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Abstract

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INVESTIGATION OF FILAMENTOUS SINGLE CRYSTALS OF BERYLLIUM OXIDE BY MEANS OF AN ULTRA-HIGH-VOLTAGE ELECTRON MICROSCOPE

In recent years a number of works have appeared devoted to the preparation and investigation of filamentous crystals of beryllium oxide. P. P. Budnikov and I. V. Shishkov ([1]) obtained filamentous crystals in the form of plates, needles, and rods by depositing BeO from the gas phase in an argon atmosphere at temperatures of 1600–1900°. Ryshkevich ([2]) and Austerman ([3]) obtained thin crystals of beryllium oxide in the form of plates, needles, and hexagonal prisms by passing water vapor over a block of polycrystalline BeO, which was heated to 1600°. The crystals grew in a furnace zone at a temperature of 1400°. Edwards and Happel ([4]) observed the growth of beryllium oxide when heating a silica boat with scaly metallic beryllium in a hydrogen atmosphere at 1500°. The crystals they obtained had the form of thin filaments or ribbons. Some crystals were hollow inside and had a metallic sphere at the tip. The diameter of the crystals ranged from fractions of a micron to 20 μ, with lengths up to 1 mm. Some crystals of branched or zigzag form reached lengths of 10 mm with diameters from 1 to 10 μ.

We obtained filamentous single crystals of beryllium oxide by high-temperature oxidation of metallic beryllium in an argon atmosphere containing 0.01% N and 0.003% O_2. The moisture content in the argon was 0.03 g/m^3 at 760 mm Hg. The metallic beryllium contained: Fe $2.6 \cdot 10^{-2}$, Mg $3.0 \cdot 10^{-2}$, Ca $3.0 \cdot 10^{-2}$, Cr $2.8 \cdot 10^{-3}$, Si $3.4 \cdot 10^{-2}$, Al $2.5 \cdot 10^{-1}$, Na $5.0 \cdot 10^{-2}$.

The oxidation was carried out in a quartz-glass vessel at a temperature of 1450–1500° for 24 hours. To prevent interaction of the metallic beryllium with the material of the vessel, the beryllium was placed on a support made of polycrystalline beryllium oxide, which at the same time served as the substrate for crystal growth. The rate of argon flow over the metallic beryllium was 10–15 l/hour. As a result of oxidation, a grayish-white cotton-like mass formed on the substrate in the immediate vicinity of the metallic beryllium.

Microscopic investigations of the material obtained showed that the cotton-like

Fig. 4

Figure 1: Fig. 4

mass consists of individual interwoven BeO crystals with lengths from a millimeter to 10–15 mm, and that the grayish tint is due to the presence of metallic spheres at the ends of the filaments. In a number of cases several filaments radiated from a single sphere, forming a spider-like structure.

Figure 1 presents a microphotograph of a filamentous crystal with a metallic sphere at the end (see insert, p. 307).

Identification of the crystals, determination of the growth direction and diameter, and transmission investigation were carried out on an ultra-high-voltage electron microscope ([5]) with an accelerating voltage of 400 kV (electron energy 557 keV).

The unit-cell dimensions, calculated from spot electron-diffraction patterns, coincided with the unit-cell dimensions for beryllium oxide: $a = 2.69$ Å and $c = 4.38$ Å. The diameter of the filamentous BeO crystals varies from hundredths of a micron to 4–5 μ,

and the diameter of the spheres at the crystal tips—from one micron to several tens of microns. The principal growth direction of the crystals, determined from spot electron-diffraction patterns taken from arbitrarily oriented crystals, coincides with the directions [0001] and $[10\bar{1}0]$.

Fig. 2 shows a spot electron-diffraction pattern from a plate-like crystal; the ring electron-diffraction pattern from the deposit was used to determine the interplanar spacings.

In dark-field indexing of spot electron-diffraction patterns from crystals with offshoots, no twinning was found, since it turned out that all reflections belong both to the main crystal and to the offshoot.

Owing to a certain bending of the crystals caused by the method of preparing the microobject, bend extinction contours appeared in the image, corresponding to portions of the crystal with equal inclination to the electron beam. The extinction contours occurred in pairs. Each contour is the projection of a certain inclined section of the crystal and can be geometrically reduced to the transverse section.

Fig. 4. Relations between the interplanar spacing d, the distance between extinction contours Δ, and the radius of curvature of the crystal ρ. *a*—projection of the crystal, visible in the microscope; *b*—diffraction pattern from both extinction contours; *c*—two positions of the reciprocal lattice of the crystal with the reflecting sphere; *g*—section of the crystal lying in the plane of the electron beam and the direction of the reflections of the diffraction pattern.

In Fig. 3 *a*—*e* the form of the extinction contours is presented as a function

of the shape of the filaments studied. The brighter region in Fig. 3*a*, *c* is the silhouette of a selector aperture 1 μ in diameter.

In the diffraction pattern obtained from each extinction contour by the selector aperture, there was one reflection corresponding to reflection only from one family of planes satisfying the Wolf–Bragg condition. Two symmetrical reflections appeared simultaneously only in the case when a portion of the image with two extinction contours was located inside the area of the selector aperture.

Knowing the wavelength and measuring the distance between two extinction contours, one can determine the radius of longitudinal bending of the crystal in the plane coinciding with the direction of the electron beam:

$$\rho = \Delta d \cdot \cos\beta / 2\lambda,$$

where ρ is the radius of curvature of the crystal; Δ is the distance between the centers of the bend extinction contours; d is the interplanar spacing; λ is the wavelength (Å); 2θ is the angle between the positions of the crystal corresponding to two extinction contours; β is the angle between the crystal axis and the direction of the bright reflections.

The appearance of an extinction contour over the whole cross section of the crystal made it possible to judge not only the character of the transverse section of the crystal but, in those cases when the crystal was hollow, also the thickness of the crystal walls, without resorting to ultrathin sections.

In addition, from the character of the extinction patterns one can, without resorting to indexing spot electron-diffraction patterns, determine the growth direction of the crystal with sufficient accuracy. It turned out that in this case, when

the extinction contour has the shape of a parallelepiped, the crystal has the shape of a plate, and the growth direction coincides with the zone $[000\bar{1}]$. When the growth direction coincides with the direction $[10\bar{1}0]$, the extinction contour has the form of a hexagon. The wall thickness of hollow hexagonal prisms does not depend on the crystal diameter. In all cases it ranged from tenths to hundredths of a micron.

The shape of the cavity in the crystal depends on the thickness of the crystal walls. In the case when the crystal walls are thin, the shape of the internal cavity repeats the external shape of the crystal. We were unable to determine the thickness of the plates from the curved extinction contour; however, it apparently does not exceed hundredths of a micron.

On the extinction contours, in several cases it was possible to observe the presence in the crystal of an axial dislocation—brighter regions having the form of a spiral, with broadenings in the form of nodes forming at the place where the dislocation turns. Figure 3e shows an axial dislocation in a crystal oriented along the axis $[10\bar{1}0]$.

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Note: Figure translations are in progress. See original paper for figures.