Letters

Impurity activated whisker growth of zirconium nitride by chemical vapour deposition

Zirconium nitride (ZrN) is known as a superhard and corrosion-resistant material. Single crystal boules have been grown by the floating-zone technique, [1] and whiskers by CVD method [2, 3]. In the present work, zirconium nitride whiskers were grown from a gas mixture of zirconium tetrachloride, nitrogen, hydrogen and argon, and the impurity effect was examined.

Fig. 1 shows the apparatus for whisker growth. A tubular quartz substrate (7 mm o.d. and 90 mm long) was held along the centre axis of a quartz reaction tube (20 mm i.d.) and the substrate was heated by a silicon carbide resistor which was inserted into the substrate tube. Zirconium tetrachloride was prepared by chlorination of zirconium sponge at 700 to 800° C *in situ* and carried by argon to the reaction zone. The surface temperature of the substrate was measured using an optical pyrometer and the flowing gas temperature ("gas temperature" hereafter) by an alumel–chromel thermocouple. Aqueous solutions of ten compounds were painted as a liquid-forming impurity on the substrate which has been scratched by abrasives, dried in air, and decomposed or reduced by hydrogen in the reaction tube below the growth temperature. The terms "length" and "diameter" of the whiskers refer to an average of about ten samples selected from the longest and the thickest in the microscope field at × 150.

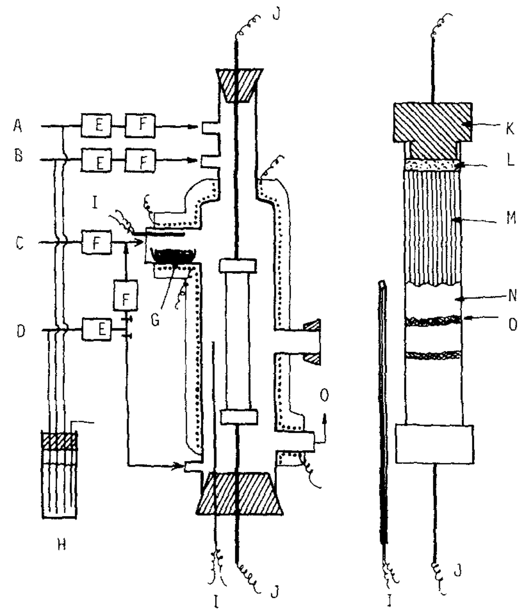

Figure 1 Schematic diagram of the experimental apparatus: (A) H_2, (B) N_2, (C) Cl_2, (D) Ar, (E) conc. H_2SO_4, (F) flow meter, (G) Zr sponge, (H) pressure controller, (I) a.c. thermocouple, (J) electrodes, (K) graphite, (L) carbon powder, (M) SiC heater, (N) quartz substrate, (O) impurity painted zone, (P) gas outlet.

TABLE I Impurity effects on whisker growth and eutectic temperature of binary compounds with zirconium or nitrogen. Growth temperature 1220° C; gas temperature 1000° C; $ZrCl_4/N_2/H_2/Ar$: 10/35/39/16 vol %; growth time 20 min.

Impurity	Eutectic temperature of binary compounds (°C)		Impurity effects*
	Zr impurity	N impurity	
Pd ($PdCl_2$)	755	–	B
Au ($HAuCl_4$)	1250	–	C
Co ($CoCl_2$)	1460	–	E
Ni ($NiCl_2$)	800	–	D
Sb ($SbCl_3$)	1430	–	B
Ag ($AgNO_3$)	1250	–	F
Fe ($Fe_2(SO_4)_3$)	800 ± 5	590	A
Mn ($MnCl_2$)	795 ± 10	500	A
Cu ($CuCl_2$)	822	–	D
Pt (H_2PtCl_6)	826	–	A

* (A) whiskers (longer than 150 μm); (B) whiskers (50 to 150 μm); (C) pillar crystals; (D) uniform coatings; (E) polygonals; (F) no-deposition.

