Chemical vapour growth of HfC whiskers and their morphology

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HfC whiskers were prepared from a gas mixture of $HfCl_4 + CH_4 + H_2 + Ar$ in the presence of metal impurities, and the growth conditions and morphology were examined. The HfC whiskers preferentially grew at an H/Cl ratio of above 8, an $HfCl_4$ gas flow rate of 10–20 standard $cm^3 min^{-1}$, a CH_4 flow rate of 10–20 standard $cm^3 min^{-1}$, and at temperatures above 1050 °C. HfC whiskers, 60–170 µm long, with a ball-like tip and periodically varying diameters, were obtained at 1250 °C using a cobalt impurity.

1. Introduction

Hafnium carbide (HfC, m.p. 3887 °C) has excellent stability against severe oxidation and corrosive atmospheres at very high temperatures. Accordingly, hafnium carbide is a very interesting candidate as a component of super-high-temperature protective coatings [1–3]. Especially, HfC whiskers are the most promising candidate for reinforcement fibres of super-high-temperature composite materials. So far, HfC has been prepared by the direct carburization of hafnium metal [4, 5], self-combustion synthesis [6], carbothermal reduction [7], magnesium-thermal reduction [8], and chemical vapour deposition (CVD) processes [9–14]. Of these processes, HfC whiskers have been prepared by a metal activated CVD process [10,12,13]. However, their detailed growth conditions, morphology and properties have not been examined.

In the present work, HfC whiskers were obtained by the metal-activated CVD process using a gas mixture of $HfCl_4 + CH_4 + H_2 + Ar$ at 1050–1250 °C, and the growth conditions and morphology were examined.

2. Experimental procedure

Hafnium tetrachloride was prepared *in situ* by the chlorination of hafnium metal powder using chlorine at 700 °C and carried by argon into the reaction tube. The horizontal reaction tube (quartz glass, 28 mm i.d. and 350 mm long), containing graphite substrate ($15 \times 100 \times 1$ mm^3) in the central part, was heated from the outside using heating elements. An impurity metal powder, of about 5 µm average grain diameter was uniformly painted on the graphite substrate.

3. Results and discussion

The HfC whiskers have been so far obtained by the nickel impurity-activated CVD process. The effect of various metal impurities other than nickel on the growth of the whiskers, was examined and the results are shown in Fig. 1, in which the reaction temperature was fixed at 1250 °C. It was observed that nickel, cobalt and vanadium impurities induced whisker growth, while other metal impurities, such as titanium, chromium, manganese, iron, niobium, molybdenum and tungsten did not produce any whiskers. Using the vanadium impurity, only a small amount of very thin and curled whiskers grew. Of the three impurities which produced whisker growth, cobalt and nickel were useful impurities for obtaining a large amount of well-formed whiskers with high reproducibility.

The effect of $HfCl_4$ and CH_4 gas flow rates on the HfC whisker growth is shown in Fig. 2 in which nickel was used as the impurity and the reaction temperature was fixed at 1250 °C. The whiskers were obtained with good reproducibility in region A at relatively small $HfCl_4$ and CH_4 flow rates (10–20 standard $cm^3 min^{-1}$). A small amount of whiskers was obtained with poor reproducibility in region B. The whiskers preferentially grew at an H/Cl gas flow ratio above 7.5

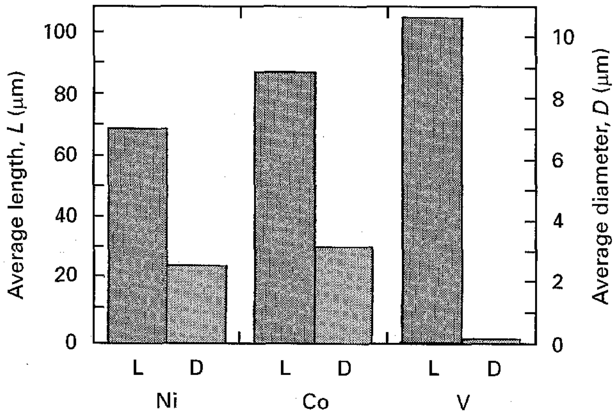

Figure 1 Effect of metal impurities on the growth of HfC whiskers. Reaction temperature 1250 °C, reaction time 20 min, $HfCl_4$ gas flow rate 10 $ml s^{-1}$ (standard $cm^3 min^{-1}$), CH_4 flow rate 20 standard $cm^3 min^{-1}$, H_2 flow rate 150 standard $cm^3 min^{-1}$.

