PII: S0272-8842(97)00042-4

Ceramics International 24 (1998) 135–138

0272-8842/97 $17.00+.00

Crystal Growth of Silicon Nitride Whiskers Through a VLS Mechanism Using SiO_2–Al_2O_3–Y_2O_3 Oxides as Liquid Phase

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(Received 4 February 1997; accepted 1 July 1997)

Abstract: Si_3N_4 whiskers were coated on Si_3N_4 whisker substrates through a VLS mechanism using SiO_2–Al_2O_3–Y_2O_3 oxides as liquid phases. Alpha-Si_3N_4 whiskers having diameters of 0.4 to 0.7 μm were used as seeds. After the seed whiskers were coated with SiO_2–Al_2O_3–Y_2O_3 oxides, the oxide-coated whiskers were heated at 1490°C N_2 including gas species generated by reacting amorphous Si_3N_4 and TiO_2 powders. Resultantly, whisker-like products were newly formed on the seeds. The morphologies of the resulting whisker growth on the seeds resembled rose-twigs and centipedes with long legs. X-ray diffraction analysis indicated that the newly formed whiskers were β-Si_3N_4. Droplets were observed on the tips of some whiskers. This suggested that the whisker growth proceeded through a vapour–solid–liquid (VLS) mechanism. © 1997 Elsevier Science Ltd and Techna S.r.l.

1 INTRODUCTION

Gas phase process such as chemical vapour deposition (CVD) has been used as one of industrially important coating techniques due to high uniformity of the coating. Figure 1 shows two types of it illustrated schematically. Usual CVD process proceeds through the vapour–solid (VS) mechanism [Fig. 1(a)]. Chemical species diffuse toward a substrate through an interfacial gas layer, then are adsorbed on the surface of the substrate and move on it. Subsequently, nucleation and crystal growth occur, accompanied by the elimination of by-products. In this process, the diffusion of the chemical species in the gas phase and the surface migration of them on the substrate are fast, compared with the vapour–liquid–solid (VLS) mechanism [Fig. 1(b)] via the liquid phase. In the VS mechanism, therefore, high deposition rate will be obtained if a reaction between the chemical species is fast enough. This often results in the deposit of coarse-grained crystals, however, because the chemical species are easy to consume for crystal growth rather than for nucleation due to their fast diffusion rate in the gas phase and fast surface migration rate on the substrate.

Crystal growth via liquid phase by the VLS mechanism has been used to prepare ceramic whiskers such as Si_3N_4 and SiC.[1–5]

To our knowledge, however, there are few studies focusing on the use of the VLS mechanism as a coating technique on substrates. As shown in Fig. 1(b), if a liquid-phase layer exist on a substrate, chemical species must be first dissolved in the liquid phase for crystal growth. Next, they diffuse in it and are adsorbed on the substrate. Finally, crystal growth occurs via nucleation in the liquid phase.

In the crystal growth from liquid phase, the higher supersaturation leads to the higher nucleation density if the growth rate of nucleus is small enough. As shown in Fig. 1(b), the diffusion rates of the chemical species in the liquid phase are probably much smaller than those in the gas phase [Fig. 1(a)]. Therefore, the rate of the supplement of chemical species to nucleus for crystal growth is very small. This probably results in high nucleation density and the formation of the finer crystals than

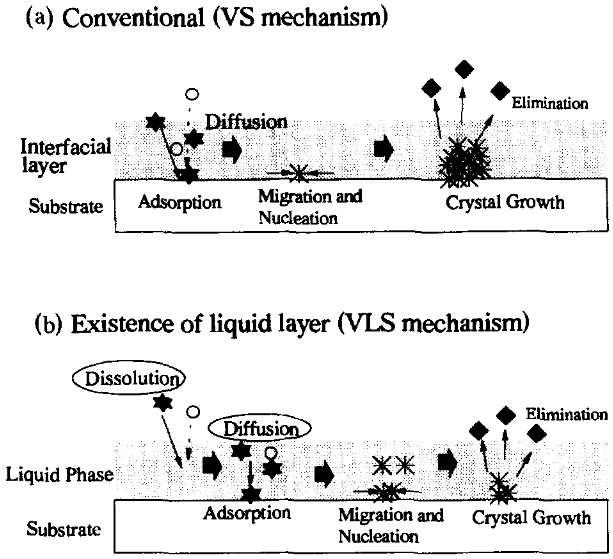

Fig. 1. Schematic illustration of two types of CVD mechanisms.

those through the VS mechanism, if the supersaturation of the liquid phase is high enough.

