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Growth of Al_2O_3 whiskers by vapour-phase reactions

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Needle-like or wool-like Al_2O_3 whiskers can be grown on a substrate by the hydrolysis of aluminium fluoride vapour. Effects of the growth conditions on the morphology of the crystals and growth processes of the whisker were investigated, and the optimum growth condition of whiskers was examined. Adequate vapour pressure conditions of the reactant gases for the growth of the wool-like whisker were found to be $P_{AlF_3} \times P_{H_2O}^{3/2} < 3.0 \times 10^{-3}$ (torr^2). Aluminium oxyfluoride was assumed to be the most probable intermediate species for the growth of Al_2O_3 whiskers. A variety of crystal morphologies are also shown and described with respect to the experimental conditions.

1. Introduction

The preparation of oxide whiskers has been extensively investigated over the last several decades using vapour-phase reactions. Among these, the growth of Al_2O_3 whiskers by vapour phase reaction has been reported by several investigators [1–4], using the following chemical reactions:

$$Al_2O_3 + 2H_2 = Al_2O + 2H_2O \quad (1)$$

$$2Al \text{ or } Al–Fe \text{ alloy} + 3H_2O = Al_2O_3 + 3H_2 \quad (2)$$

$$2AlCl_3 + 3CO_2 + 3H_2 = Al_2O_3 + 3CO + 6HCl \quad (3)$$

Webb and Forgang [2] obtained Al_2O_3 whiskers of 1 to 3 mm long and 3 to 50 μm diameter using Reaction 2. Wiedemann and Sturzenegger [3] synthesized Al_2O_3 whiskers, using aluminium-containing alloys in wet hydrogen to lower the partial pressure of aluminium. Campbell [4] has developed a continuous formation process for Al_2O_3 whiskers, using Reaction 3.

In the reactions described above, aluminium suboxides, especially Al_2O, have been considered to be the most probable intermediate species for the vapour-phase mass transport. Many experiments on the growth mechanism of alumina whiskers have been carried out [5–9], but the mechanism still remains to be solved. Alumina crystals have been designated as A_1, A_2, A/C and C whisker, because of their relationship to the crystal axes in the hexagonal system.

In a preceding paper [10], it was found that alumina crystals, which had various morphologies, i.e. wool-like whiskers, needle-like whiskers, jointed needle-like crystals, coagulated powder and thin films, could be prepared from the AlF_3–H_2O system, depending on growth conditions. In that paper, the fibrous crystals with diameters greater than about 5 μm were called needle-like whiskers, and those below 5 μm were called wool-like whiskers, even if both morphologies were similar. In the present work, the growth conditions and thermodynamics for growing whiskers were studied in detail by changing the vapour pressures of AlF_3 and H_2O. A variety of crystal morphologies was also examined with respect to the experimental conditions.

2. Experimental details

The apparatus has been previously described in detail [10]. The graphite tube, which was used as a reactor, consisted of a region for vaporization of AlF_3 and a region for growth of Al_2O_3. AlF_3, which was evaporated in a furnace at a given temperature ranging from 710 to 820° C, was introduced into the reactor with argon gas and reated with water vapour, introduced through another inlet with argon gas, on a polycrystalline alumina substrate. The desired vapour pressure of H_2O was prepared by bubbling argon gas through water at 0° C and diluting the moist gas by appropriate mixing with dry argon gas. All experiments were carried out at atmospheric pressure. The experimental conditions were as follows: growth temperature 1400° C, growth time 3 h, AlF_3 vapour pressure 1.0×10^{-4} to 1.0×10^{-2} torr, H_2O vapour pressure 8×10^{-3} to 5×10^{-1} torr, argon gas flow rate 150 to 400 ml min^{-1}. The morphology of the crystals was examined by optical microscopy and scanning electron microscopy. The products were identified by X-ray and electron diffraction patterns. The impurities in the whiskers were detected with an X-ray microanalyser.

