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Ruby Whisker Growth and Characteristics*

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Chromium-doped α-Al_2O_3 (ruby) whiskers have been grown by a vapor phase reaction. The ruby whisker growth morphologies were studied by means of optical and x-ray microscopy. Neutron activation analysis was employed to determine the chromium concentrations. Several unusual whisker shapes and surface configurations were observed and are discussed.

CHROMIUM–DOPED α-Al_2O_3 (ruby) whiskers were grown by codeposition from the vapor phase in the presence of hydrogen. The experimental growth conditions were similar to those used to grow sapphire whiskers by Webb and Forgeng.[1] Aluminum (99.993%) and chromium (99.95%) metal chips were placed at either end of an alumina combustion boat, contact between the two metals taking place only at the center of the boat. A purified hydrogen flow rate of 140 cc/min was maintained while the temperature was gradually raised over a 24-h period to 1450°C. Whisker growth commenced at about 1200°C. The oxygen required for the reaction comes either through or from decomposition of the mullite furnace tube.[2] The ratio of the partial pressure of water vapor to hydrogen, P_{H_2O}/P_{H_2}, was determined at the exhaust end of the furnace to be 1.5×10^{-3}.

Red and pink ruby whiskers were found to grow only above the interface region between the two metals. No red or pink ruby whiskers were observed to grow when the chromium and aluminum chips were randomly mixed in the combustion boat or when various alloys of these metals were used. Similarly, α-Al_2O_3 whiskers observed to grow from ruby rods by DeVries and Haskell[3] showed no coloring due to Cr^{3+}. Calculations of the free energies for the various oxides of chromium under the reaction conditions present in our experiment ($P_{H_2O}/P_{H_2}=1.5\times10^{-3}$) show that oxidation of chromium to Cr_2O_3 is just possible, and may take part in the ruby whisker growth process.

The ruby whiskers reached lengths of 0.5 cm, and were observed to grow from the oxidized metal surface in the combustion boat. The wool-like overgrowth generally found in pure sapphire whisker growth was absent from the regions where ruby whiskers grew. X-ray analysis (Laue back-reflection and rotating-crystal), neutron-activation analysis, and the color of the whiskers[4] (reflecting the Cr^{3+} doping density) affirm that the whiskers are ruby. Figure 1 shows some typical pink and red whisker morphologies. In Fig. 1(a), a tapered hexagonal c-axis whisker (top) of uniform Cr^{3+} concentration, is compared with the central section of a pure sapphire whisker (bottom). The ruby whisker of Fig. 1(a) is quite similar to pure sapphire in its morphology, i.e., the hexagonal cross section tapers to a fine end while maintaining its hexagonality. At higher Cr^{3+} concentrations, however, this regular geometrical shape is altered; this is discussed later.

A slight difference in surface texture may be seen between the sapphire and the ruby whisker in Fig. 1(a). The surface configuration of the ruby may be more clearly seen in Fig. 1(b) which shows a ruby blade which has grown perpendicular to the c axis. In many cases, the ruby whiskers showed a textured surface. Although this is not common in the growth of sapphire whiskers, Barns and Ellis[5] observed a similar roughness on gallium phosphide whiskers which they termed an "overgrown surface." An even more striking example of this surface configuration is shown in Fig. 3(a). The average chromium concentration in whiskers of the type shown in Fig. 1(a) and (b) was 2.5±0.5% by weight, as determined by neutron-activation analysis on a sample of 10 ruby whiskers weighing 850 μg. Fine ruby whiskers have also been observed, as shown in Fig. 1(c), and have diameters of the order of 10 μ. For one particular growth run, the chromium concentration in this form was about 4%.