On the basis of the above presumption, we coated fine-grained Si_3N_4 whiskers on Si_3N_4 whisker substrates.[6] In the present study, we investigated the effect of liquid phase thickness on the dimensions of coated whiskers.

2 EXPERIMENTAL PROCEDURE

The concept for the Si_3N_4 whisker coating is illustrated in Fig. 2. An oxide layer, which melts and forms a liquid phase at high temperature, is coated on the Si_3N_4 whisker substrate. The oxide-coated whiskers are heated at temperatures above the melting point of the oxide in source gases. After the dissolution of the source gases in the resulting liquid phase, nucleation and crystal growth occur on the surface of the substrate in the liquid phase, from which whiskers grow.

Alpha-Si_3N_4 whiskers (single crystals) having diameters of about 0.4 to 0.7 μm, which were prepared by a reaction of amorphous Si_3N_4 with TiO_2 powders,[7] were used as seeds. Next, two kinds of ethanol solutions of metal alkoxides of the Si–Al–Y–O system were prepared; tetraethoxysilane (TEOS, produced by Sasaki-Kagakuyakuhin Co. Japan) and alkoxides-derivatives, including Al and Y (Hautoform MS–Al and MS–Y, produced by Fuji–Kagakuyakuhin Co. Japan), were mixed with a composition of SiO_2:Al_2O_3:Y_2O_3 = 4:2:4 (weight ratio). As-prepared solution was diluted with ethanol one (Solution A: no dilution) or four times (Solution B) to prepare solutions with different

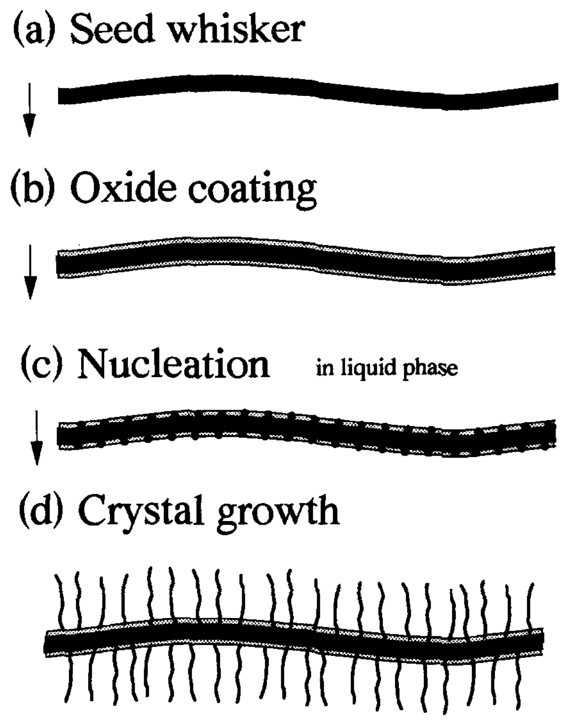

Fig. 2. Illustrations of a surface modification of ceramic whiskers using a VLS mechanism.

oxide content. The oxides content are summarised in Table 1.

The seed whiskers were dipped in the solutions, and were then drawn and dried. The treated whiskers were calcined at 500°C for 1 h in air to convert the alkoxides to an oxide. A reported phase diagram indicates that the resulting oxide glass on the seed whiskers melts at about 1400°C.[8] Finally, the Si_3N_4 whiskers coated with the SiO_2–Al_2O_3–Y_2O_3 glass were heated with the compacted bodies of an amorphous Si_3N_4 (produced by Mitsui–Toatsu Co. Japan) and TiO_2 (produced by Tayka Co. Japan) powders at 1490°C, 700 Torr for 2 h in N_2. Obtained products were observed with scanning electron microscope (SEM), and were identified by X-ray diffraction.

