Growth Morphology of Alumina Whiskers

Takashi HAYASHI,* Masatoshi IWATA, and Hajime SAITO
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464
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Synopsis. Alumina whiskers were grown on a substrate by hydrolysis of aluminium fluoride vapor. The present paper describes some observations concerning the growth and morphology of alumina whiskers. The most frequently observed types in this work were A_2-whiskers and C-whiskers.

The growth of alumina whiskers by vapor phase reaction has been accomplished by several investigators.[1-4] The growth of alumina whiskers occurs with the main crystallographic direction, and the corresponding crystals are sometimes referred to as A_1, A_2, A/C and C-type whiskers. C-whiskers grow in the c direction, [0001], of the hexagonal system, and A_1- and A_2-whiskers grow in the c plane in a $[10\bar{1}0]$ direction and in a $[11\bar{2}0]$ direction, respectively, and A/C-whiskers grow by approximately equal alteration of the growth direction in the A and C direction.

The size, morphology and crystallographic orientation of whiskers depend strongly on the experimental growth conditions. In the preceding paper,[5] we reported the growth of alumina whiskers by the hydrolysis of aluminium fluoride vapor. The present paper describes some observations concerning the growth and morphology of alumina whiskers.

The apparatus has been previously described in detail.[5] 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 1070 °C, was introduced into the reaction chamber with a carrier gas (Ar gas) and reacted with H_2O vapor, introduced through another inlet with a carrier gas, on a polycrystalline Al_2O_3 substrate. The desired vapor pressure of H_2O was obtained by bubbling the carrier gas through water at 0 °C and diluting the moist carrier gas with the appropriate flow of dry carrier gas. The experimental conditions were as follows: Growth temp: 1400 °C, Growth time: 3 h, AlF_3 vapor pressure: 10^{-4}—10 Torr,† H_2O vapor pressure: 10^{-3}—20 Torr, Ar gas flow rate: 100—200 ml/min. The morphology of the crystals formed was examined by optical microscopy.

Influence of AlF_3 vapor pressure, P_{AlF_3}, and H_2O vapor pressure, P_{H_2O}, on the morphology of the crystals was investigated and the relation between P_{AlF_3} and P_{H_2O} is shown in Fig. 1. Alumina crystals which had various morphology, *viz.* fine powder, bulk crystals, platelet crystals and whiskers, were formed on the substrate, depending on the growth conditions. With the simultaneous decrease of AlF_3 and H_2O vapor pressure, the crystals changed their forms from powder to bulky or platelet crystals and finally to whiskers. Adequate vapor pressures of AlF_3 and H_2O for both needle crystal and whisker growths were found to be below about 5 Torr. Whiskers only were formed under the lower vapor pressures, *i.e.* $P_{AlF_3}<1$ Torr, $P_{H_2O}<1$ Torr. The morphology of the crystals formed depended also on the growth region on the substrate. In the narrow region at which direct impingement of reactant gases occurred, the formation of fine powder or coarse polycrystalline deposits tended to occur, while whiskers tended to grow in the regions which ran along the flow of mixture gases towards the outlet.

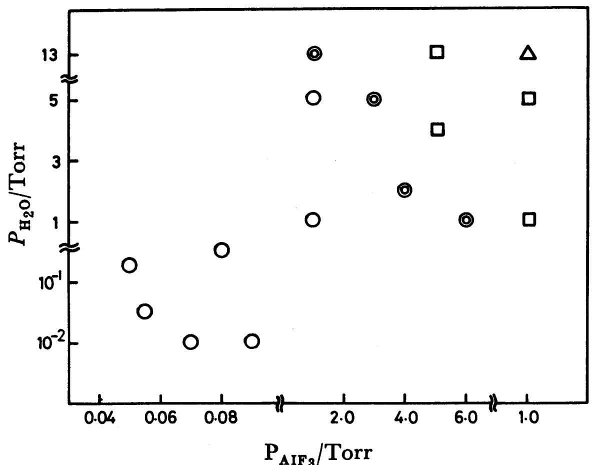

Fig. 1. Influence of P_{AlF_3} and P_{H_2O} on the morphology of grown crystals. Ar(AlF_3): 150 ml/min, Ar(H_2O): 200 ml/min. △: Powdery polycrystal, □: bulk crystal, ◎: needle crystal, ○: whisker.