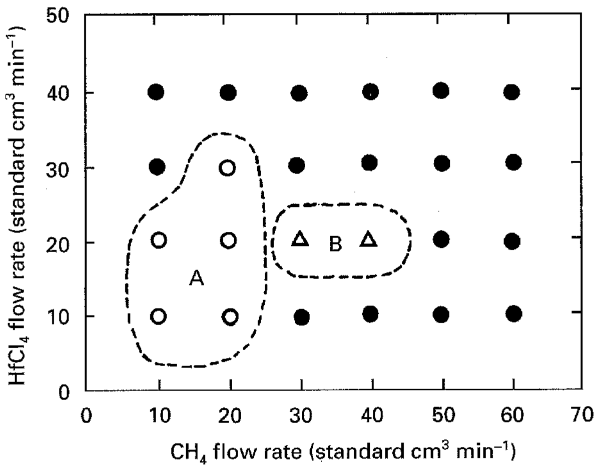

Figure 2 Effects of $HfCl_4$ and CH_4 gas flow rates on the growth of HfC whiskers. Nickel impurity; reaction temperature 1250 °C, H_2 flow rate 150 standard $cm^3 min^{-1}$. (○) region A, a large amount of whisker growth with good reproducibility; (△) region B, a small amount of whisker growth with poor reproducibility, (●) no deposition.

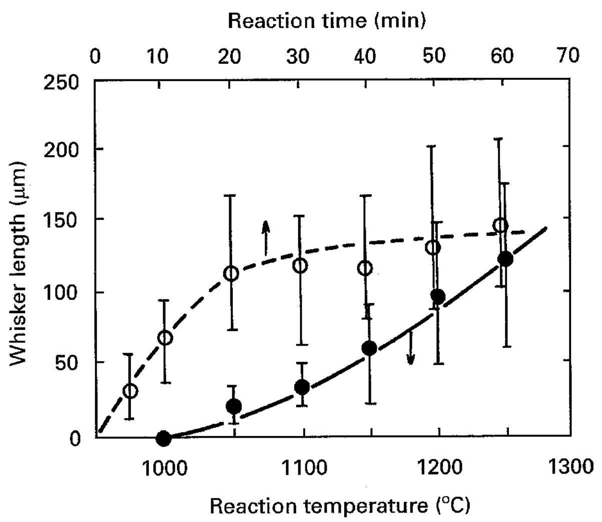

Figure 3 Effects of reaction temperature and reaction time on HfC whisker growth. $HfCl_4$ gas flow rate 6 standard $cm^3 min^{-1}$, CH_4 flow rate 10 standard $cm^3 min^{-1}$, H_2 flow rate 150 standard $cm^3 min^{-1}$. (●) reaction time 30 min, (○) reaction temperature 1250 °C.

and reaction temperatures above 1050 °C. The effects of reaction temperature and reaction time on the whisker length are shown in Fig. 3, in which reaction time and reaction temperature were fixed at 30 min and 1250 °C, respectively. Whisker length monotonically increased with increasing reaction temperature, and whiskers about 120 μm long were obtained at 1250 °C. The whisker length sharply increased with increasing reaction time up to 20 min and then gradually increased. On the other hand, the whisker diameter was not affected by the reaction temperature and reaction time, and was in a range 2–5 μm.

Fig. 4 shows the representative HfC whiskers and an enlarged view of the whiskers tip obtained using nickel impurity at 1250 °C. A ball-like deposit was usually observed on the tip of the whiskers. Fig. 5 shows an interesting view of the ball-like deposits. Secondarily grown small ball-like deposits or whiskers,