3 RESULTS AND DISCUSSION

Figure 3 shows the comparison of the morphologies of the seed whiskers [Fig. 3(a)] and the resulting product. In the case of solution B, a number of

Table 1. The concentration of alkoxides prepared for oxide coating

Oxide	Content of oxides (kg m^{-3}) Solution A	Solution B
SiO_2	55.35	13.84
Al_2O_3	27.67	6.91
Y_2O_3	55.35	13.84

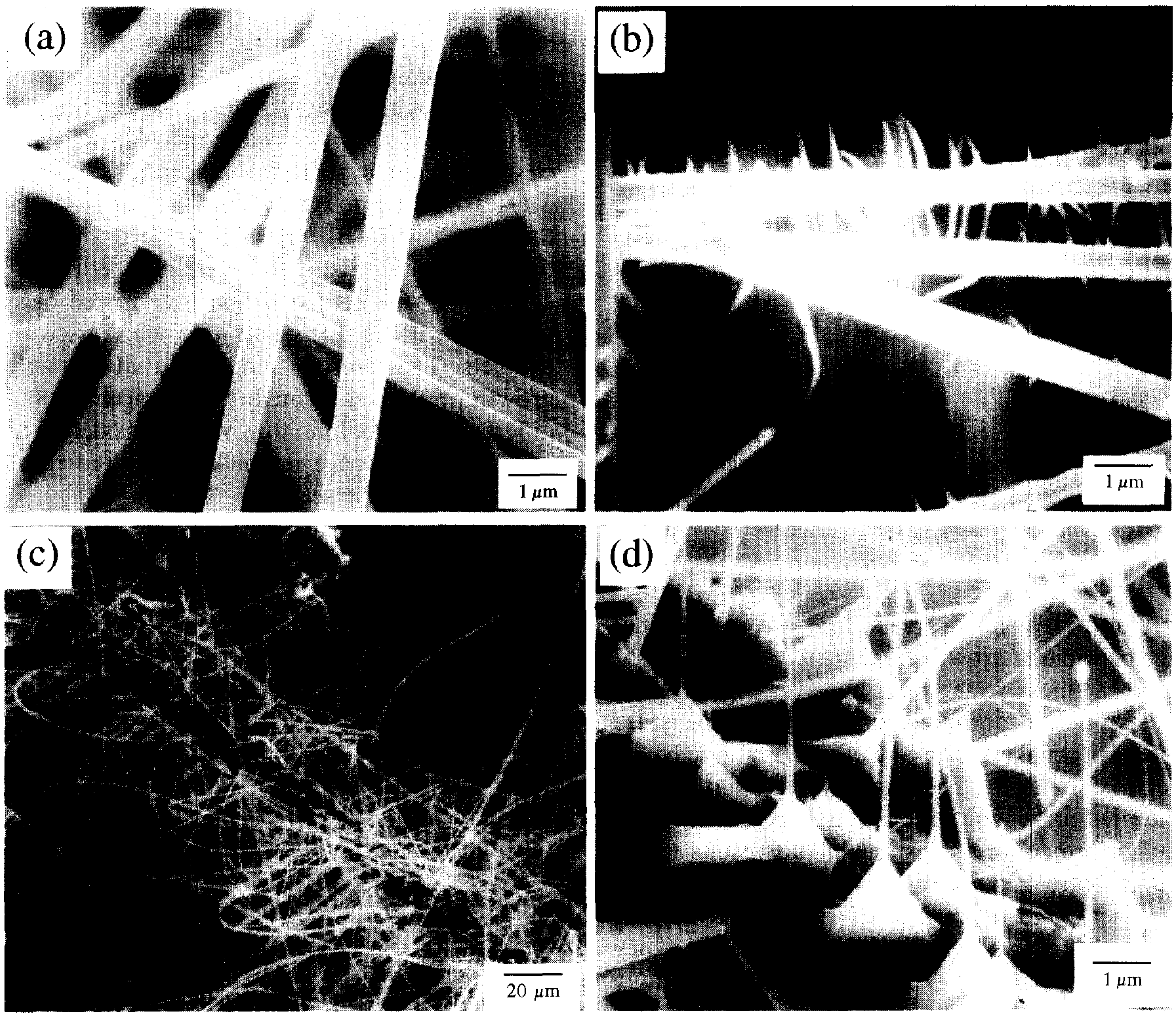

Fig. 3. SEM micrographs of (a) seed whiskers, (b) fine-grained whiskers from solution B, (c) long whiskers from solution A and (d) short whiskers from solution A.

fine-grained whisker-like products were formed on the surface of the seed whiskers. The morphology of the growth was just like rose-twigs [Fig. 3(b)]. There is no significant variation in thickness of the seeds before and after the whisker coating. This indicates that a thin oxide layer was coated on the seeds. X-ray diffraction indicated that the newly formed whiskers are the β-Si_3N_4.

