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Projekt pt.: **„Zintegrowany Program UTHRad.”,** POWR.03.05.00-00-Z105/17
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Course title: Materials Engineering and Application

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LECTURE №8

Single crystal growing

The single crystals can help to study the structure and properties of metals and alloys, the mechanisms of plastic deformation and fracture, and to investigate the nature of interatomic bonds in metals, alloys, and compounds. The topology studying of the Fermi surface requires obtaining high-purity and perfect metal single crystals. Working with high-purity and single-crystal materials allows you to discover new properties that do not appear on similar polycrystalline objects. The single crystals of metals, alloys and compounds are not only unique objects of research in the field of solid state physics, but also real materials of new technology, which in some cases have already found practical application.

The first metal was obtained by artificial single crystals growth at the beginning of the 20th century. These were single crystals of fusible metals, which immediately became objects of basic research. However, metal single crystals, unlike semiconductor ones, did not find technical application for a long time. That began only in the 1960s, when the synthesis of sufficiently large and high-purity single crystals of refractory metals was carried out. At present, the role of metal single crystals in science and technology is constantly growing. At the same time, requirements are increasing for the purity, perfection of the structure and geometry of the grown single crystals. The impurities deep cleaning and obtaining single crystals is the way to create materials with desired properties along with alloying. It should be emphasized that the issues of obtaining metallic single crystals and their deep cleaning are inextricably linked. There is a direct relationship between the degree of perfection of a single crystal and the level contained impurities. The main methods for purifying metals from impurities are hydrometallurgical

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processes, ion exchange, dissociation of galloid compounds, liquid extraction, electrolysis, sublimation, vapor deposition, vacuum smelting. The effectiveness of each of the abovementioned methods is determined by the physicochemical properties of the base metal and the impurities contained therein.

The single crystals grown from a melt

On a rotating speed, supercooling is generated by controlled heat removal from the surface of the crystal and the meniscus of the melt adjacent to it (Czochralski method, Fig. 8.1, a). By pulling through a slit on the surface of the melt, shaped crystals are obtained, for example, pipes or plates (Stepanov's method, Fig. 8.2, b). When single crystals are grown inside the melt, supercooling is obtained, for example, with running water of the seed holder (Kyropoulos method, Fig. 8.3, c). In directed crystallization the container with the melt is moved horizontally or vertically from the hot to the cold zone of the furnace. While crystallization begins in a specially narrowed front of the container, it provides a single-crystal ingot (the Stockberger-Bridgman method, Fig. 8.1, d; method "boats," Fig. 8. e, f).

In the so-called method of hiding, the container itself may be made of crystallizing material that is cooled externally with water, while its inside is melted by high-frequency currents; single crystals are grown by pulling to seed or by slow cooling. In the zone melting method, the molten zone moves from the seed through a polycrystalline ingot. Zone melting can be carried out in the container or without it, as shown in Fig. 8.1, h. In the latter case, the meniscus of the melt is held by capillary forces, and sometimes by electromagnetic "support." For refractory substances, melting of the powder is used, pouring into a hot plasma, with the deposition of the resulting drops of the melt onto the seed (Verneuil method, Fig. 8.1, f). Single crystals in the form of fibers with a thickness of 10–200 μm are obtained by drawing through a die or from a drop of melt formed on a rod (1.5–2 times greater thickness) when heated by a laser beam ("pedestal" method, Fig. 8.1, g). The growth rate from the melt is ca. 0.1 ÷ 1 cm/h. Homogeneous crystals are obtained from a melt of a stable chemical compound. In the presence of impurities, to obtain homogeneous crystals, it is advisable to use the drawing method, ensuring that during growth, the shape of the phase boundary remain constant. The main efforts in the growth of single crystals from a melt are directed to controlling the temperature field by the melt mixing method (natural and forced convection), and controlling the growing atmosphere.