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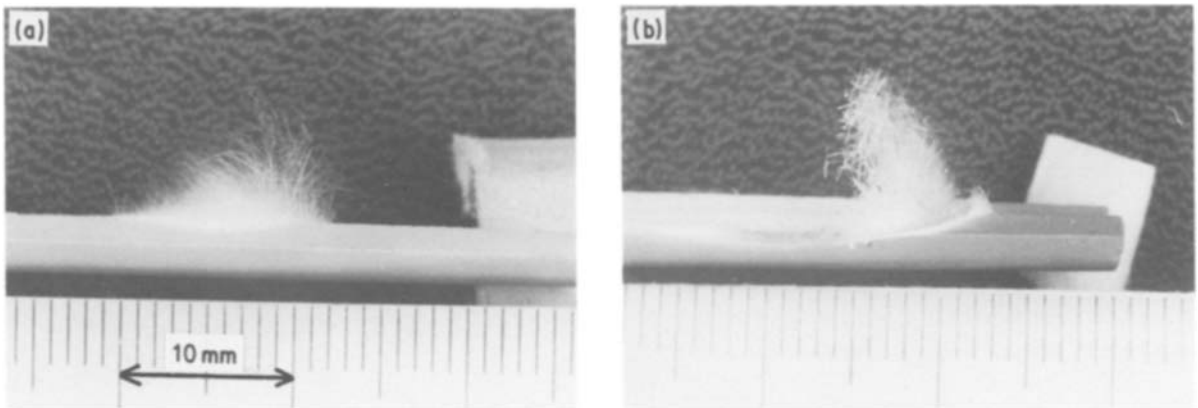

Figure 1 (a) Wool-like whiskers and (b) needle-like whiskers formed on the alumina substrate.

3. Results and discussion

3.1. Influence of growth conditions on crystal morphology

It was found that the pressure level needed to be below a critical value in order to obtain only whiskers and to eliminate the formation of platelets and dendrites. Many whiskers grew straight from suitable sites on the surface of the substrate, as shown in Fig. 1. Wool-like whiskers were usually 1 to 4 μm diameter and several millimetres long, whereas needle-like whiskers were 10 to 30 μm diameter and 5 to 12 mm long. This length is approximately equal to the diameter of the reactor. The morphology of the grown crystals depended strongly on the growth conditions. At first, the influences of vapour pressure of H_2O (expressed as P_{H_2O}) and the flow rate of argon gas containing AlF_3 (expressed as $Ar(AlF_3)$) on the morphology were investi gated. The flow rate of the moist argon gas ($Ar(H_2O)$) and P_{AlF_3} were kept constant at 150 ml min^{-1} and 7.6×10^{-2} torr, respectively. It was found that P_{H_2O} for the growth of wool-like whiskers needed to be below about 5×10^{-2} torr. At vapour pressures above this value, the number of wool-like whiskers tended to decrease with increase in P_{H_2O}, in comparison to the number of needle-like whiskers which tended to increase remarkably. Fig. 2 shows the relation between P_{AlF_3} and P_{H_2O} for whisker growth at constant $Ar(AlF_3)$ and $Ar(H_2O)$ flow rates of 250 and 150 ml min^{-1}, respectively. The correlation between vapour pressures of AlF_3 and H_2O was deduced, as mentioned below, from the experimental data. Suitable vapour pressures of AlF_3 and H_2O for the growth of wool-like whiskers were below about 8×10^{-2} and about 10^{-1} torr, respectively. At a constant P_{AlF_3}, the relative number of wool-like whiskers formed tended to decrease with increase in P_{H_2O}. It was found that a higher P_{AlF_3} required a lower P_{H_2O} to form mainly wool-like whiskers. Increasing both P_{AlF_3} and P_{H_2O} simultaneously caused morphological change of the grown crystals from wool-like to needle-like whiskers.