In Table I, the impurity effects observed at 1220° C for a 20 min growth are summarized, together with the eutectic temperatures of the relevant binary alloys. Gold impurity induced the crystals to form pillars (Fig. 2), cobalt to form polygons, while nickel and copper gave uniform coatings rather than whiskers. Platinum, iron and manganese were the most effective in growing thin whiskers or phylloid crystals at temperatures below 1200° C (Fig. 3a and b), or pillar crystals at temperatures above 1200° C (Fig. 3c). The experiments were subsequently carried out using platinum metal as an impurity unless otherwise described, because it gave a high reproducibility in growth experiments.

The lowest growth temperature of the whiskers was about 1000° C under activation with impurity

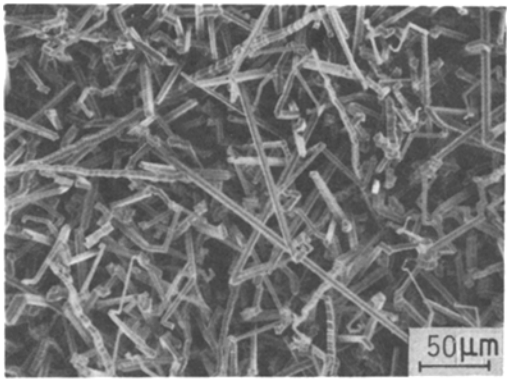

Figure 2 Appearance of pillar-like crystals grown with Au impurity. Temperature: 1220° C.

metals. The influence of gas temperature on the whisker growth is shown in Fig. 4, in which the substrate temperature was maintained at 1220° C. The whisker length increased with increasing gas temperature and attained a maximum at 1000 to 1020° C, becoming shorter again above 1020° C, probably due to the competitive deposition of zirconium nitride on the inner wall of the reaction tube. The experiments were, therefore, conducted at a gas temperature of 1000° C.

When the ratio $N_2/(ZrCl_4 + N_2)$ in the feed gas was varied under a fixed rate of $ZrCl_4 + N_2$ of 1.86 ml sec^{-1}, the length of the whiskers increased with the ratio $N_2/(ZrCl_4 + N_2)$ and attained a maximum at a ratio of 0.75 (Fig. 5), which is 2.25 times the stoichiometric ratio of the reaction,

$$ZrCl_4 + \tfrac{1}{2} N_2 + 2 H_2 = ZrN + 4 HCl, \quad (1)$$

i.e. zirconium nitride whiskers grow preferentially from a nitrogen-rich atmosphere, and such a tendency is in agreement with that observed in polycrystalline deposition of zirconium nitride [2].

The effect of the ratio $H_2/ZrCl_4$ in the feed gas on whisker growth is shown in Fig. 6. The whisker length increased with increase of the ratio $H_2/ZrCl_4$ and attained a maximum at a ratio of 3.0 to 3.5, which corresponds to 1.5 to 1.75 times the stoichiometric ratio of Reaction 1. The effect of the total gas flow rate on whisker growth is shown in Fig. 7, in which the gaseous concentrations of zirconium tetrachloride, nitrogen, hydrogen and argon were fixed at 10, 35, 39 and 16 vol %, respectively. Whisker length increased with increase in the total flow rate and attained a maximum at 4 ml sec^{-1} which corresponds to a linear velocity of about 8 cm sec^{-1} at the growth temperature, while the diameter gradually increased with increase in the total flow rate. Under a low linear velocity, the reactants are exhausted by the deposition on the inner wall before arrival at the substrate. On the other hand, under a high linear velocity the concentrations of the reactants over the substrate

