficient $D_0^{\alpha\beta}$, sample shape R_0 and oxygen partial pressure P_{O_2} etc. All these parameters appearing in our model have clear physical meaning. Therefore, our new model can be used to discuss quantitatively for various factors including temperature T, oxygen partial pressure P_{O_2}, sample shape etc. on oxidation behavior. While the traditional models like Jander's etc cannot lead to an accurate formula to deal with a whisker like equations used here.

Besides, our model can extract the activation energy ΔE more accurately and easily than that of the traditional models that have already been proved in our previous papers [14].

5. Discussion

(1) The oxidation behavior of AlN whiskers was quite different in the experimental temperature range assigned, depending on the kinetic factor and the morphological development during oxidation process. At the temperature of 1323–1373 K, the oxidation reaction mainly occurred at the surface of AlN whiskers and was chemically controlled. At higher temperature, i.e. 1423 K the chemical reaction goes fast and the diffusion path goes longer, thus a combining chemical reaction controlled and diffusion controlled appears. At 1473 K, AlN whiskers were peeled off into small fragments, the oxidation behavior behaved as powder. Therefore, the oxidation behavior at this temperature was initially controlled by chemical reaction model then by powder diffusion model.

(2) The new model has been employed to treat the oxidation behavior of AlN whiskers and the observed theoretical curves seemed to be in good agreement with the experimental ones, indicating the validity of the new model.

(3) Compared with the oxidation behavior of AlN powder reported in our recent work [15], AlN whiskers possess better oxidation resistance by comparing the new index of the "characteristic oxidation time". At the temperature of 1423 K, the "characteristic oxidation time" is 7200 s for AlN whiskers and 4600 s for AlN powder [15]. From the above analysis, one may find that, the "characteristic oxidation time" presented in this work is able to give a good description for the "oxidation resistance" of AlN with different shapes.

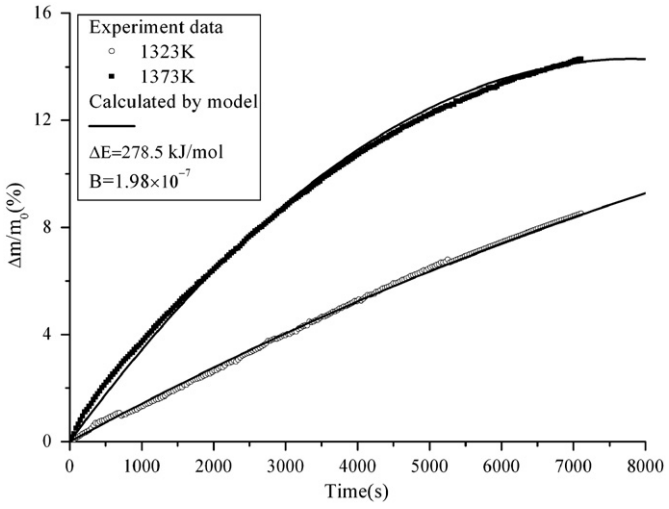

Fig. 5. A comparison of experimental data with model for isothermal oxidation curves at the temperature range of 1323–1373 K.

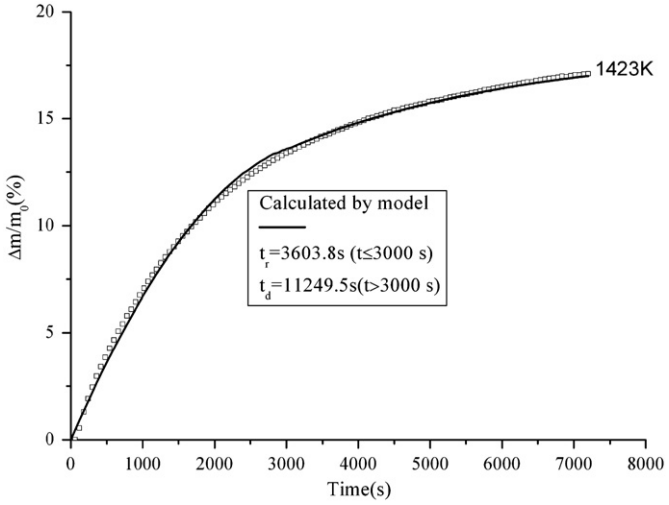

Fig. 6. A comparison of experimental data with model for isothermal oxidation curves at 1423 K.

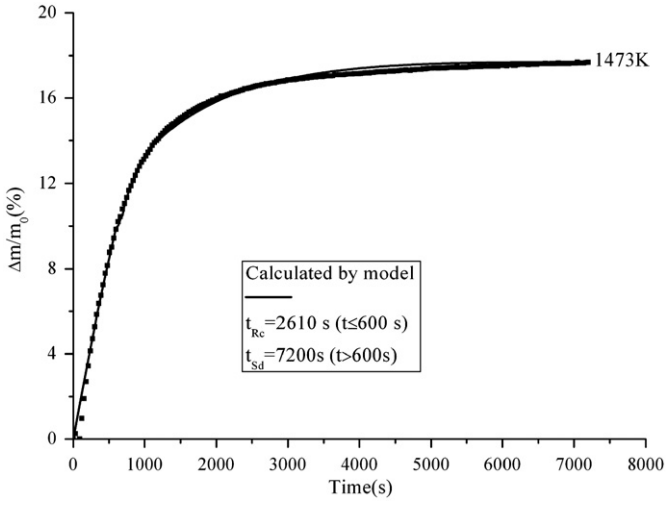

Fig. 7. A comparison of experimental data with model for isothermal oxidation curves at 1473 K.

(4) As fiber materials, AlN whiskers are required to possess various kinds of good properties including mechanic and physicochemical properties. Based on the above quantitative analysis, it can be seen that the "oxidation resistance" is also an important property that should be considered along with other mechanical and physicochemical properties when it works as a reinforcing material agent in an environment containing oxygen at an elevated temperature.

6. Conclusions

(1) AlN whiskers have been prepared by heating a mixture of Al_2O_3 and Al in a graphite crucible under a flowing nitrogen atmosphere. The synthesized product has been identified by the XRD, the SEM and the EDS. The whiskers obtained at 1873 K were hexagonal in cross-section shape. The synthesized whiskers are long straight filaments with diameters between 1 and 5 μm and length in the cm range.

(2) The oxidation behavior of AlN whiskers in air has also been investigated, which varies depending on the temperature range and the morphologies of AlN whiskers after oxidation. It was chemical reaction controlled at lower temperature, while at higher temperature, some cracks appeared and the oxidation was controlled by chemical reaction and diffusion. Further increase in the temperature to1473 K, AlN whiskers were peeled into smaller parts, which increased the oxidation rate and hence showed powder-like oxidation behavior.

(3) Our new kinetic treatment has been used to analyze the experimental results, from which it can be seen that there is a good agreement between the experimental data and the theoretical prediction. A new index of the "characteristic oxidation time" used to measure the "oxidation resistance" has been introduced that has clear physical meaning and is easy to use. The new model has also been compared with the tradition models used in the literatures.

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