3.2. Growth process

The formation of alumina by the reaction of AlF_3 with H_2O may be represented by the following overall reaction:

$$2AlF_3 + 3H_2O = Al_2O_3 + 6HF \quad (4)$$

Where $\Delta G^\circ = -39.5$ kcal mol^{-1} at 1700 K. As previously discussed, AlOF was considered to be the most probable intermediate species in the reaction from

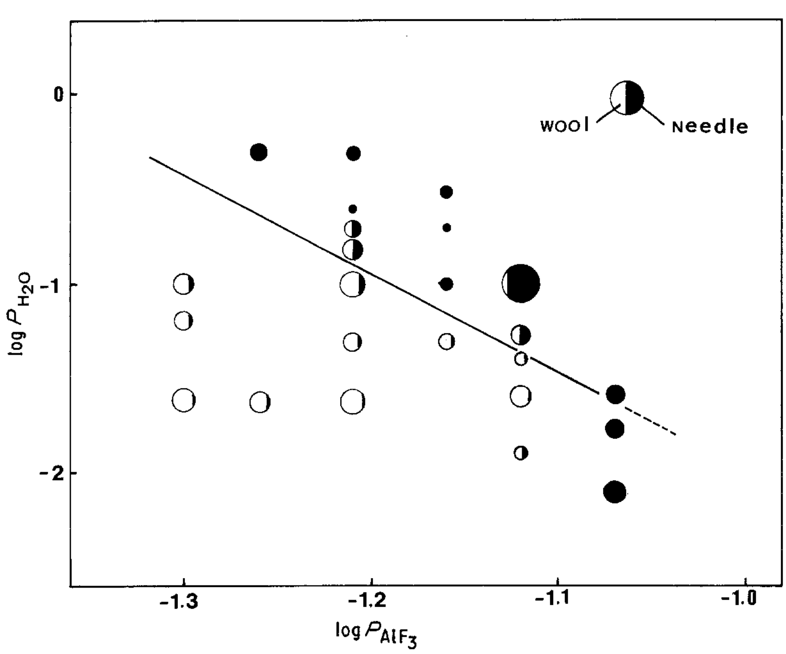

Figure 2 Relation between P_{AlF} and P_{H_2O} for whisker growth; $Ar(AlF_3) = 250$ ml min^{-1}, $Ar(H_2O) = 150$ ml min^{-1}. The size of the circles represents the relative yield of whiskers obtained, and the black and white areas represent the relative ratios of needle-like whiskers and wool-like whiskers, respectively.