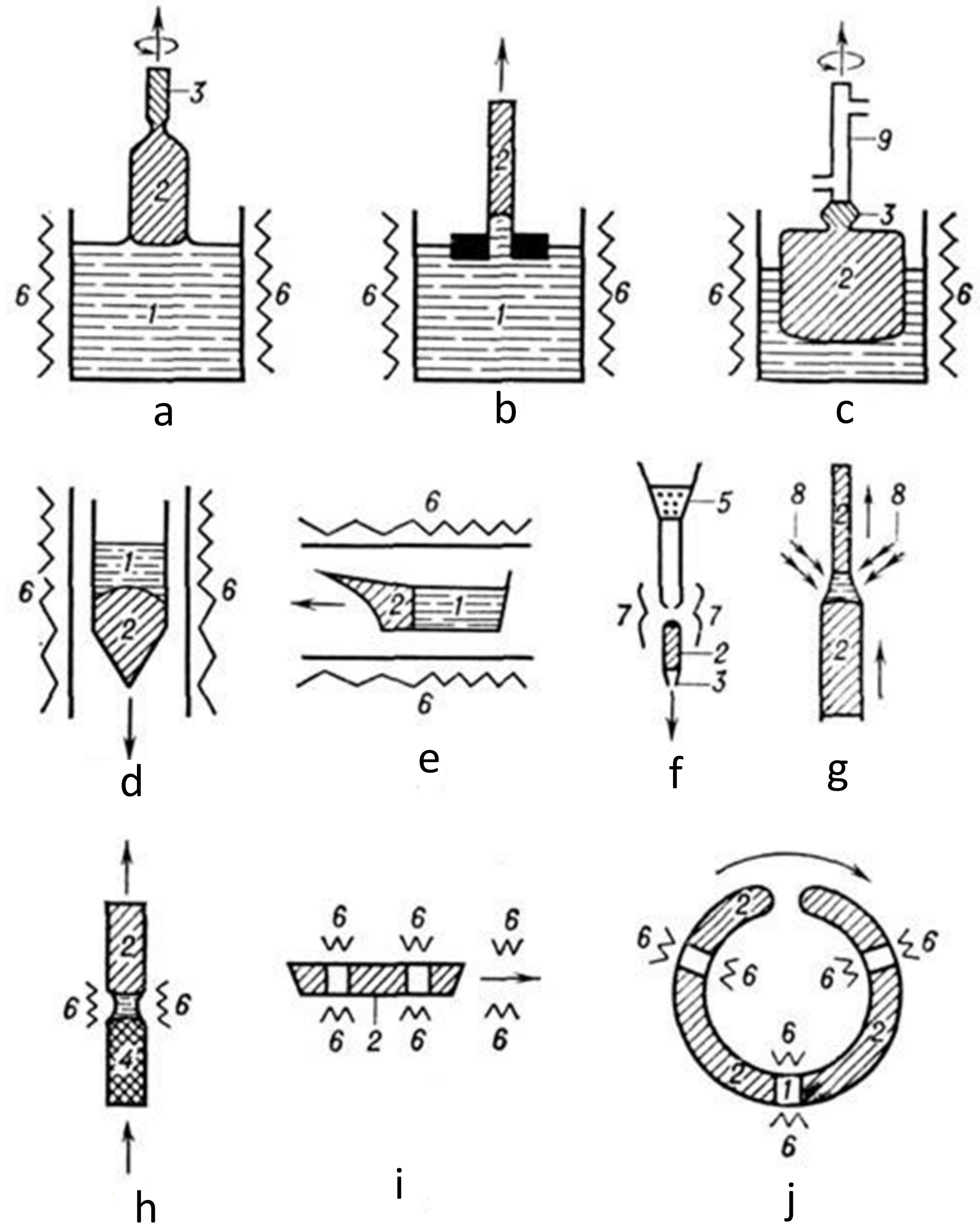

Fig. 8.1. Single crystal growth from melt: a - Czochralski method; b - Stepanov's method; c - the method of Kyropoulos; d - the Stockberger-Bridgman method; e - the method of “boat”; f- is the Verneuil method; g - the method of “pedestal”; h - zone melting without a crucible; 1 - melt; 2 - single crystal; 3 - seed; 4 - polycrystal; 5 - powder; 6 - electric heater;7 - gas heater; 8 - laser radiation; 9 - water-cooled seed holder

