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Abstract

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GROWTH OF METALLIC SINGLE CRYSTALS UNDER HIGH HYDROSTATIC PRESSURE

The growth of single crystals of a substance, in particular metals, under high hydrostatic pressure is of great interest.

On the basis of thermodynamic considerations one may assume that the number of defects in the crystal structure decreases with increasing pressure.

Since

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p,$$

then

$$\Delta S = -\int_{p_1}^{p_2} \left(\frac{\partial V}{\partial T}\right)_p dp,$$

where S is the entropy of the substance, p the pressure, T the temperature, and V the volume of the substance.

In view of the fact that the coefficient of thermal expansion $(\partial V/\partial T)_p$ decreases with pressure, the entropy will also decrease with pressure. Consequently, with increasing pressure there will be a tendency toward an increase in the regularity of the crystal lattice, since crystals grown under high pressure should, in principle, possess a smaller number of defects in the crystal structure. As far as we know, this question is being raised in the scientific literature for the first time and requires experimental verification, which is the subject of our future work.

On the other hand, it is known that under the action of high pressure the properties of crystals can change substantially ($^{1-4}$). In particular, changes in the crystal lattice are observed—allotropic transformations, as well as hardening phenomena, occurring both as a result of the action of high pressure on an already formed crystal ($^{5-9}$), and as a consequence of crystallization under pressure ($^{10-13}$).

Fig. 1. Graphite heater

Figure 1: Fig. 1. Graphite heater

If the crystalline modification obtained under the action of high pressure is retained at low pressures (14–16), then a single crystal grown at high pressure (in the stability region of the new phase) will make it possible to investigate the physical properties of this modification, associated with the anisotropy of its structure, as well as the transition of this modification upon heating into the phase stable at low pressure. If, however, the modification obtained at high pressure cannot be retained at atmospheric pressure, then the study of traces of the new phase, if these traces (dimensions, orientation, etc.) are preserved, will make it possible to draw deeper conclusions about the processes of phase transformations in crystals.

Single crystals grown at high pressures make it possible, by comparison with single crystals obtained at normal pressure, to trace the influence of structural defects on the physicomechanical properties along various crystallographic axes, and also to carry out microscopic and x-ray studies of dislocations. These considera-

significantly broaden the range of substances from which it is of interest to grow single crystals at high pressures.

For a comparative study of the properties of single crystals, the apparatus for growing single crystals was designed so that crystals could be obtained on it both at normal and at high gas pressure. The specifics of operation at high pressures (the very limited possibility of controlling the process inside the high-pressure vessel) determined the nature of the technique (17–20) and the design of the furnace for growing single crystals.

Fig. 1. Graphite heater

Single crystals of Al and Zn were grown from the melt. The crucible was a conical graphite heater of a vertically arranged furnace (see Fig. 1). The conical shape of the heater-crucible provided a temperature gradient in the furnace during its operation of 7-10 deg/mm, and the symmetry with respect to the vertical axis provided isothermality in the horizontal sections of the heater. Cooling of the melt was carried out by reducing the electrical power supplied to the furnace. With the aid of an adjustable transformer, displacement of the temperature front ($T = T_{\text{cr}}$, where T_{cr} is the crystallization temperature) from bottom to top was ensured at a rate of 0.8-1 mm/min. At high pressure (10,000 atm.) the velocity of motion of the front ($T = T_{\text{cr}}$) was 0.5-0.7 mm/min. The rate of motion of the temperature front ($T = T_{\text{cr}}$) determined the growth rate of the crystals.

Initially, the growth of single crystals was established in vacuum (10^{-2}—10^{-3} mm Hg) and at normal pressure in nitrogen and argon. Under these conditions the operating characteristics of the furnace were found and the technique for growing single crystals was worked out. The electric-current powers

Fig. 2. Schematic of the setup for growing metallic single crystals under high hydrostatic pressure.
1 —millivoltmeter; 2 —high-pressure vessel; 3 —power-supply panel; 4 —combined lead-through obturator; 5 —gas cylinder; 6 —low-pressure filter; 7 —gas compressor of L. F. Vereshchagin' s system; 8 —high-pressure filter; 9 —pressure gauge (manganin or pointer). Instruments introduced into the experimental circuit for growing single crystals at constant pressure (indicated by a dotted line): 10 —electronic potentiometer; 11 —auxiliary high-pressure vessel; 12 —pressure gauge (manganin or pointer); 13 —millivoltmeter

needed for melting Zn and Al samples (cylinder, $d = 4$ mm, $l = 50$ mm) at normal pressure were 0.3 kW for Zn and 0.8 kW for Al, and the times required to obtain each of these crystals were 100 and 150 min.

At high gas pressures (Ar or N_2), the current powers required to reach the same temperatures in the furnace placed in the high- ···

pressure, increased approximately linearly with increasing pressure and were 1.8 and 3.0 kW at 10,000 atm. The times required under these conditions to obtain Zn and Al crystals were, respectively, 280 and 480 min.

The growth of single crystals at high pressures (Fig. 2) was carried out in two different regimes: with variable and with constant pressure. In the first case, melting of the specimen occurred at constant pressure, while crystal growth occurred at variable pressure (the decrease in furnace temperature during crystallization naturally led to a drop in gas pressure in the high-pressure vessel). It was assumed that, under such a growth regime, the single crystals would contain a smaller amount of gas than specimens grown at constant pressure. Constancy of the high pressure in the second regime for obtaining single crystals was ensured by introducing into the apparatus an auxiliary high-pressure vessel with internal heating, connected to the first vessel. At the time when the pressure in the bomb in which the crystal was grown began to fall (as a result of the decrease in furnace temperature), the pressure in the second bomb was increased (by additionally raising the temperature), thereby compensating for the pressure drop in the first bomb. The stability of the pressure level was $±$50 atm.

The grown single crystals had the shape of cylinders ($d = 4$ mm, $l = 50$ mm) with a cone (angle 30°) at the end. The structure of the specimens was determined by X-ray methods.

The results of a comparative study of single crystals grown at normal and high pressures, as well as a detailed description of the apparatus for obtaining single crystals, will be the subject of subsequent communications.

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