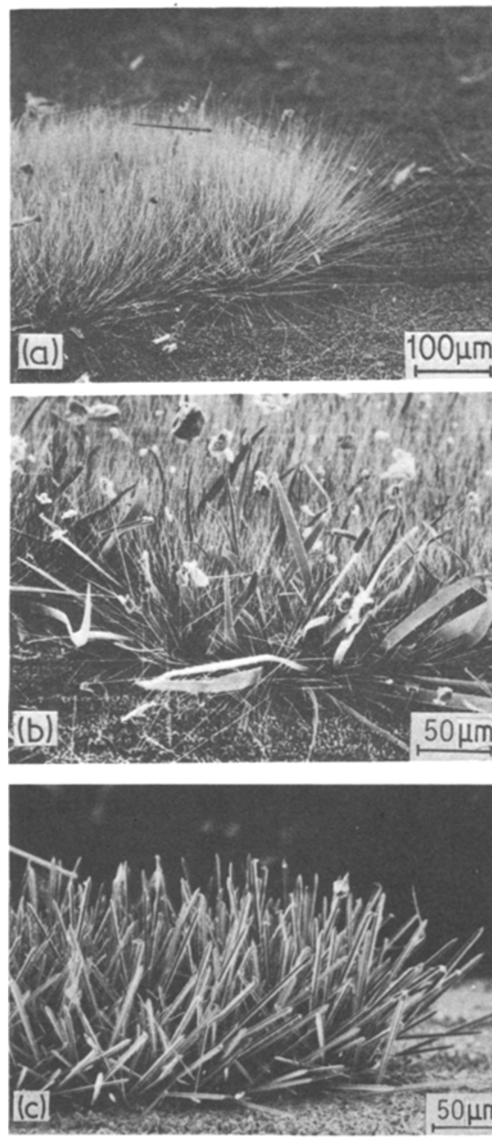

Figure 3 Appearances of whiskers and pillar-like crystals grown with Pt impurity. (a) Thin whiskers; (b) phylloid crystals, temperature 1180° C; (c) pillar-like crystals, temperature 1250° C.

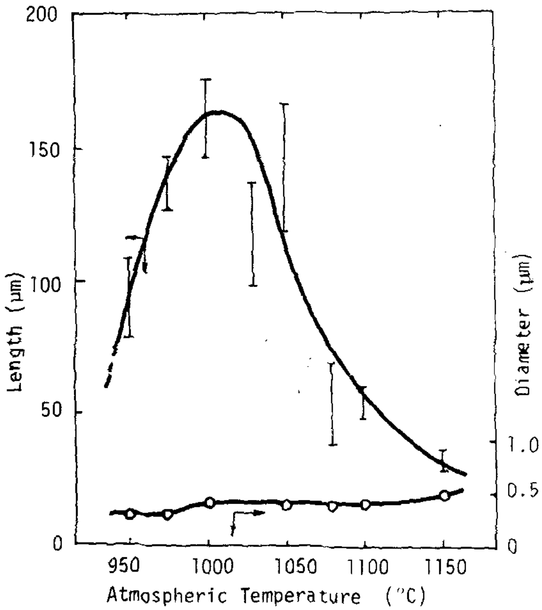

Figure 4 The effect of gas temperature on whisker growth. Growth temperature 1220° C, $ZrCl_4/N_2/H_2/Ar$ = 10/35/39/16 vol%; growth time 20 min.

