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The morphology and growth mechanism of TiC whisker prepared by chemical vapour deposition

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TiC whiskers with good quality and high yield are prepared by a modified chemical vapour deposition (CVD). The whisker morphology and factors affecting its formation have been investigated. Various whisker morphologies such as Wool-, Hassock-, Cluster-, bar-, Hedgehog-, and bamboo-like, are observed under different conditions. The morphologies of TiC whiskers are markedly affected by the gas flow rate and the C/Ti ratio, which is supposed to be related to concentration variation and the formation of Ni-Ti eutectic liquid phase. The growth characteristics of TiC whiskers are also affected by the stability of deposition parameters. It is found that in the course of whisker growth on nickel substrate, the well known VLS mechanism is not necessarily dominant. It is effective in the initial stage, but then might change to the VS mechanism with the dissipation of liquid droplets at the whisker tips. The deposition temperature plays an important role in changing from the VLS to the VS mechanism.

1. Introduction

Whiskers are used as reinforcement in composite materials for increasing their strength and toughness. In ceramic matrix composites (CMC), the main effect of the whiskers is to toughen the brittle ceramic matrix. The required properties of the whiskers for use in CMC are their size and morphology, the compatibility with matrix materials and the interfacial bonding between matrix and whiskers. At present, many carbide and nitride whiskers, such as SiC and Si_3N_4, have been used for both metal matrix composites (MMC) and ceramic matrix composites (CMC) [1–3]. In comparison with SiC and Si_3N_4 whiskers, however, the newly developed TiC whisker has much higher strength (especially high temperature strength), corrosion resistance, better thermal and electrical properties, and better compatibility with alumina matrix [4–6]. Therefore, in recent years, many experiments have been made on the preparation of the TiC whiskers [7–9].

Whisker morphology, such as shape, size, aspect ratio, and smoothness, has important effect on the toughening of CMC, which is usually achieved through a combination of crack defection, crack bridging, and whisker pull out. The whisker morphology is related to the growth mechanism, and they both are affected by the deposition parameters. In the present experiment, TiC whiskers are economically prepared by a modified CVD method, is based on the reaction: $TiCl_4(g) + CH_4(g) = TiC(s) + 4HCl(g)$. The intention of this paper is to study the morphologies and the effects of deposition parameters on the characteristics of the TiC whiskers prepared by the modified CVD method. The growth mechanism of the whiskers is also discussed in detail.

2. Experimental procedure

Instead of the horizontal reaction tube used by other authors [7–9] and in our previous works [10–11], the modified CVD method uses a vertical graphite tube of 30 mm in inner diameter heated by a nickel-chromium alloy coil. The inner diameter of the gas inlet is reduced greatly, so that the flow rate increases significantly. The $TiCl_4$-CH_4-H_2- (and/or Ar) gas mixture is used as reactant and a pure hollow nickel cylinder as substrate which is placed near to the gas inlet around the inner reaction tube wall. The TiC whiskers are obtained by this new method with high yield and consequently lower cost, due to the appropriate movement of vapor phase for the deposition.

The morphologies of TiC whiskers are observed with a scanning electron microscope (SEM). The structure and growth direction of the TiC whiskers are examined by a transmission electron microscope (TEM). The contents of the components and impurities of the TiC whiskers are determined by energy-dispersive spectroscopic (EDS) analysis.

3. Results and discussion

3.1. Whisker morphology

The geometric features such as size and aspect ratio of the TiC whiskers prepared by the modified CVD method are desirable, as shown in Table I. The whisker microphotographs indicate that whiskers obtained under different conditions may have different morphologies. Various morphologies, such as Wool-, Hassock-, Cluster-, and bar-like are observed, as shown in Fig. 1.

It is found that the gas flow rate dependence of the morphology is noteworthy. With low gas flow rate,