A variety of growth characteristics of the ruby whiskers are illustrated in Figs. 2 and 3. Figure 2(a) shows a c-axis whisker with a marked Cr^{3+} concentration gradient along its length. The light pink base of the whisker is of hexagonal cross section, and is typical of sapphire whisker growth. Toward the top of the whisker, where the chromium concentration increases (the chromium concentration is higher in darker regions), the whisker tends to lose its regular hexagonal cross section and becomes more cylindrical. This is in contrast to the ruby whisker of Fig. 1(a) which has a uniform Cr^{3+} concentration of 2.5% along its length. From the whisker of Fig. 2(a), it would appear that the transition from hexagonal to round cross section takes place in ruby at a chromium concentration between 3% and

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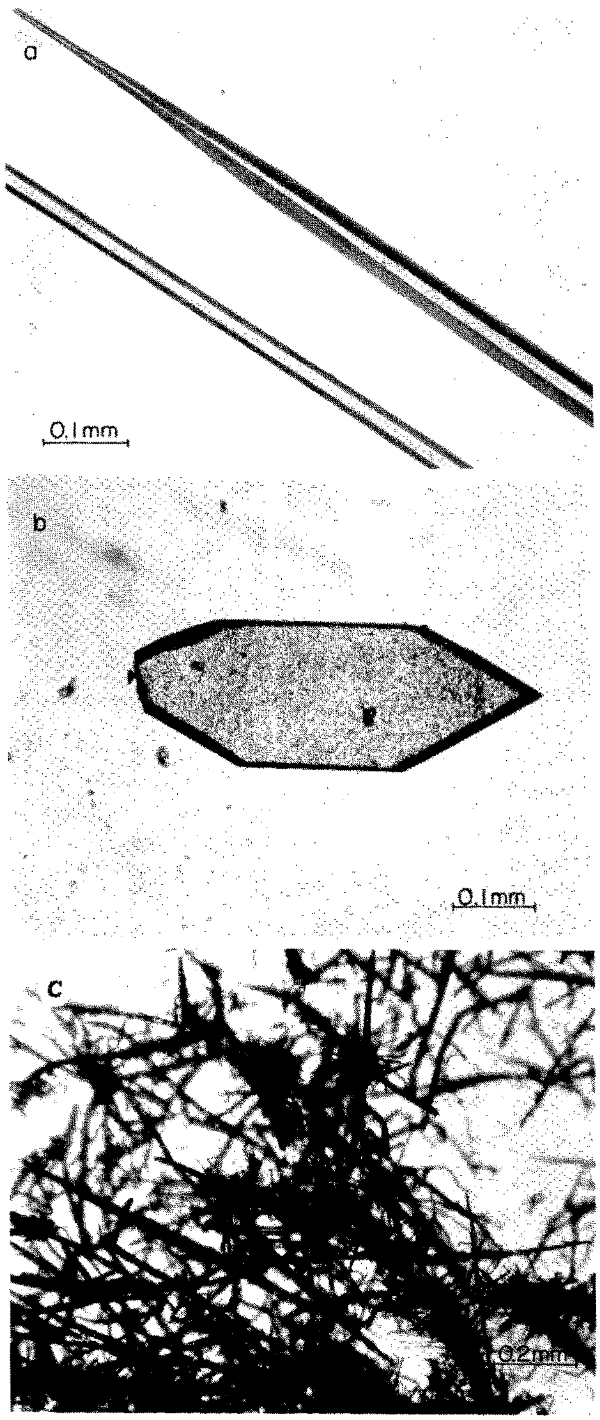

FIG. 1. Typical ruby whisker morphologies. (a) Tapered hexagonal ruby whisker (top) compared with section of pure sapphire whisker. (b) Hexagonal red ruby blade, growth perpendicular to c axis. (c) Fine pink ruby whiskers.

