CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR P. P. BUDNIKOV and N. V. SHISHKOV

1961

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR P. P. BUDNIKOV and N. V. SHISHKOV

SOME OBSERVATIONS ON THE CRYSTALLIZATION OF BERYLLIUM OXIDE FROM THE GAS PHASE

Some refractory oxides, single crystals of which are difficult to obtain by crystallization from the melt because of the high melting temperature, crystallize comparatively readily from the gas phase, yielding very perfect single crystals ([1], [2]). The temperature at which such crystals are obtained may be considerably lower than the melting temperature of the oxide.

We observed the growth of beryllium oxide crystals from the gas phase at 1900, 1800, and even 1600°. The experiments were carried out at atmospheric pressure in an argon atmosphere.

Compact polycrystalline beryllium oxide of 99.9% purity was placed in a hollow graphite block and held at constant temperature for 10 hours or more in a furnace with graphite resistance heating.

The growing BeO crystals were located on the inner wall of the lid of the block, which had a temperature 10–50° lower than that of the sample.

The crystals had sizes up to 5 mm and varied in form, although plates and rods predominated (Fig. 1, *a*—*e*). Rod-shaped crystals often grow in groups in one direction, forming columnar intergrowths. Among other forms, short hexagonal prisms no larger than 100×100 μ are encountered.

The mechanism of crystal growth from a gaseous medium is generally considered ([3]) to be condensation of the substance at the tip of the growing crystal.

From photographs in transmitted light (Fig. 1 *a*—*v*) it is seen that a characteristic phenomenon in the process of BeO growth from the gas phase is the formation of dendritic branches and so-called "whiskers." As Hardy notes ([3]), it is unknown whether metal "whiskers" have the same orientation as the primary crystal on which they grow. But from the photographs (Fig. 1) it is evident that offshoots and "whiskers" of BeO form a quite definite angle with the primary crystal, namely 60, 90, or 120°. This corresponds to crystallization of the branch in the directions of the *a* axes of the unit cell of the primary crystal.

In some photographs the crystals are opaque because of the presence on their surface of a film of carbon evaporated from the graphite block. In what form the

Figure 1

Figure 1: Figure 1

Fig. 2. Single-crystal beryllium oxide ribbon. 150×

Figure 2: Fig. 2. Single-crystal beryllium oxide ribbon. 150×

carbon is deposited on beryllium oxide is unclear; however, chemical interaction between carbon and BeO with formation of beryllium carbide Be_2C is excluded, since this reaction proceeds only above 1950°.

A very characteristic initial stage of carbon deposition on BeO is observed on thin plates (Fig. 1 *e*, *d*). In transmitted light a thin gray film of carbon forms a pattern whose basic element is a regular triangle with side $1 \div 5 \cdot 10^{-4}$ cm. According to Ortont ([4]), the same pattern is characteristic of the surface of hexagonal packing formed from elementary tetrahedra (for example, Mo_4^{6-}). It may therefore be assumed that the deposit formed as a result of condensation of carbon vapors on BeO reveals the relief of the crystal surface, just as do electron-microscopic replicas. This is confirmed by the similarity of the pattern to the triangular growth terraces observed by Varma ([5]) on the surface of a zinc blende crystal. Another cause of the formation

Fig. 1. Beryllium oxide crystals grown from the gas phase on a graphite surface;
a, b –340×; *c, d* –200×; *e, f* –440×.

DAN, vol. 138, No. 5, Budnikov and Shishkov

of the figure may be selective adsorption of carbon by certain areas of the flat surface of the single crystal, although this is less likely.

In most cases the rows formed by the figures of carbon deposition on the surface of a BeO plate are oriented parallel to its longitudinal axis, which is the *c* axis, and in some cases are arranged at an angle of about 30° to the axis of the crystal. In the latter case the branch grows perpendicular to the geometric axis of the plate.

Fig. 2. Single-crystal beryllium oxide ribbon. 150×

In Fig. 1d a rod-shaped crystal is shown, whose axis coincides with the *c* axis of the BeO unit cell. By means of its branch the crystal joined with a plate, on which an offshoot is also visible. It is noteworthy that the growth of the branch was not stopped by the obstacle encountered–the plate–and the build-up of the branch proceeded to the sides, with the formation of a shapeless deposit at the point of contact. This photograph serves as proof of the mechanism of crystal growth from the gas phase by condensation of material at its tip.

BeO single crystals obtained from the gas phase are very strong and can undergo large elastic deformations without destruction, as is seen from Fig. 2. As

Ryszkiewicz reports [2], the bending strength of BeO "whiskers" is 150,000 kg/cm^2. In view of the very high strength of single crystals obtained from the gas phase, this method of growing oxide crystals may become highly promising if ways are found to increase the growth rate and methods of controlling the condensation process at high temperatures.

Moscow Chemical-Technological Institute
named after D. I. Mendeleev

Received
25 II 1961

CITED LITERATURE

1. V. A. Timofeev, A. F. Zalesskii, in: *Collection: Growth of Crystals*, **2**, Publishing House of the Academy of Sciences of the USSR, 1959.
2. E. Rischkewitsch, *Trans. Brit. Ceram. Soc.*, **59**, 8, 303 (1960).
3. G. K. Hardy, *Successes in the Physics of Metals*, **3**, Moscow, 1960.
4. B. F. Ormont, *Structures of Inorganic Substances*, 1950.
5. A. Varma, *Crystal Growth and Dislocations*, Foreign Literature Publishing House, 1958.

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