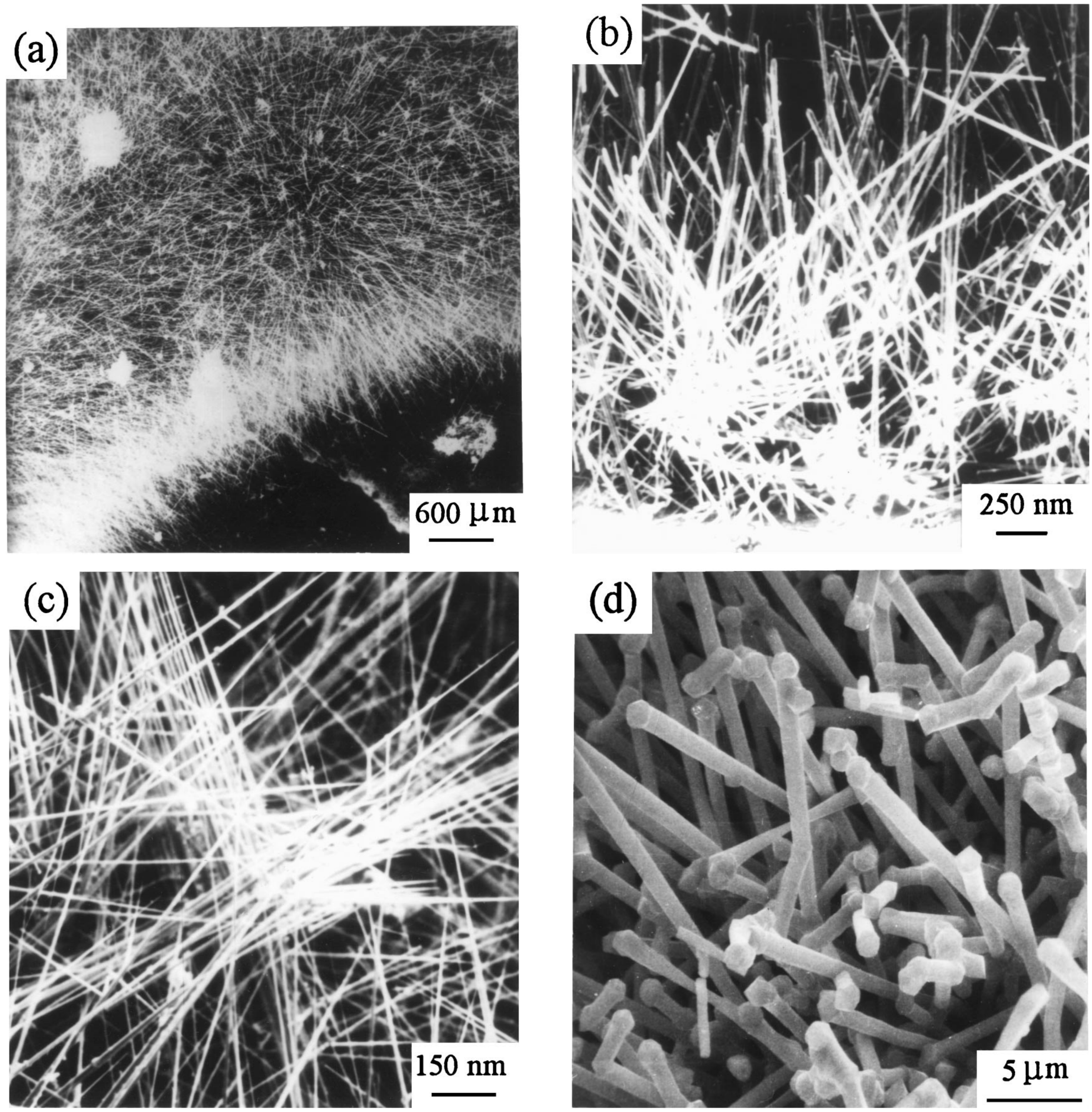

Figure 1 The morphologies of (a) wool-, (b) hassock-, (c) cluster-, and (d) bar-like TiC whiskers.

TABLE I The characteristics of the TiC whiskers (75 min)

Deposition temperature (°C)	Diameter[a] (μm)	Aspect ratio (L/D)	Growth direction[b]
1125	0.01–1.0	100–1000	[1 0 0]
1150	0.05–1.7	100–1000	[1 0 0] [1 1 1]
1200	0.1–2.0	200–1000	[1 0 0] [1 1 1]

[a]SEM, [b]TEM

typical Wool-like morphology is obtained at 1125 °C with a C/Ti ratio of 1.7 : 1 (Fig. 1(a)). However, with high gas flow, typical Hassock- and cluster-like morphology are observed for the same deposition temperature and C/Ti ratio (Fig. 1(b), 1(c)), and bar-like morphology can be observed at above 1200 °C and the same C/Ti ratio (Fig. 1(d)). The effect of gas flow rate on the morphology is likely due to the change in the concentration of the gas phase. At a higher gas flow rate, more CH_4 and $TiCl_4$ are carried to the central region by the flowing gas. Thus, the concentration in the central region is higher than that in the annulus region between the central region and the nickel substrate cylinder. High concentration favors the one-dimensional growth of whiskers, and leads directly to the whisker growth from the bottom of the annulus to the central region. So the whisker growth morphology may be hassock-, cluster-, or bar-like. Low gas flow rate has little effect on the distribution of the concentration of the gas phase, so the whiskers can grow more randomly, and the morphology is wool-like.

Apart from the total gas flow rate, the flow ratio, in particular the ratio of the flow rate of $TiCl_4$ to that of methane (C/Ti), plays a key role in determining the morphology of TiC whiskers. Fig. 2 shows the morphologies of the TiC deposits with various C/Ti at the same location at the temperature of 1125 °C. When the C/Ti ratio is more than 2.0, the