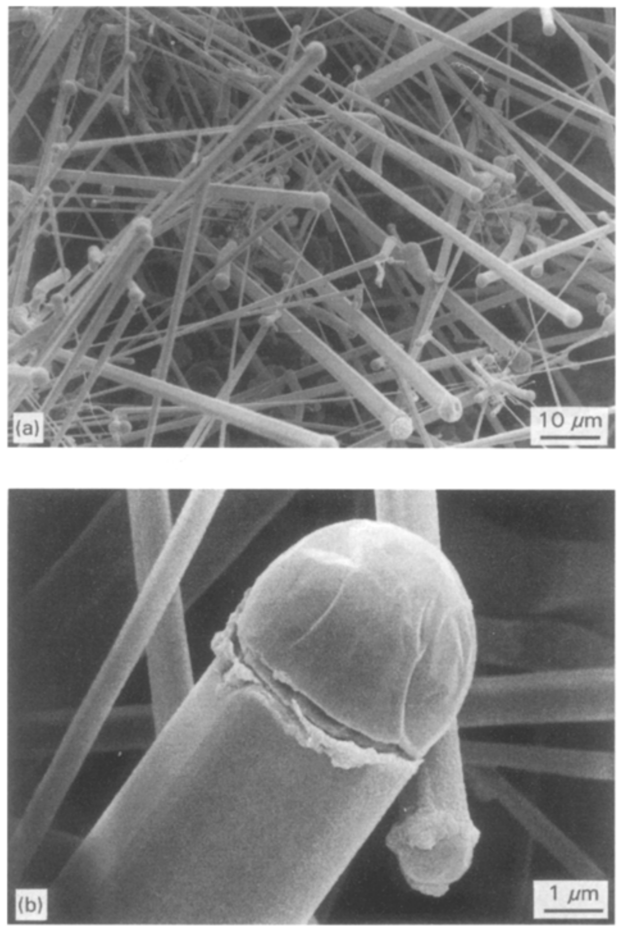

Figure 4 (a) Representative HfC whiskers and (b) an enlarged view of the whisker tip. Nickel impurity, reaction temperature 1250 °C.

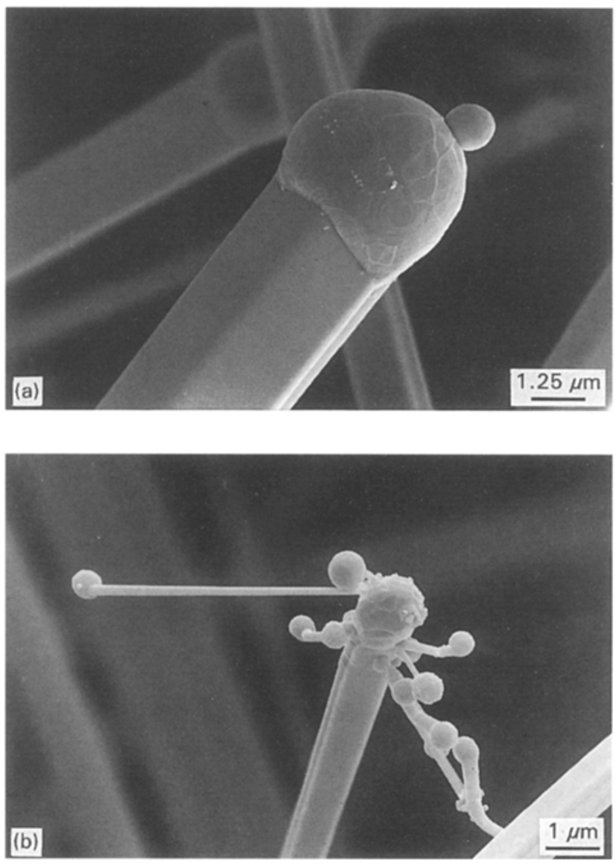

Figure 5 (a) A ball-like tip having secondarily grown smaller ball-like deposit and (b) whiskers having a smaller ball-like tip. Nickel impurity.

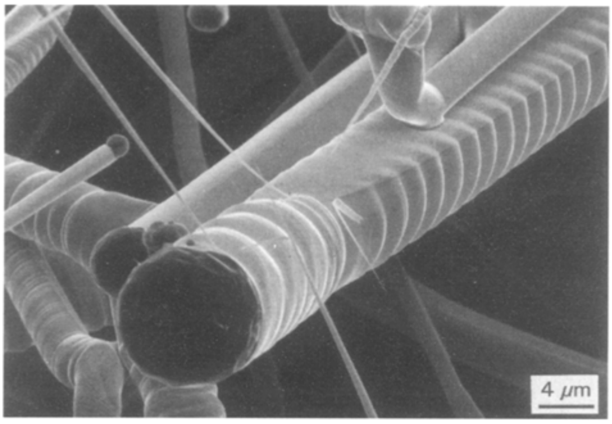

Figure 6 HfC whiskers having periodically thick and thin diameter. Cobalt impurity, reaction temperature 1250 °C.

