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Abstract

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Many methods are known for obtaining filamentous single crystals—crystallization from the gas phase, from melts, from solutions, splitting massive crystals along cleavage planes, etc. Of particular interest, apparently, is the spontaneous growth of filamentous single crystals. Cases have previously been described of the spontaneous growth of CuO crystals during oxidation of high-purity copper (1) and of α-Fe_2O_3 during oxidation of pure iron (2). It is believed that filamentous crystals are formed as a result of large differences in the volumes of the metal and oxide, leading to the development of strong stress and plastic deformation of the oxide on the metal surface.

In our studies we observed the spontaneous growth of filamentous single crystals of magnesium oxide on the surface of periclase specimens with a spinel bond. Specimens measuring $65 \times 115 \times 230$ mm were fired by us in a tunnel kiln at a temperature of 1650°. It is interesting that, after some time, filamentous single crystals began to appear on the surface of the specimens cooled to room temperature.

Examination of the specimens showed that they consist of a dark core surrounded by a light zone (Fig. 1a, see insert facing p. 1041). The filamentous crystals grew at the boundary between the dark and light zones. In the macrophotograph of a periclase specimen with a spinel bond, zone 2, on which the filamentous crystals grew, is clearly visible, located between zone 1—the light zone—and zone 3—the dark zone.

As a result of macroscopic examination it was found that the light zone consists of very large grains of periclase, in the spaces between which there are interlayers consisting of magnesioferrite, spinel of the $MgAl_2O_4$ type, and magnesium orthosilicate and $CaMgSiO_4$. Figure 1b shows a microphotograph of a fired magnesite specimen, in which large single crystals of periclase are clearly visible. The dark zone of the specimen consists of finer periclase grains containing a certain amount of FeO in the form of a solid solution. Figure 1c shows a microphotograph of the dark zone of the specimen. The light inclusions between the periclase grains are a small amount of iron oxide reduced to metal.

The filamentous crystals obtained grew in the form of quadrangular or hexagonal prisms, and also as skeletal two-dimensional plates (Fig. 1e). Quite often the crystals have a screw-like form. The length of some crystals reached 5 mm, with a thickness on the order of several microns. In general, the thickness of the crystals did not exceed 10μ.

Figures 1c, d, and e show microphotographs of filamentous single crystals formed on the surface of fired magnesite during its cooling. By their coloration, the filamentous crystals formed on the surface of the specimen are divided by color into colorless, light-yellow, and dark-brown. The refractive index of the colorless crystals is $N = 1.740$—1.745, which corresponds to an FeO concentration in the crystals of 0.9—1.8% (3). The refractive index of the light-yellow and dark-brown ···

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Fig. 1. Specimens of crystals.
a –1/2×, b –200×, c –200×, d –400×, e –140×, f –140×.

new crystals reaches $N = 1.760$ (FeO content in the form of a solid solution in periclase up to 3.1%).

Determination of the growth direction of the whisker single crystals in the specimen showed that the $\langle 100 \rangle$ direction predominates. Crystals with the growth direction $\langle 110 \rangle$ are encountered more rarely. Crystals with the growth direction $\langle 111 \rangle$ were not found.

It may be assumed that the whisker crystals of magnesium oxide on the surface of the magnesite specimen grow as a result of strong compression of layer 2 (Fig. 1a) between zones 1 and 3. The growth of whisker crystals under compression of massive single crystals of magnesium oxide was described by Hulse [4]. It should be noted, however, that the length of the whisker crystals obtained by the method of compressing a massive single crystal was no more than 700 μ, and the growth direction coincided with $\langle 100 \rangle$. In the case described by us, stress in a large polycrystalline specimen is formed because, during firing, oxygen has time to diffuse only to a certain depth. In this process zones are formed: a light zone, in which a certain amount of FeO contained in the batch as an impurity is oxidized to Fe_2O_3, forming magnesioferrite at the boundaries of the periclase grains; a dark zone, in which unoxidized FeO enters the magnesium oxide lattice in the form of a solid solution; and a third, light zone–an intermediate zone. Upon cooling of the fired magnesite refractory, owing to the difference in volume expansions of the inner and outer zones, such large pressures are created in it that plastic flow of magnesium oxide occurs. The large number of whisker single crystals with the growth direction $\langle 100 \rangle$ shows that the compressive pressure required for crystal growth in this direction is much smaller than in the $\langle 110 \rangle$

direction.

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