4%. This may not be true in general, however, since the transition probably depends on the whisker diameter and the rate of growth. A similar impurity-dependent effect has also been observed by Brenner in copper whiskers containing silver.[6]

A periodic concentration gradient is evident in the photograph of Fig. 2(b) where the bulging parts of the bamboolike structure are richer in chromium. We believe that this results from fluctuations in local growth conditions while codeposition is taking place. A ruby whisker exhibiting a 60° change in growth direction is seen in Fig. 2(c). This effect is frequently observed in pure sapphire whiskers.[7] Finally, the ruby blade of Fig. 2(d) bears hexagonal surface markings, but in contrast to sapphire, the markings in the ruby blade are distorted due to the presence of chromium. This is analogous to the transition in whisker shape observed in Fig. 2(a).

Several other surface configurations were frequently observed. Figure 3(a) shows two faces of a 0.5-cm-long deep red ruby whisker which was determined to be a single-crystal whisker growing in a stable[8] $(1\bar{1}01)$ orientation. In spite of its surface roughness, the sharp Laue spots indicated a high degree of crystalline perfection. Figure 3(b) shows a hexagonal clear whisker with pinkish-brown spots which appear to be surface markings. Symmetry in the spots leads us to believe that many of the rows appearing in the photograph are reflections. The average chromium concentration in these whiskers is about 0.1%. The rotating-crystal x-ray pattern obtained from these spotted whiskers was identical to that obtained from pure α-Al_2O_3 whiskers, thus shedding no light on the nature of this configuration. Tensile tests have shown that the spotted whiskers have an average tensile strength of about 300 000 psi (for 10 μ diam), as compared to 600 000 psi for pure sapphire whiskers of the same diameter.[9] No measurements were made on the tensile strengths of the red ruby whiskers (2.5% chromium). From handling, however, the latter appear to be weaker than the spotted whiskers. This observed effect of grown-in impurities on mechanical properties is in qualitative agreement with that observed by Brenner in copper whiskers.[6]

In conclusion, it has been shown that ruby whiskers of various morphologies, containing a range of chromium concentrations up to 4%, may be grown by a vapor-phase reaction. The study of such highly doped whiskers may shed further light on crystal growth and properties.

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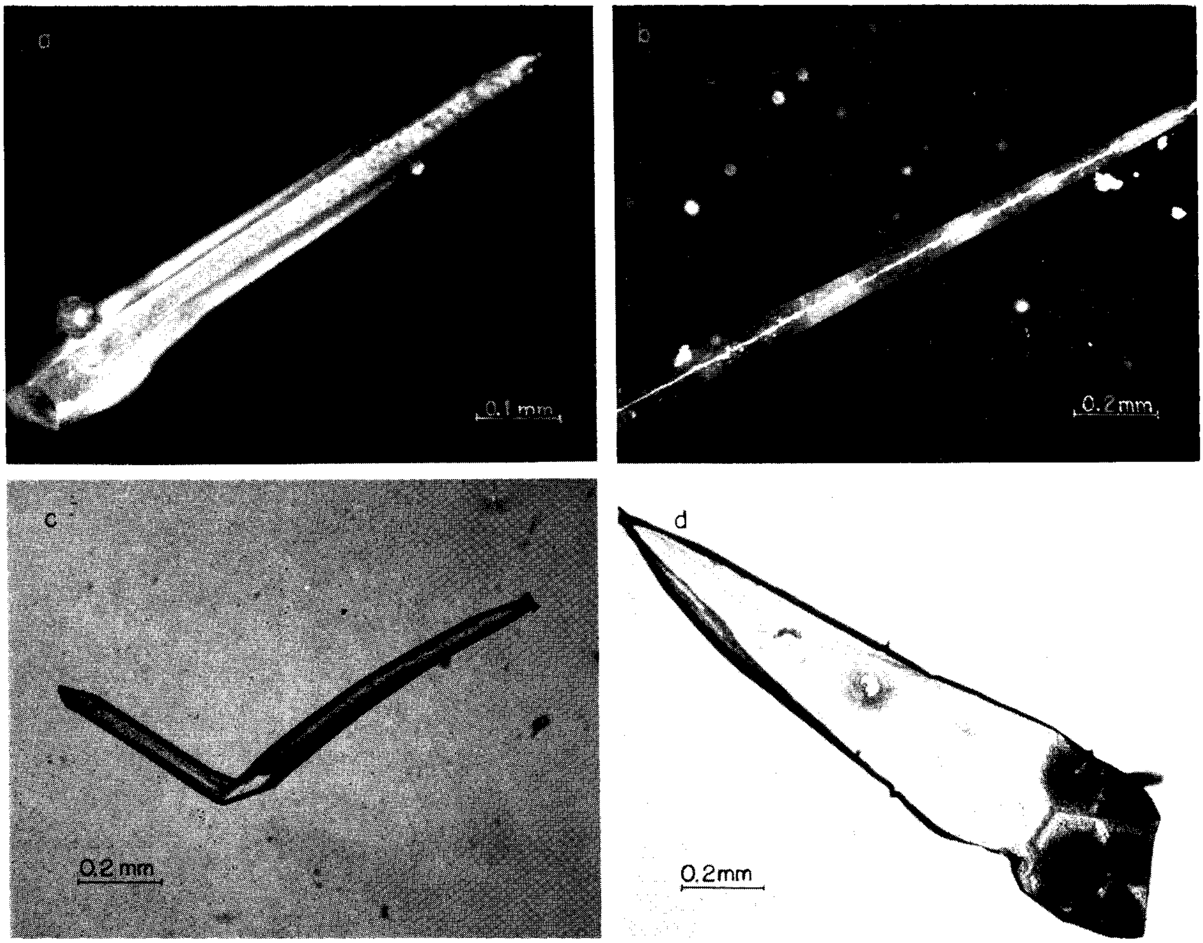