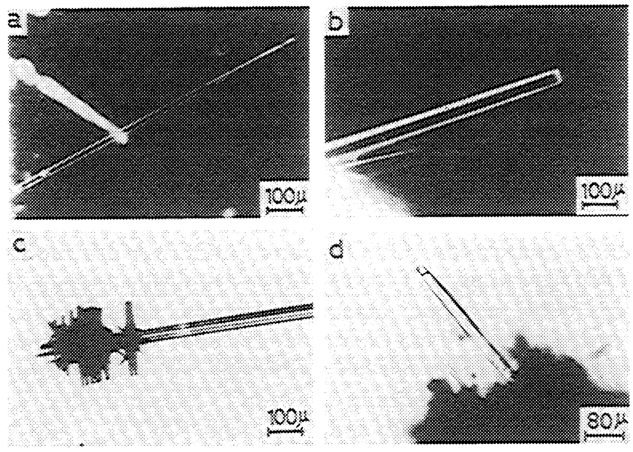

Fig. 2. Optical micrographs of whiskers. (a): Tapered whisker, (b): thin ribbon-like whisker, (c): branched whisker, (d): whisker having a droplet at its tips.

Many whiskers grew straight and grew up to the length of several mm (maximum 7—8 mm) with diameters up to 50 μm. Typical optical micrographs of alumina whiskers are shown in Fig. 2. The most frequently observed types were A_2- and C-whiskers. As expected from its morphology their cross sections showed rectangular and hexagonal shapes, respectively. In the whiskers formed in the present work, both platelet

† 1 Torr = 133.322 Pa.

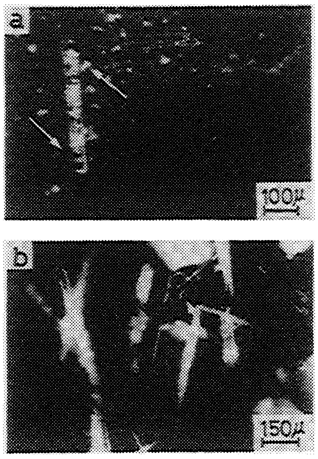

Fig. 3. Optical micrographs of kinked whisker. (a): 90° growth kinks, (b): 60° growth kinks.

and hexagonal forms were observed. Two types exist in the former: pillar and needle-like whiskers. On the other hand, the C-whiskers having many branches on the lateral surfaces near the whisker tip were occasionally observed in the latter. These branched whiskers, inclined at right angles and at about 45° to the crystal axes, were considered to be A-whisker and A/C-whiskers,[6] respectively. These branching tended to occur easily near the whisker tip when the C-whisker reached a certain length. Such secondary whisker growth is similar to the results reported by Sears[6] in which A-type whiskers grow predominantly at the thickened tip of C-whiskers. In some cases, although very rare, a whisker which had a small globule at its tip was observed. It is thought that they grew according to the VLS mechanism in the presence of impurities.

Besides the straight whiskers, kinked whiskers having 60°, 90°, and 120° angles were sometimes observed, as shown in Fig. 3. The possible angle between A_1 growth direction and A_2 growth direction are 30°, 90°, and 150°. It was considered by optical technique that 90° growth kink (Fig. 3,a) occurred by changing the growth direction such as A_1-A_2-A_1 direction or A_2-A_1-A_2 direction, but not such as A-C-A direction. That is, in the case of an A_1 or A_2-whisker which is bounded by both {0001} and {1120} or {1010} types of columnar surfaces two-dimensional nucleation should occur on the {1120} or {1010} surfaces at a lower supersaturation than on the {0001} surfaces, because the surface energy is least for the most closely packed surface {0001}.[6] Also, A-type whiskers would change growth direction by 60°,[6] as shown in Fig. 3,b, because the possible angles between one A growth direction and another A growth direction are 60° and 120°.

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