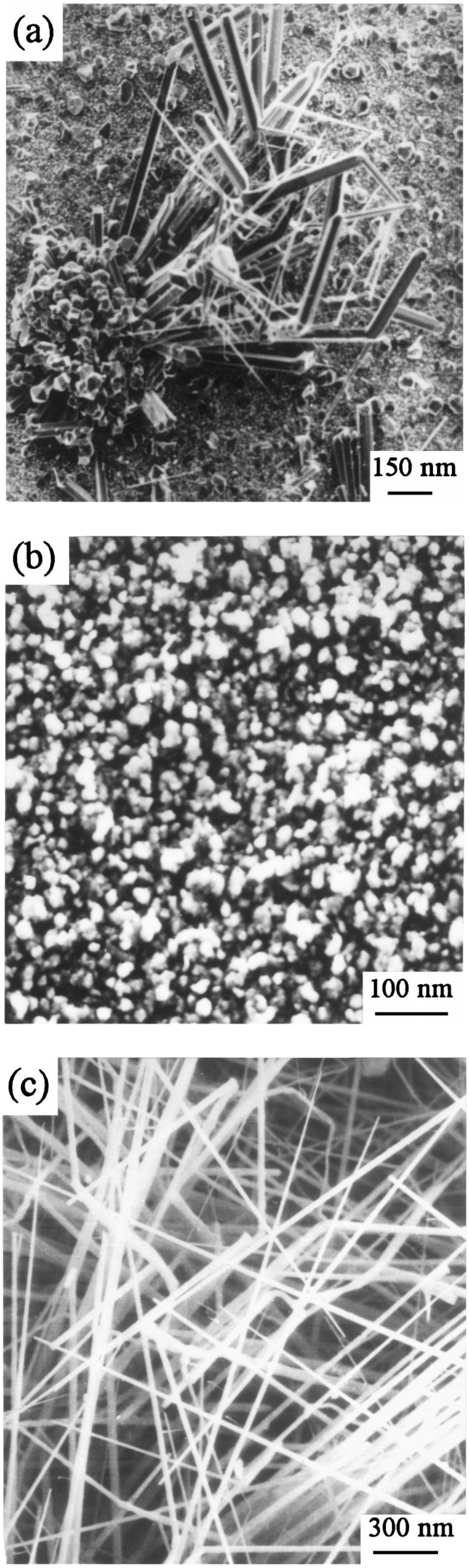

Figure 2 Scanning electron micrograph of the deposits with various C/Ti (1125 °C, 60 min): (a) C/Ti = 2.5, (b) C/Ti = 1.06, (c) C/Ti = 1.7.

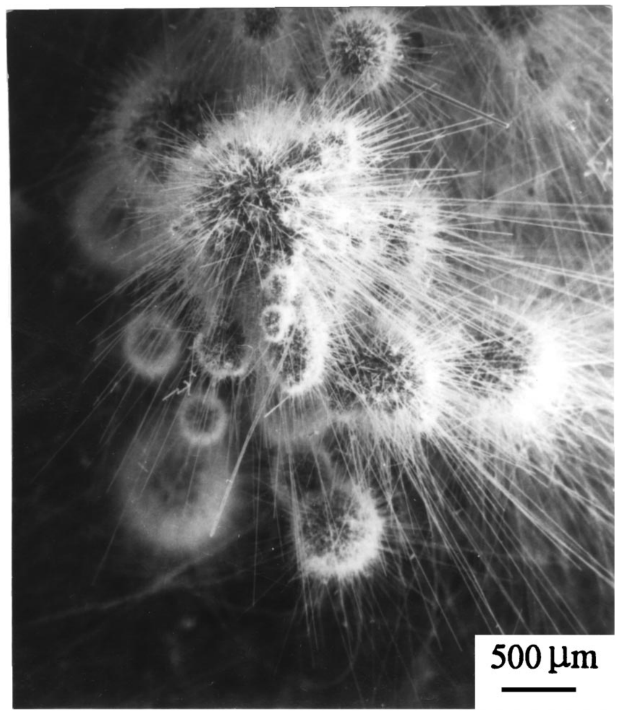

Figure 3 Hedgehog-like whisker growth on the carbon rich regions.

TiC whiskers sporadically scatter in the substrate, as shown in Fig. 2(a). Binary Ni-Ti eutectic liquid droplets formed in the initial stage of the whisker growth initiates TiC whiskers growing according to the VLS mechanism [11]. With the depletion of the titanium, resulting from the reduction of $TiCl_4$ with H_2, fewer liquid droplets are available as nucleation sites. Wokulski *et al*. [8] explained that it was difficult for TiC whisker to grow at high C/Ti ratios due to sedimenting carbon hindering its growth. But our experimental result is in contrast to this conclusion. In a specially designed experiment, we intentionally deposited some carbon on nickel substrate prior to the formation reaction of TiC whisker, and found that the TiC whiskers with high yield grew as hedgehog-like in the carbon rich regions, as shown in Fig. 3. Therefore, the small amount of whiskers deposited at the high C/Ti may be due to a deficiency of titanium rather than excessive carbon. When the C/Ti ratio is approximately 1.0 or less, TiC whiskers will not form due to insufficient carbon (see Fig. 2(b)). Instead, titanium will react with the nickel substrate to form a low melting point Ni-Ti binary eutectic alloy microcrystal. The optimum value of the C/Ti is about 1.7 in this experiment. The morphology of whiskers obtained at this C/Ti is shown in Fig. 2(c).

The stability of deposition parameters, especially the gas flow rate, has an important effect on the morphologies of TiC whiskers. Smooth and straight whiskers are obtained with the gas flow rates controlled stably. When the gas flow rates are changed irregularly, some other whisker shapes can be observed. Fig. 4(a) shows a micrograph of bamboo-like whiskers. The diameters of these whiskers are periodically thin and thick. Similar periodic diameter change was reported in the literature [12–14]. The periodicity in the diameter of these whiskers was regarded to be related to the perturbation of supersaturation [12]. The periodic changes of