In the case of solution A, the newly formed whiskers on the seeds were much longer than those obtained from the solution B, and the morphology of the growth was just like centipedes having long legs [Fig. 3(c) and (d)].

Clearly, the diameters of the seeds increase. This is probably because a thick oxide layer was coated although its thickness was determined. No droplets were found on the tips of the fine-grained whiskers from solution B [Fig. 3(b)] and relatively long whiskers from solution A [Fig. 3(c)]. Droplets were found on the tips of relatively short whiskers from solution A [Fig. 3(d)].

Regarding whisker growth through VLS mechanisms, the following mechanism is suggested.[9] Gas species are dissolved in liquid droplets on a substrate, and then they are supplied to the surface of the substrate, where crystal growth starts. Accompanied by the crystal growth, the droplets are lifted-up. If the components of the droplets are not all dissolved in the grown crystals, further crystal growth is continued. If not, the droplets are consumed and ultimately disappear.

Whisker growth in the present study would be ascribed to the mechanisms shown in Fig. 4. With a thin oxide layer, the droplets on the tips of whiskers are quickly consumed, accompanied by whisker growth. Since the Si–Al–Y–O component of the liquid phase is partly dissolved in the Si_3N_4 whiskers. It is widely known that SiO_2–Al_2O_3–Y_2O_3 oxides are conventional sintering aids for liquid phase sintering of Si_3N_4 ceramics, when a part of them is dissolved in Si_3N_4; SiAlON ceramics are formed.[10] Therefore, the whiskers are

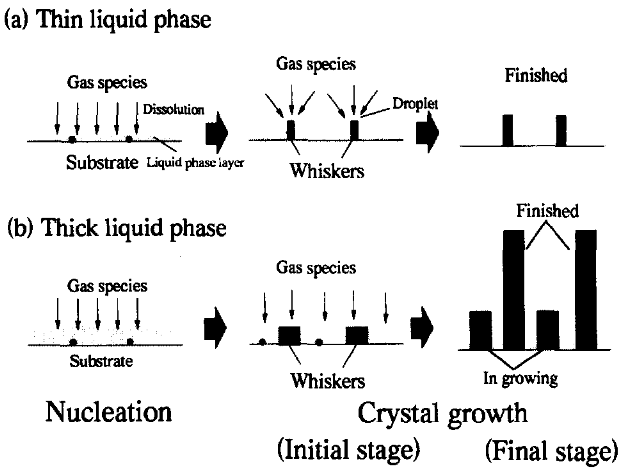

Fig. 4. The comparison of whisker growth mechanisms; (a) thin oxide layer, (b) thick oxide layer.

short and have no droplets, and are in the final stage of whisker growth [Fig. 4(a)].

With a thick oxide layer, however, the droplets are easy not to consume, since large droplets are probably formed on the tips of whiskers due to the thick oxide layer. Therefore, whisker growth is continued for a long time and is finished when the droplets are entirely consumed. This results in the growth of long whiskers having no droplets. On the other hand, relatively short whiskers having droplets are also seen with the long whiskers. They probably start to grow after a considerably long duration; the liquid layer remains on the substrate even though most of it is consumed in the growth of many long whiskers. The short whiskers are in an initial stage of whisker growth and have possibility of further elongation with the increase in duration [Fig. 4(b)].

4 CONCLUSION

Si_3N_4 whiskers were coated on α-Si_3N_4 whisker seeds, on which SiO_2–Al_2O_3–Y_2O_3 oxides were coated, through a VLS mechanism using gas species generated by reacting amorphous Si_3N_4 and TiO_2 as source powders. With a thin oxide layer, the coated whiskers were fine-grained and had no droplets on the tips of the whiskers. With a thick oxide layer, the coated whiskers consisted of short whiskers with droplets and long whiskers with no droplets. These results indicated that the whisker growth proceeded through a VLS mechanism. The differences in molphology were considered to be caused by difference in thickness of the resulting liquid layer on the seeds.

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