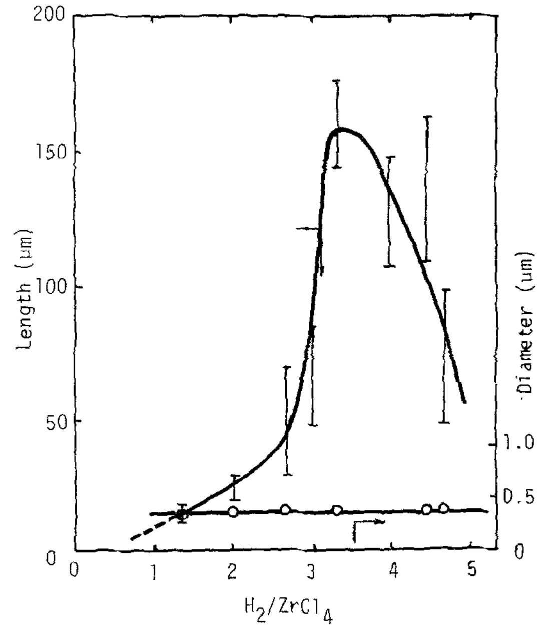

Figure 6 The effect of hydrogen flow rate on whisker growth. Growth temperature 1220° C; gas temperature 1000° C; $ZrCl_4$:0.43 ml sec^{-1}, N_2 :1.43 ml sec^{-1}, H_2 + Ar: 2.24 ml sec^{-1}.

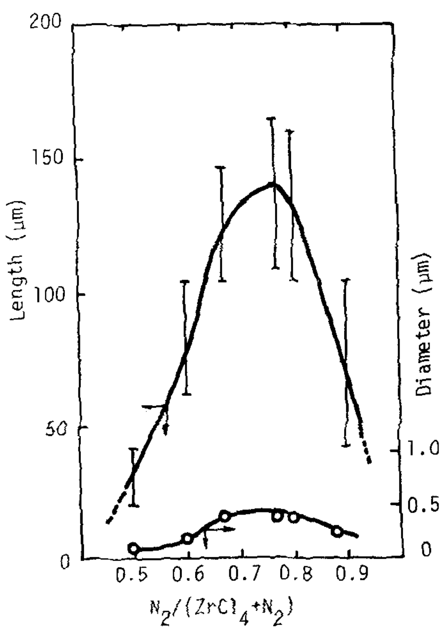

Figure 5 The effect of gas flow ratio $N_2/(ZrCl_4 + N_2)$ on whisker growth. Growth temperature 1220° C, gas temperature 1000° C, $ZrCl_4 + N_2$: 1.86 ml sec^{-1}, H_2: 1.94 ml sec^{-1}, Ar:0.3 ml sec^{-1}; growth time 20 min.

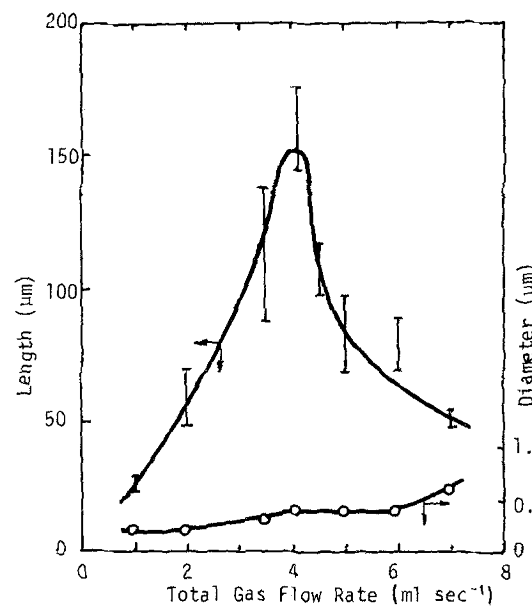

Figure 7 The effect of total gas flow rate on whisker growth. Growth temperature 1220° C; gas temperature 1000° C; $ZrCl_4/N_2/H_2/Ar$:10/35/39/16 vol%; growth time 20 min.