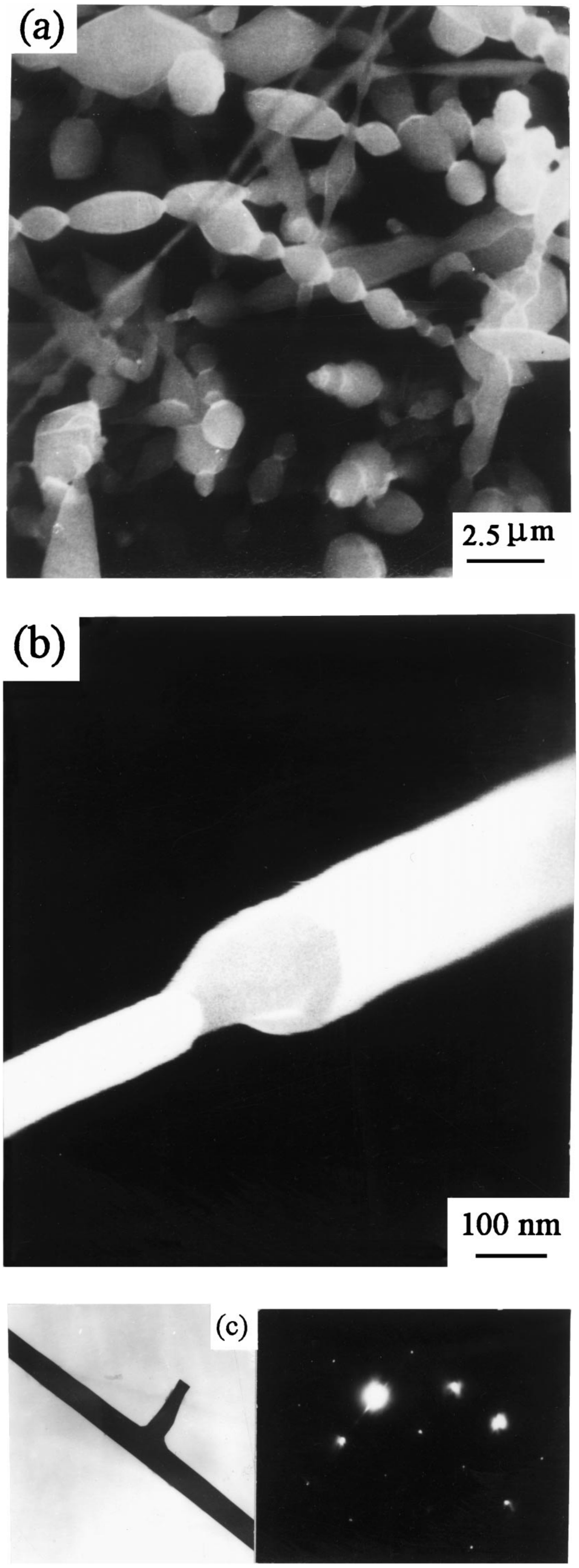

Figure 4 Scanning electron micrograph of (a) bamboo-like TiC whiskers and (b) whisker with sharp diameter shrinkage due to the fluctuation of the deposition parameters. (c) TEM micrograph of branch whisker growth from the mother whisker and their identical growth direction of ⟨1 0 0⟩.

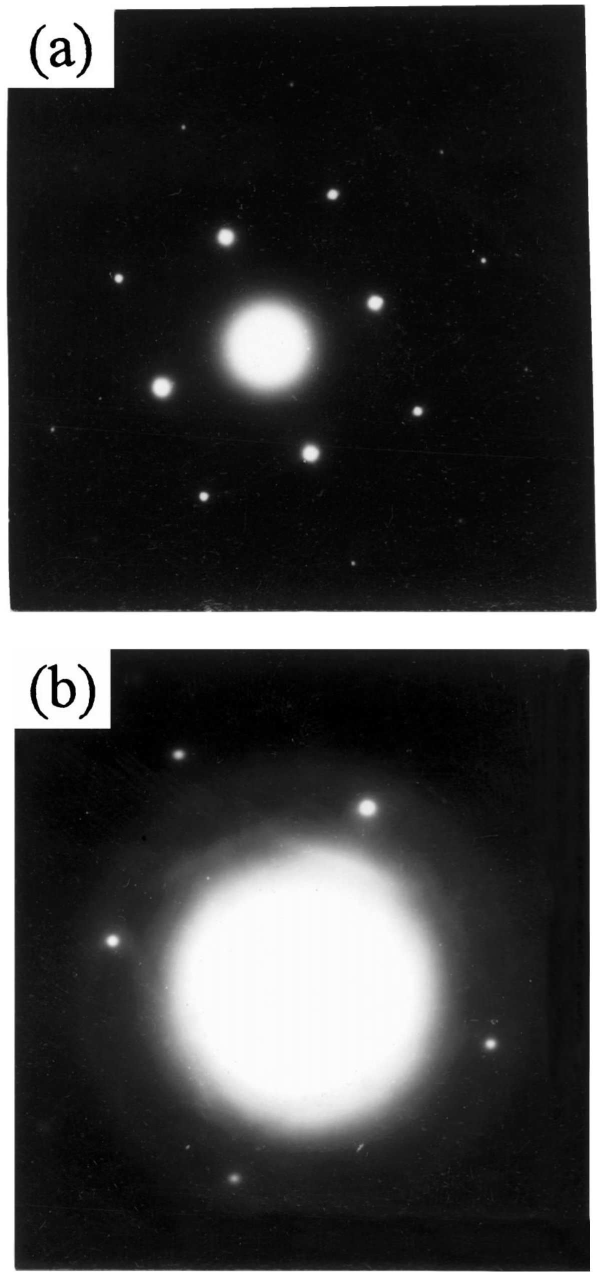

Figure 5 TEM micrograph of (a) TiC whiskers with growth direction of ⟨1 0 0⟩ and (b) with growth direction of ⟨1 1 1⟩.

whisker diameters in the present study may also be due to the fluctuation of supersaturation. Fig. 4(b) shows that the whisker diameter decreases greatly when the flow rate of $TiCl_4$ vapor is reduced suddenly. As shown in Fig. 4(c), TiC whiskers with branches are observed. The formation of these whiskers is also due to the undulation of deposition parameters. Although shape change exists in a single whisker, the growth direction is identical along the whole whisker (see Fig. 4(c)). The TEM images show that the growth directions of the whiskers obtained in the present experiment are mainly ⟨1 0 0⟩ and ⟨1 1 1⟩, as shown in Fig. 5.