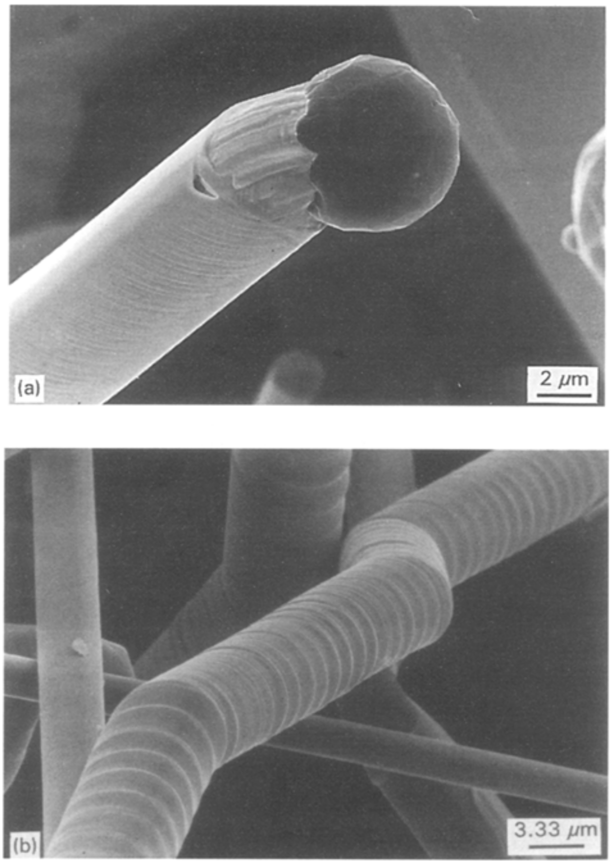

Figure 7 (a) Inclined ball-like tip and (b) kinked whisker. Cobalt impurity, reaction temperature 1250 °C.

having a small ball-like tip, were sometimes observed on the primary ball-like deposits, as shown in Fig. 5a and b. These secondarily grown deposits or whiskers may be caused by a partial instability or fluctuation in the liquid droplet during the growth of the whiskers.

Fig. 6 shows representative HfC whiskers obtained using cobalt impurity. It is interesting that when using cobalt impurity, whiskers with periodically thick and thin diameters (with striation patterns) were usually observed as shown in Fig. 6. The presence of a large amount of cobalt and a small amount of hafnium and carbon was usually observed on the ball-like tip using an electron probe microanalyser. Accordingly, the whiskers obtained using cobalt impurity, were grown

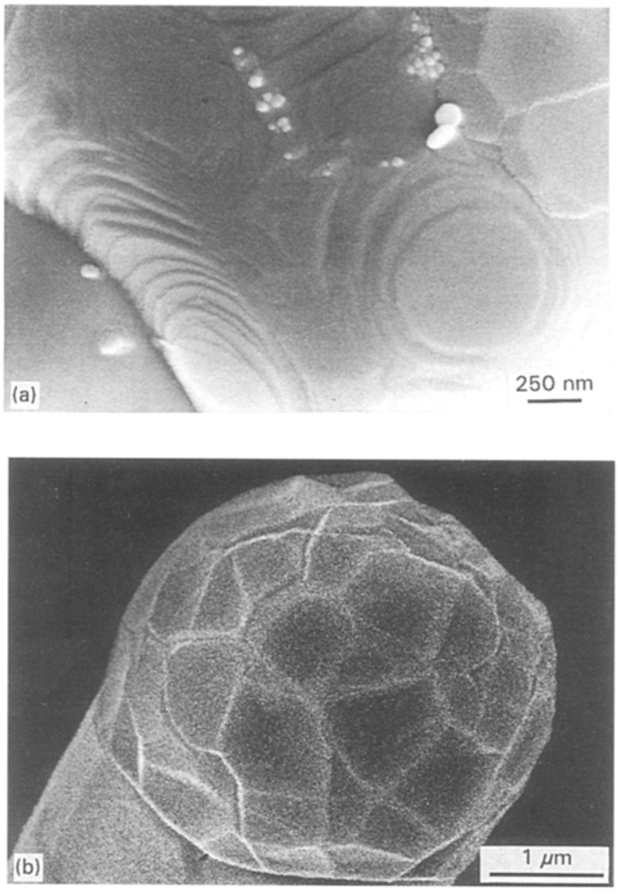

Figure 8 Enlarged views of the regularly shaped ball-like tip. Impurity: (a) Ni, (b) Co. Reaction temperature 1250 °C.