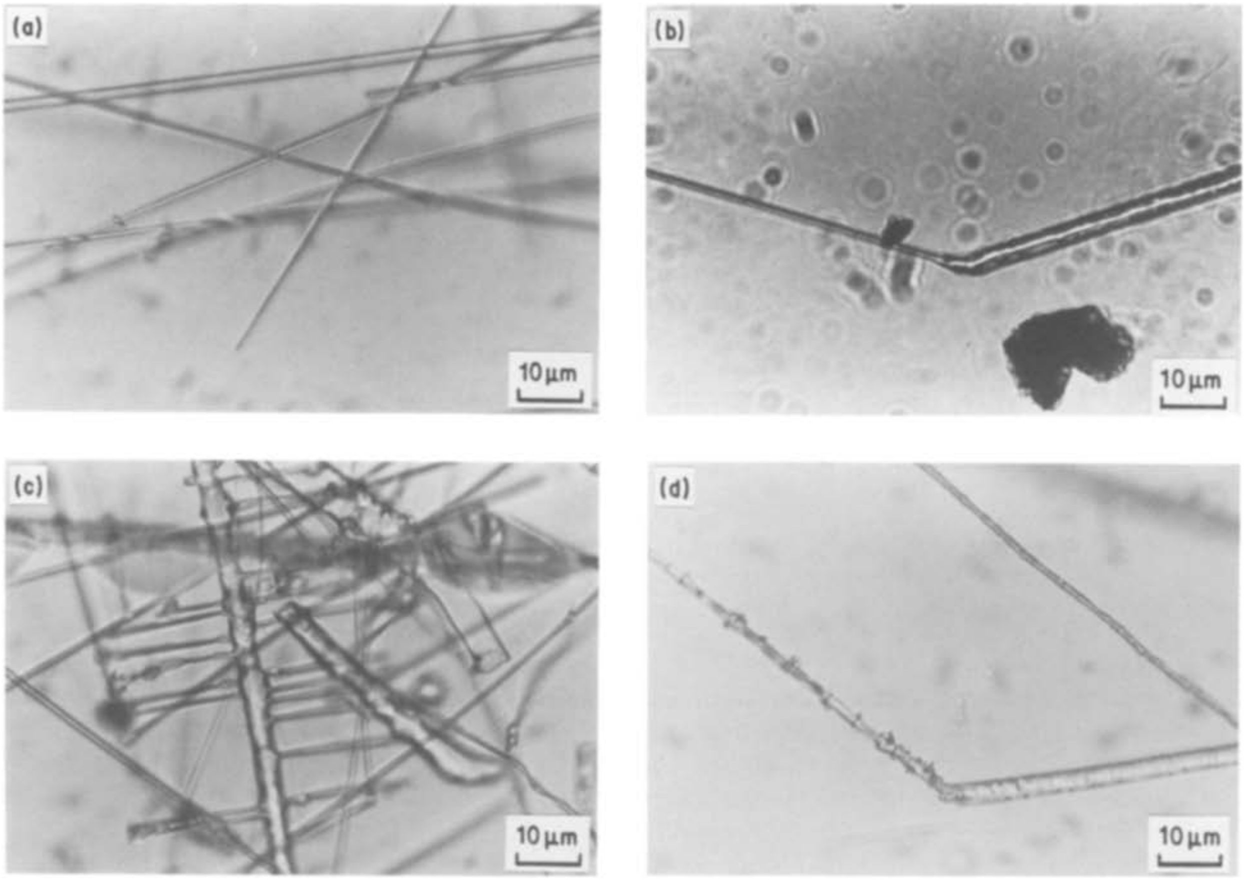

Figure 3 Optical micrographs of wool-like whiskers: (a) straight whiskers; (b, c) kinked whiskers; (d) branched whiskers.

thermodynamical calculations. The vapour pressure of Al_2O, which is usually considered to be the predominant intermediate species, is about one-twentieth that of AlOF in the conditions of this work. Hence, the following reactions have to be considered:

$$AlF_3 + H_2O = AlOF + 2HF \quad (5)$$

where $\Delta G^\circ = 30.4\,\text{kcal}\,\text{mol}^{-1}$ at 1700 K. Since the free energy change in Reaction 5 is positive, the products will be unstable. If we considered the possible deposition reactions and their free energies, the following reactions may occur:

$$2AlOF + H_2O = Al_2O_3 + 2HF \qquad \Delta G^\circ = -95.3\,\text{kcal}\,\text{mol}^{-1} \quad (6)$$

$$3AlOF = Al_2O_3 + AlF_3 \qquad \Delta G^\circ = -123.2\,\text{kcal}\,\text{mol}^{-1} \quad (7)$$

It was deduced that the disproportionation reaction of AlOF, such as Reaction 7, might occur preferentially under the conditions where the ratio of AlF_3 to H_2O was larger than that of Al/O in Al_2O_3, i.e. 2/3.

For whisker growth, the control of supersaturation is a prime consideration, because the degree of supersaturation, Σ_T, is expressed by the partial pressure, P_a, of the growth species (AlOF) produced by the reaction, and the equilibrium partial pressure, P_e, of the growth species at a given temperature:

$$\Sigma_T = P_a/P_e \quad (8)$$

Here, the growth of alumina whiskers is implicitly assumed to proceed via Reactions 5 and 6. From Reaction 5,

$$P_a(\text{AlOF}) = \frac{K_2 P_{AlF_3} P_{H_2O}}{P_{HF}^2} \quad (K_2 = \text{equilibrium const.}) \quad (9)$$

From Reaction 6,

$$P_e(\text{AlOF}) = \frac{P_{HF}}{K_3^{1/2} P_{H_2O}^{1/2}} \quad (K = \text{equilibrium const.}) \quad (10)$$

Hence,

$$\Sigma_T = \frac{K_2 P_{AlF_3} P_{H_2O}^{3/2} K_3^{1/2}}{P_{HF}^3} \quad (11)$$