3.2. Growth mechanism

There are two well-accepted whisker growth mechanisms: the Vapor-Solid (VS) mechanism and the Vapor-Liquid-Solid (VLS) mechanism. The vapor-solid process is the basis of the axial screw dislocation growth, and the spherical liquid droplet on the whisker tip is the inherent characteristic of the VLS mechanism.

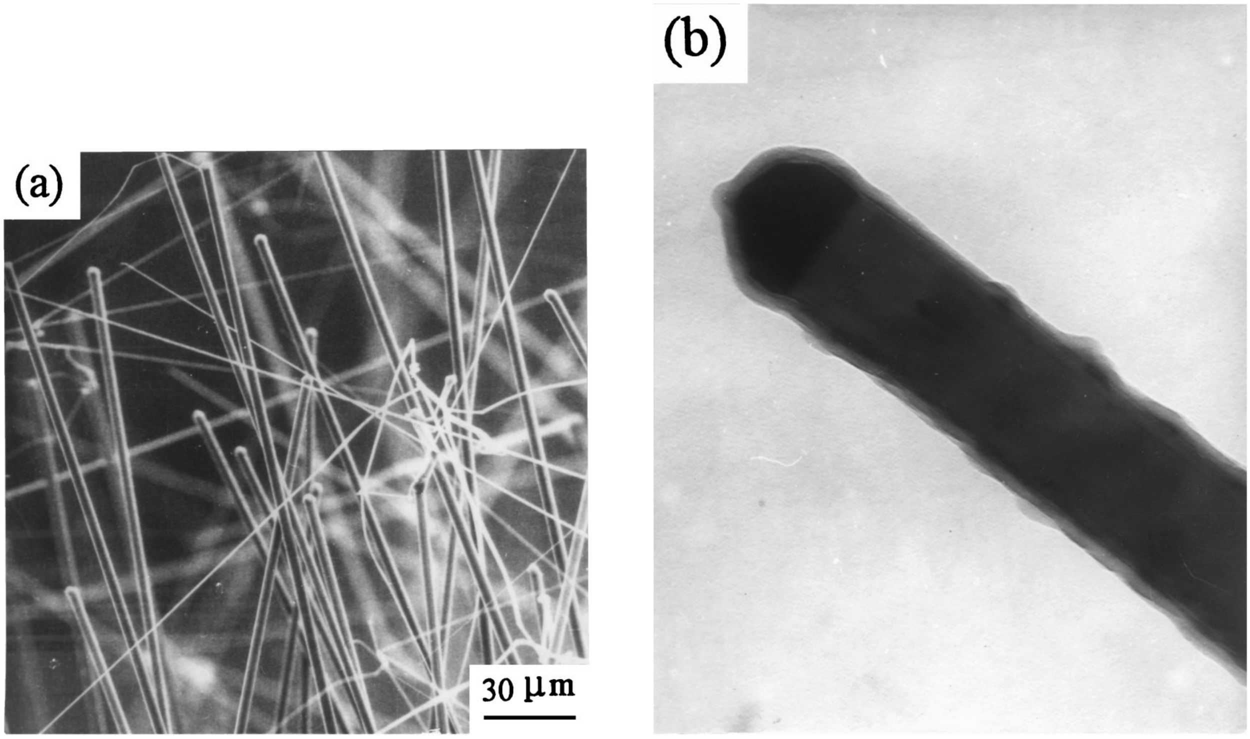

Figure 6 (a) Scanning electron micrograph of TiC whiskers growth by the VLS mechanism. (b) TEM micrograph of a spherical liquid droplet on a whisker tip.