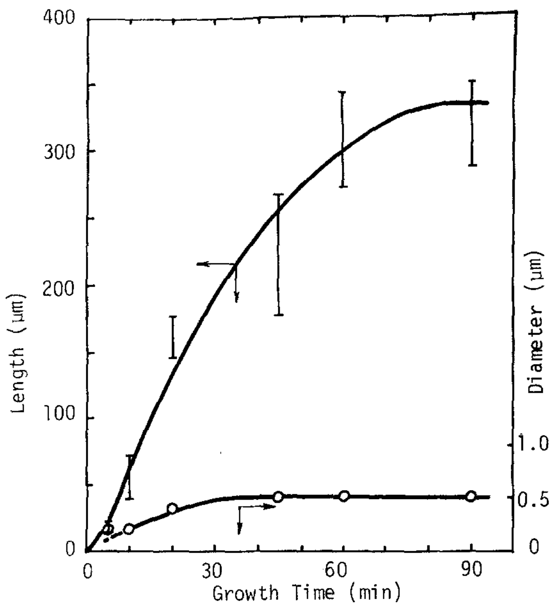

Figure 8 Time dependence of whisker growth. Growth temperature 1220° C; gas temperature 1000° C; $ZrCl_4$/N_2/H_2/Ar:10/35/39/16 vol%; total flow rate:4.1 ml sec^{-1}.

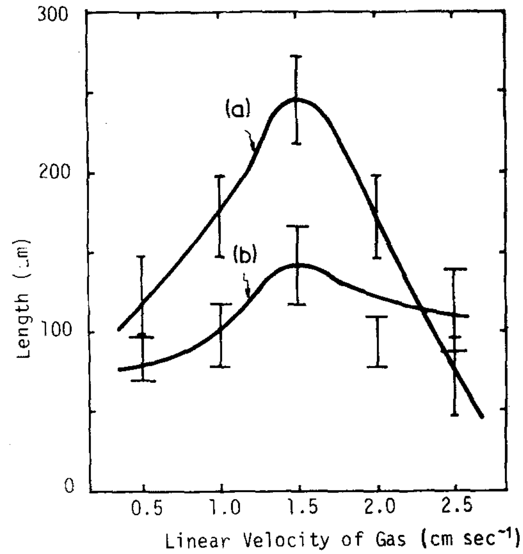

Figure 9 The effect of substrate thickness on whisker growth. Substrate thickness: (a) 10 mm o.d., (b) 7 mm o.d. Growth temperature 1220° C; gas temperature 1050° C; $ZrCl_4$/N_2/H_2/Ar:10/35/39/16 vol%; total gas flow rate: 4.1 ml sec^{-1}; growth time 20 min. Linear velocity is calculated from the feed rate at room temperature.

are so high that coatings become the main deposits. Therefore, the longest whisker is grown at a medium linear velocity.

As Fig. 8 shows, the whisker length increased monotonically with increasing time, and attained a constant value of 300 to 350 μm after 60 min, while the diameter remained at about 0.5 μm until 90 min. The growth termination may be attributed to the temperature gradient over the substrate surface.

Whisker growth on substrates of 7 and 10 mm o.d. was compared (Fig. 9). The maximum length of whiskers grown on the thicker substrate was twice that on the thinner substrate, while the maximum length was attained at a linear velocity of about 1.5 cm sec^{-1} on both substrates. The thicker the substrate, the larger the heating energy necessary. Therefore, the temperature gradient over the thicker substrate surface may be more gentle than that over the thinner substrate, and the impurity drops may remain even on the tip of the longer whisker. This result is of practical importance for obtaining longer whiskers.

An intensity distribution of the X-ray diffraction peaks of the as-grown whiskers was similar to that cited in the "powder diffraction file" (Fig. 10b).

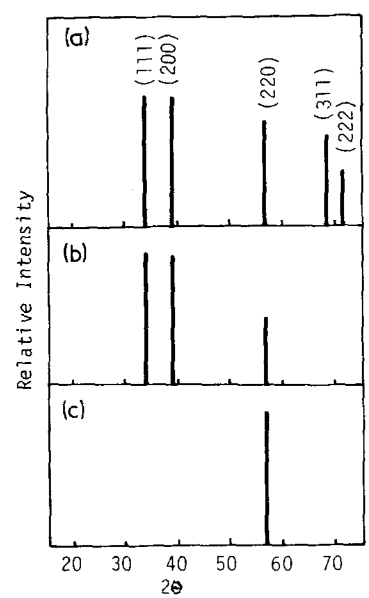

Figure 10 X-ray diffraction profiles. (a) ASTM data for ZrN; (b) as-grown whiskers; (c) whiskers dispersed on glass. Growth conditions of whiskers: growth temperature 1220° C; gas temperature 1000° C; $ZrCl_4$/N_2/H_2/Ar: 10/35/39/16 vol%; total gas flow rate:4.1 ml sec^{-1}, growth time 20 min.