Since $K_1 = K^2 K_3$ (K_1 is the equilibrium constant of Reaction 4), Reaction 11 can be expressed as

$$\Sigma_T = \frac{K_2 P_{AlF_3} P_{H_2O}^{3/2}}{P_{HF}^3} \quad (12)$$

This derivation suggests that the supersaturation ratio, Σ_T, can be controlled by adjusting the partial pressures of the input gases. As estimated graphically from the vapour pressure for growth (Fig. 2), adequate vapour pressure conditions of the reactant gases for the formation of wool-like whiskers were found to be:

$$P_{AlF_3} P_{H_2O}^{3/2} < 3.0 \times 10^{-3}\,\text{torr}^2$$

Also, since the reaction was made of graphite, it is considered that the reaction $H_2O + C = CO + H_2$, $\Delta G^\circ = 26\,\text{kcal}\,\text{mol}^{-1}$ at 1700 K, takes place on the surface of graphite which leads to a decrease in the

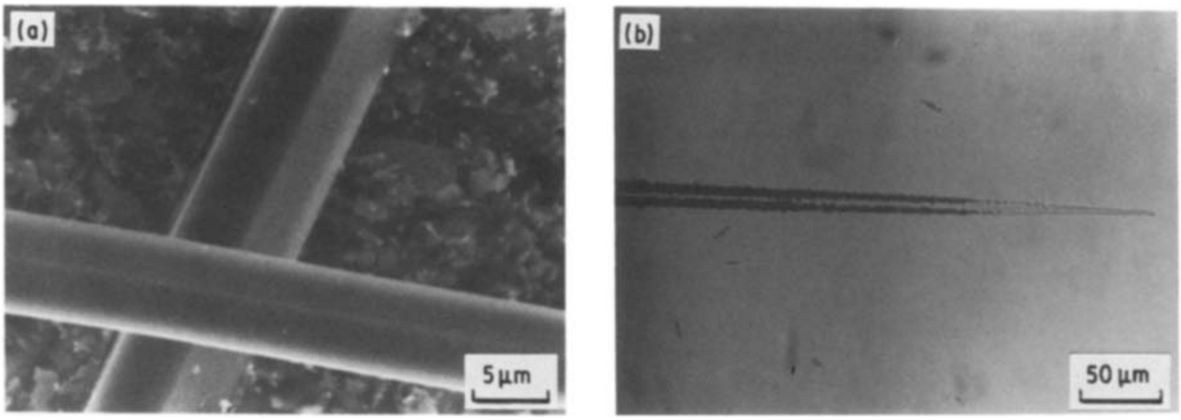

Figure 4 Optical micrographs of needle-like whiskers: (a) whiskers with hexagonal forms; (b) tapered whiskers.

vapour pressure of H_2O. Therefore, the actual vapour pressure of H_2O was considered to be lower than its calculated vapour pressure.

3.3. Morphology of products

The crystals formed were identified as Al_2O_3 by X-ray diffraction and electron diffraction. Typical photographs and scanning electron micrographs of Al_2O_3 whiskers are shown in Figs 3 and 4. Most whiskers grew straight and their side surfaces were generally smooth, but whiskers having kinks, branches or knots perpendicular to the growth direction were frequently observed (Figs 3b, c, and d). Furthermore, curved and bent filament-like whiskers tended to form easily under conditions of high carrier gas flow rate, due to the turbulence of gas flow around the substrate. Needle-like whiskers, which seem to be C-whiskers from observation of the well-developed side faces with hexagonal forms, were frequently observed under relatively high vapour pressures of AlF_3 and H_2O (Fig. 4a). Two types of whisker could be formed: one type is that which had a uniform cross-section over its length, and the other is that which is tapered. The tapered whiskers shown in Fig. 4b seem to be A_2-whiskers in the $[1 1 \bar{2} 0]$ direction as reported by Sears and DeVries [11]. No impurities were detected by EPMA of whiskers formed under the usual conditions. Some whiskers formed under a high water vapour pressure, however, had glassy beads which were composed of silicon and aluminium as a contaminant from the mullite tube, as shown in Fig. 5.