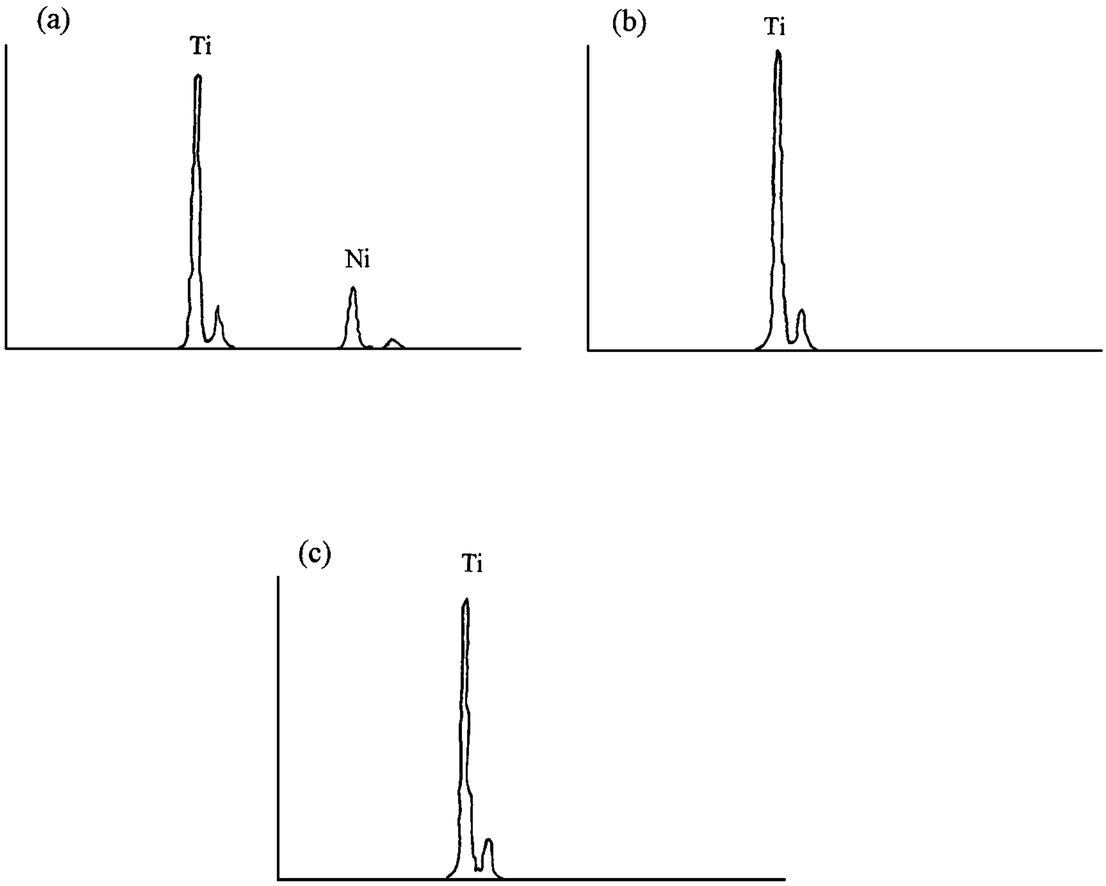

Figure 7 EDS spectra of (a) the apex and (b) the root of a whisker with liquid globule tip, (c) the apex of a whisker with facet and microstep tip.

At low deposition temperatures (below 1125 °C), nearly all of these whiskers bore liquid globules on their tips, as shown in Fig. 6. The EDS analysis shows that nickel exists in the liquid globules, but not in the whisker roots, as shown in Fig. 7(a), Fig. 7(b), respectively. So it can be ascertained that the VLS mechanism is responsible for the whisker growth at low deposition temperatures.

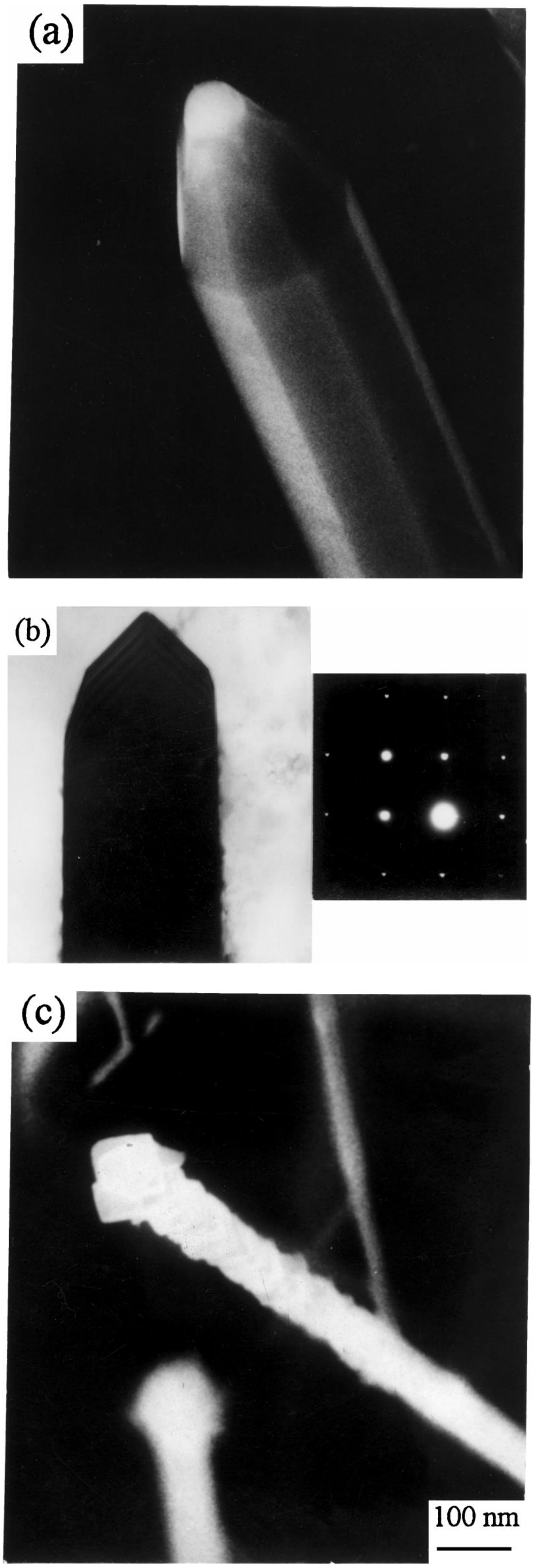

Figure 8 (a) Scanning electron micrograph of a whisker tip surrounded by facets, (b) TEM micrograph of whisker with microsteps at tip, and its electron diffraction pattern. (c) Whisker with layers in both whisker tip and root.