When a collection of thin whiskers was thoroughly disintegrated in a few drops of water, poured onto a holder glass and dried, the X-ray diffraction diagram showed only one peak assigned to the (2 2 0) plane (Fig. 10c); therefore, the growth axis is supposed to be ⟨1 1 1⟩ or ⟨1 0 0⟩. Thick pillar-shaped crystals grown at a temperature above 1200° C showed the same diffraction profile as the thin whiskers, which had an appearance of square pillars with an average size of 0.5 μm edge length (Fig. 11). On the basis of these observations on crystal shape, the growth direction of the whiskers is considered to be ⟨1 0 0⟩, being in agreement with that reported by Miyoshi *et al.* [3].

Impurity metals such as platinum, iron and manganese form low eutectic binary alloys with zirconium or nitrogen as can be seen in Table I. Since zirconium nitride whiskers grew exclusively in the presence of impurity metals, their growth mechanism must be closely connected with the VLS mechanism. In Fig. 11, the tips of pillar-shaped crystals are shown on which a short-thin whisker with a droplet can be seen, and the growth procedure is supposed to be that of the VLS mechanism in the axial direction, followed by VS growth in the radial direction.

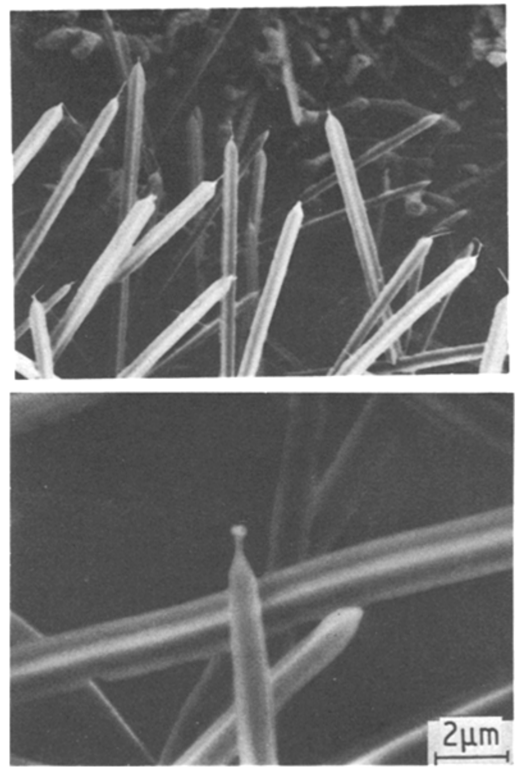

Figure 11 The tip of a whisker.

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Received 8 August
and accepted 2 November 1978

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On the thermal fracture of ice

Brittle materials are susceptible to catastrophic failure induced by thermal stresses. This is well known for ceramic materials in engineering applications which involve relatively high temperatures [1]. Thermal fracture, also occurs in ice, which can fail in a brittle manner even at temperatures close to its melting point. Thermal fracture of ice can be demonstrated experimentally by the immersion of ice-cubes in water or alcohol. The resulting thermal fracture frequently is accompanied by acoustic emission easily perceived by the human ear.

The low thermal stress resistance of ice can be demonstrated by a numerical example. Consider a piece of ice of spherical geometry initially at −20° C suddenly immersed in H_2O at a temperature of 25° C. For an estimate of the heat-transfer coefficient, it will be assumed that heat transfer to the ice occurs by laminar convection. The heat-transfer coefficient, h, can be expressed [2] as