4. Conclusions

The vapour-phase growth of Al_2O_3 whiskers by hydrolysis of aluminium fluoride vapour has been studied at 1400° C. Wool-like and needle-like whiskers, without accompanying platelet and dendrites, were grown on a polycrystalline alumina substrate. The wool-like whiskers grew to lengths of several millimetres with diameters of 1 to 4 μm, while the needle-like whiskers grew to lengths up to 12 mm with diameters of 10 to 30 μm. Wool-like whiskers were formed preferentially under conditions of low vapour pressures of the reactant gas, i.e. $P_{AlF_3} \times P_{H_2O}^{3/2} < 3.0 \times 10^{-3}$ torr^2.

Most whiskers grew straight on the substrate under the usual conditions, but under conditions of the high carrier gas flow rate, curved and bent whiskers tended to grow more easily due to the nonuniform gas flow around the substrate. Furthermore, whiskers with kinks, branches or knots were also formed. The most frequently observed types were A_2-whiskers and C-whiskers.

References

1. R. C. DeVRIES and G. W. SEARS, *J. Chem. Phys.* **31** (1959) 1256.
2. W. W. WEBB and W. D. FORGANG, *J. Appl. Phys.* **28** (1957) 1449.

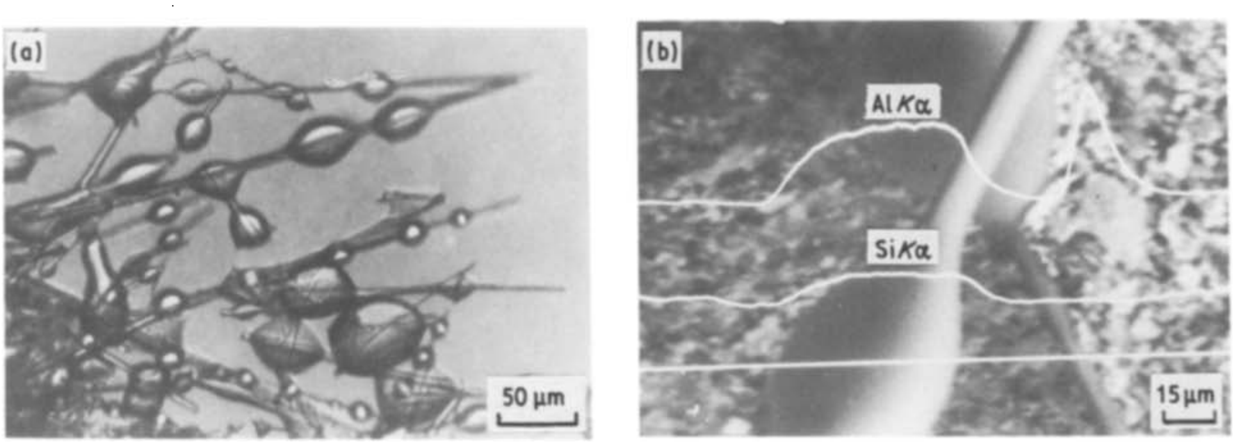

Figure 5 (a) Optical micrograph and (b) EPMA analysis of whiskers with glassy beads.

3. H. G. WIEDMANN and E. STURZENEGGER, *Naturwissenschaften* **61** (1974) 65.
4. W. B. CAMPBELL, *Chem. Eng. Prog.* **62** (1966) 68.
5. R. D. DRAGSDORF and W. W. WEBB, *J. Appl. Phys.* **29** (1958) 817.
6. P. L. EDWARDS and R. J. HAPPEL, *ibid.* **32** (1962) 826.
7. D. J. BARBER, *Phil. Mag.* **10** (1964) 75.
8. S. MINAGAWA and T. GEJYO, *J. Amer. Ceram. Soc.* **52** (1969) 282.
9. S. MINAGAWA, *ibid.* **55** (1972) 77.
10. I. YAMAI and H. SAITO, *J. Crystal Growth* **45** (1978) 511.
11. G. W. SEARS and R. C. DeVRIES, *J. Chem. Phys.* **39** (1963) 2837.

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