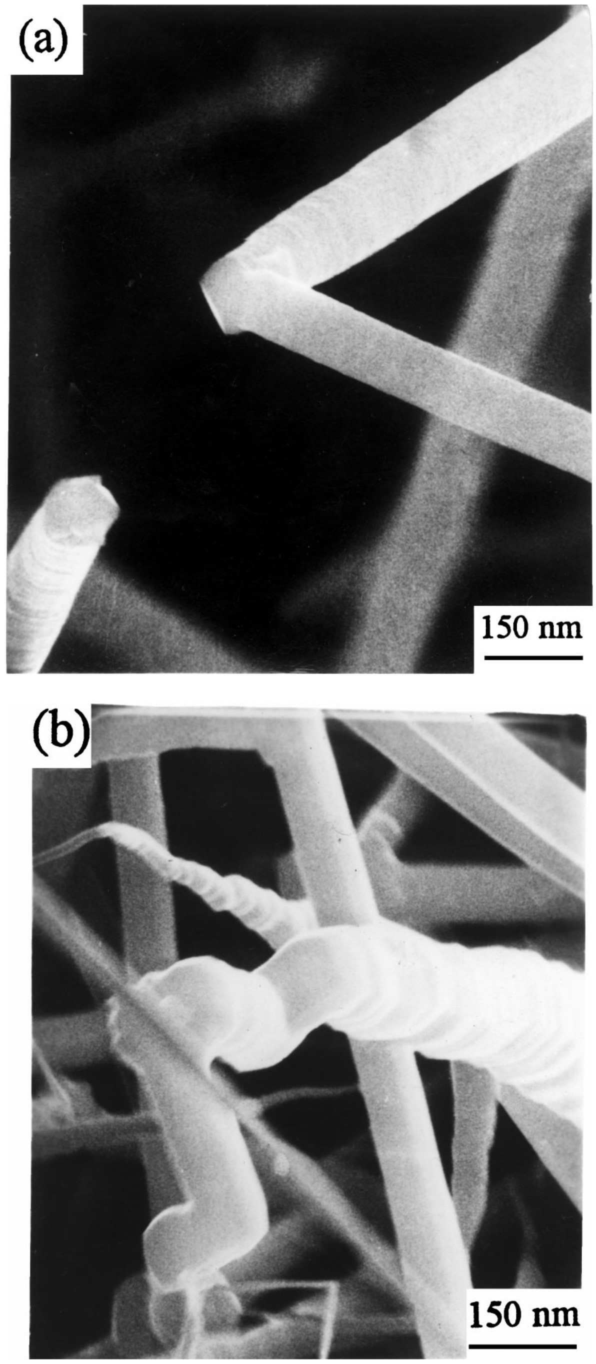

Figure 9 Scanning electron micrograph of (a) the TiC whiskers growth by the VS mechanism (layers in the root whisker) changing to the VLS mechanism with the aid of liquid droplet, (b) the whisker with repeated orthogonal crooks.

The SEM and TEM images show that apart from spherical liquid droplets on the whisker tips, many whisker tips surrounded by facets are also observed around 1150 °C, as shown in Fig. 8(a). Even layers and microsteps are observed in the whisker tips and the whisker roots growth from them, as shown in Fig. 8(b), (c). The TEM image shows that these whisker roots and tips both have the same growth direction (Fig. 8(b)), and the EDS analysis shows no presence of nickel in these tips, as shown in Fig. 7(c). This indicates that the VS mechanism may operate in the whisker growth process in this case. Kato and Tamari [15] regarded that the whisker tips being surrounded by facets might be related to the change of the whisker growth mechanism from the VLS to the VS mechanism. Wang *et al*. [13] suggested that a chemical reaction played a role in facilitating the VS

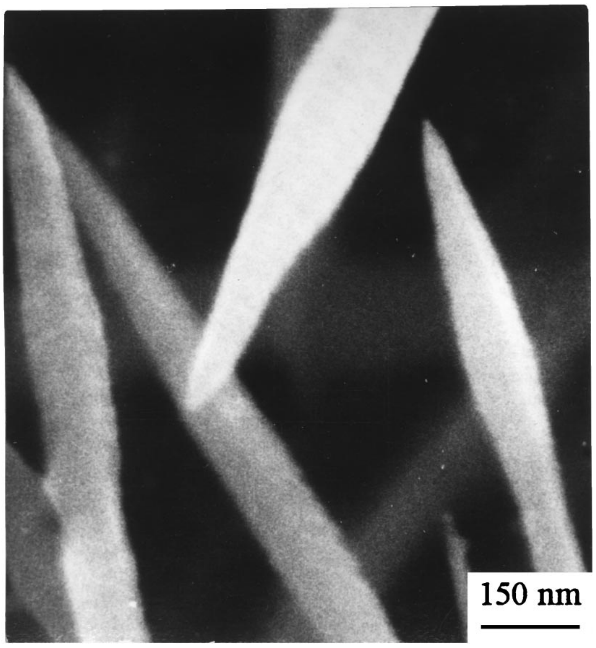

Figure 10 Scanning electron micrograph of TiC whiskers with tapered tips.