FIG. 2. Ruby whiskers displaying significant characteristics. (a) Hexagonal ruby whisker approaching round shape with increasing chromium concentration. (b) Bamboo-like structure with alternating pink and red areas corresponding to varying chromium concentrations. (c) Ruby whisker with 60° change of growth direction. (d) Bladed ruby whisker showing distorted hexagonal markings.

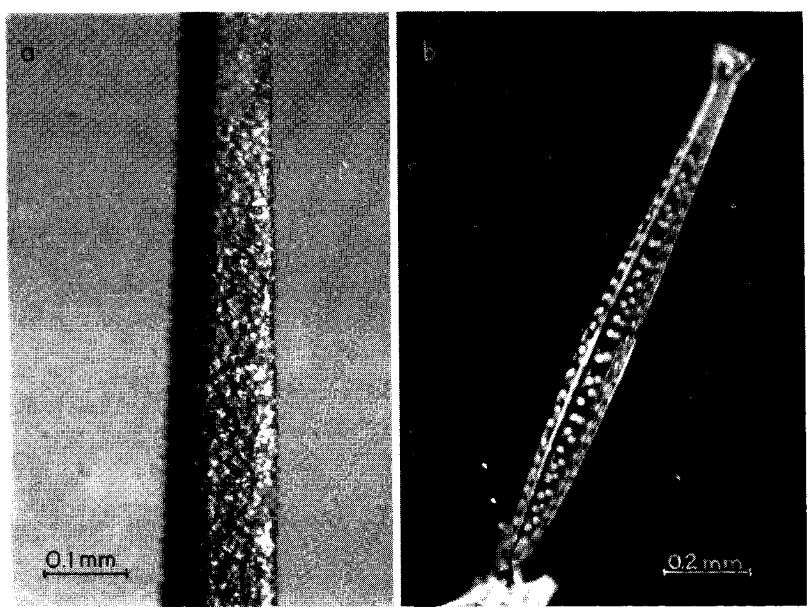

FIG. 3. (a) Section of 0.5-cm-long red ruby whisker growing in a $(1\bar{1}01)$ orientation. (b) Clear hexagonal whisker with pinkish-brown spots which appear to be surface markings.