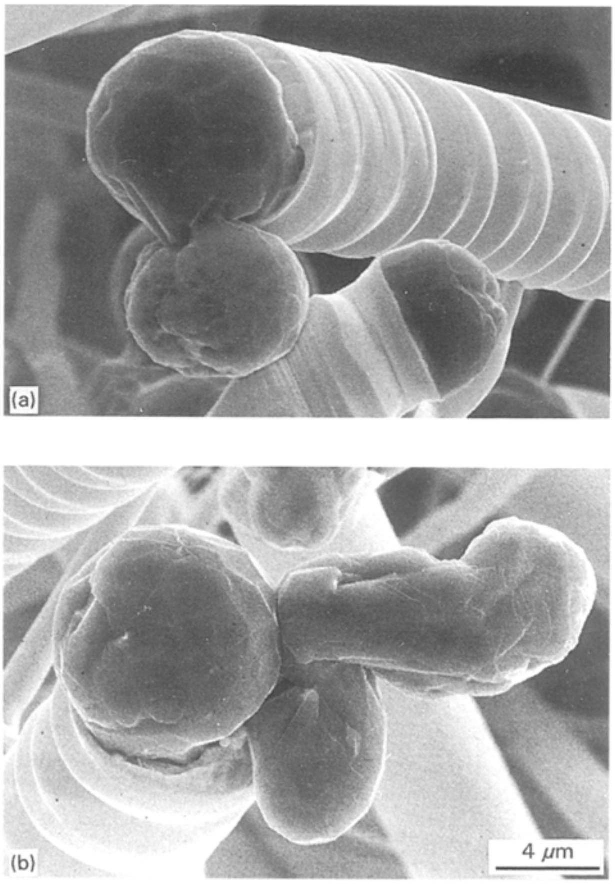

Figure 9 Enlarged view of the irregularly shaped ball-like tip. Cobalt impurity, reaction temperature 1250 °C.

by the VLS mechanism proposed by Wagner and Ellis [15, 16], as in the case using nickel impurity [10]. The formation of the striation patterns observed on the surface of the whiskers as shown in Fig. 6 may be caused by a periodic instability such as a periodic change in the liquid droplet diameter while the reasons or the driving force are not yet known. Fig. 7a shows an interesting tip part of the whiskers obtained using cobalt impurity. The centre of the ball-like deposit tilts at an angle away from the whisker axis. Whiskers that were kinked at small angles were sometimes observed, as shown in Fig. 7b. These whiskers may be formed by the tilting of the droplet from the whisker axis during the growth of the whiskers.

Fig. 8 shows an enlarged view of the ball-like deposits observed on the whisker tip. The well-formed ball-like tip usually has distinct growth steps or polygonal facets, as shown in Fig. 8. These steps or facets may be formed by the crystallization of the droplet when the temperature was lowered. On the other hand, irregular branching of the deposits was sometimes observed, as shown in Fig. 9.

The lowest eutectic temperatures for the respective binary compounds were as follows: 1212 ± 12 °C for Hf–Co, 1274–1317 °C for Co–C and 2210 ± 50 °C for Hf–C. The ball-like deposits observed on the whisker tip were composed of Hf–Co–C ternary compounds, as already shown. The high eutectic temperature of the binary compounds suggests that the Hf–Co–C compound has a higher melting point than the reaction temperature of 1250 °C. Accordingly, it may be considered that the ball-like deposits do not arise from a perfect liquid state, but from a quasi-liquid state with a very high viscosity which has a higher diffusion velocity than the bulk solid state, in order to cause the VLS growth. These quasi-liquid states of the ball-like deposits may affect their morphology.

4. Conclusion

HfC whiskers were prepared by the metal impurity-activated chemical vapour deposition method. The growth conditions and morphology were examined. Cobalt and nickel were the most effective impurities for the growth of the whiskers. Whiskers 60–170 μm long and 3–5 μm thick were obtained at 1250 °C.

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