nucleation. Although several viewpoints exist regarding the possible reaction process, it is commonly accepted that the reduction of $TiCl_4$ and methane decomposition may exist in the TiC formation reaction [7, 11]. That is

$$TiCl_4(g) \xrightarrow{H_2(g)} TiCl_3(g) \xrightarrow{H_2(g)} TiCl_2(g) \xrightarrow{H_2(g)} TiCl(g) \xrightarrow{H_2(g)} Ti(g)$$

$$CH_4(g) \rightarrow CH_3(g) \rightarrow CH_2(g) \rightarrow CH(g) \rightarrow C(g)$$

The energy barrier for VS nucleation might be lowered by the reaction between certain reduction and decomposition products, such as TiCl and CH. The energy required for VS nucleation may facilitate the VS mechanism. Therefore, we presume that a tendency for the VLS mechanism to change to the VS mechanism exists in the whisker growth process at relative high deposition temperature. It is quite possible that TiC whiskers grow by the VLS mechanism at the initial growth stage, then change to the VS mechanism with the liquid droplet disappearing from the whisker tips. Fig. 9 shows that once new liquid droplets form on the tips of the whiskers growing by the VS mechanism, these whiskers will be back to grow in accordance with the VLS mechanism, which accompanies the change of growth directions and the formation of crooks (Fig. 9(a)). The undulation of the deposition parameters, in particular the deposition temperature, often induces this. Even repeated orthogonal crooks can be observed when the deposition parameters fluctuate periodically, as shown in Fig. 9(b). This indicates that the dissipation of liquid droplets in the whisker growth process may determine the change from the VLS to the VS mechanism. The liquid droplet may disappear due to the escape of nickel from the eutectic liquid alloy. The nickel escapes either by evaporation [7] or reaction to produce certain vapor phase of nickel alloy [9].

When the deposition temperature is increased up to 1200 °C (the vapor pressure of Ni(s) at 1200 °C is 2×10^{-5} Torr), an interesting result is found. The TiC whiskers not only grow on nickel substrate, but also on the inner wall of the graphite reaction tube. Nearly all of whisker tips become more and more tapered and no droplet has been found on the whisker tips, as shown in Fig. 10. It indicates that the VS mechanism holds in this case. The liquid droplets disappearing from the tips of the whiskers may be due to the increase of the evaporation speed of nickel atoms with temperature, or the depletion of nickel taking part in the reaction.

4. Conclusion

TiC whiskers with good quality and high yield are prepared by a modified CVD method. Various whisker morphologies are observed under different conditions. The major factors affecting the whisker morphology are the gas flow rate and the C/Ti ratio. Typical wool-like growth morphology of whiskers is obtained at a lower gas flow rate, while hassock-, cluster-, and bar-like whiskers are obtained at a higher flow rate. The difference in morphology can be ascribed to the difference in concentration of the vapor phase. The effect of the C/Ti on the whisker morphology is related to the formation of Ni-Ti eutectic liquid phase which initiates whisker growth. Furthermore, the stability of deposition parameters also affects the whisker morphology and growth mechanism. The whiskers prepared in this experiment are perfect single crystals. The main growth directions are $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,1 \rangle$. The VLS mechanism is not necessarily dominant in the whisker growth process. At low deposition temperature, the TiC whiskers grow on the nickel substrate accoding to the VLS mechanism. With the increase in temperature, the VLS mechanism operates at the initial stage, then changes to the VS mechanism with the dissipation of liquid droplets at the whisker tips. The deposition temperature plays an important role in determining the change from the VLS to the VS mechanism.

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References

1. G. C. WEI and P. F. BECHER, *Amer. Ceram. Soc. Bull.* **64** (1985) 298.
2. H. MATSUBARA, Y. NISHIDA, M. YAMADA, I. SHIRAYANAGI, and T. IMAI, *J. Mater. Sci. Letters* **6** (1987) 1313.
3. K. XIA and T. G. LANGDON, *J. Mater. Sci.*, **31** (1996) 5487.
4. T. TAKAHASHI, K. SUGIYAMA and H. ITOH, *J. Electrochem. Soc.* **117** (1970) 541.
5. F. W. VAHLDICK, *J. Less-Common Metals* **12** (1967) 429.
6. D. T. MORELLI, *Phys. Rev. B* **44** (1991) 5453.
7. N. TAMARI and A. KATO, *J. Crystal Growth* **46** (1979) 221.

8. Z. WOKULSKI and K. WOKULSKA, *J. Crystal Growth* **62** (1983) 439.
9. Z. WOKULSKI, *J. Crystal Growth* **82** (1987) 427.
10. J. S. PAN and Y. H. CHEN, *Acta Mater. Composite Sin.* **12** (1995) 1.
11. Y. H. CHEN, J. S. PAN and X. Y. HUANG, *J. Crystal Growth* **172** (1997) 171.
12. E. I. GIVARGIZOV, *J. Crystal Growth* **20** (1973) 217.
13. L. WANG, H. WADA, and L. F. ALLARD, *J. Mater. Res.* **7** (1992) 148.
14. S. MOTOJIMA, Y. OGAWA, S. GAKEI, and H. IWANAGA, *Mater. Sci. and Eng. B* **30** (1995) 13.
15. A. KATO and N. TAMARI, *J. Crystal Growth* **49** (1980) 199.

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