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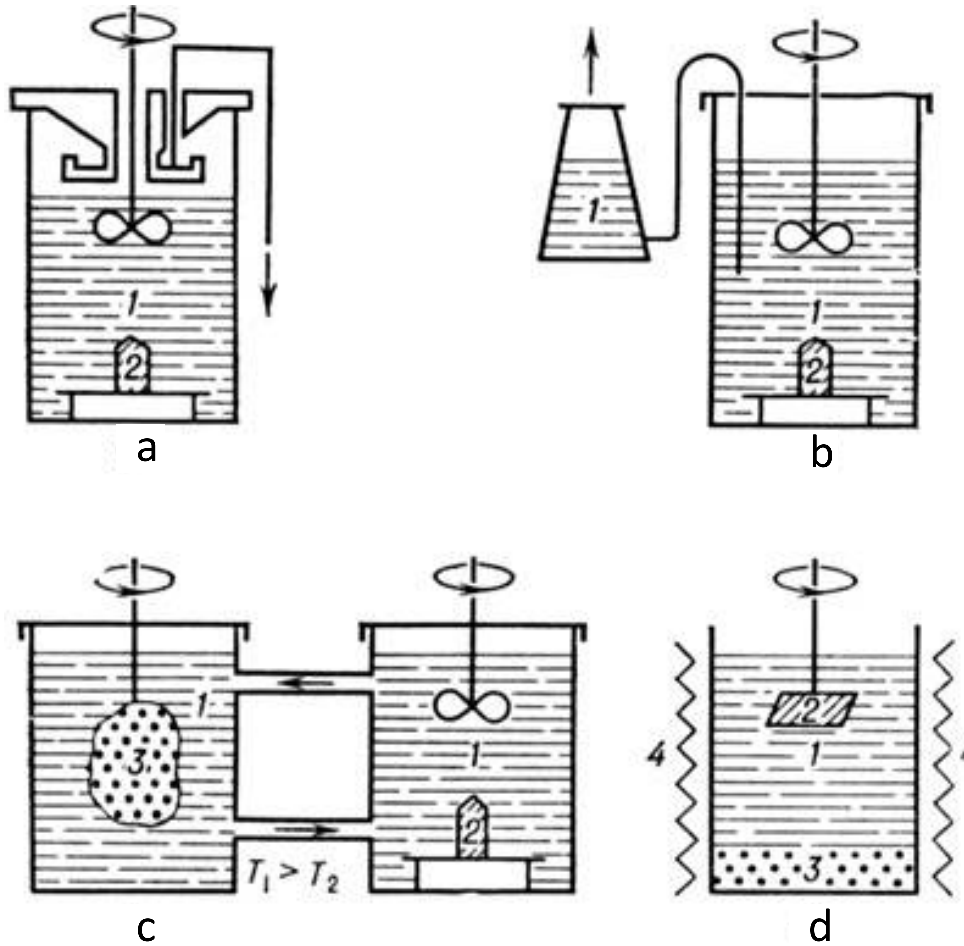

Fig. 8.2. Growing a single crystal from a solution: a - is a solvent evaporation method; b - the method of "recharge"; c, d - temperature gradient method; 1 - solution; 2 - single crystal; 3 - powder; 4 - heaterGrowing single crystals from a solution

Subcooling is obtained by lowering the temperature through evaporating the solvent, as illustrated in Fig. 8.2a, or by “feeding” a more concentrated solution as in Fig. 8.2b. In the so-called temperature gradient method, shown in Fig. 8.2 c-d, a hotter zone is obtained in the apparatus, where the substance dissolves and is transferred by diffusion or convection to the growing crystal.

The hydrothermal growth of sparingly soluble substances is carried out in autoclaves at high temperatures and pressures. Growth rate is ca. 0.1 ÷ 1 mm/day. To obtain a perfect crystal from a solution, it is necessary that the supply of a substance to a growing surface would not limit the growth rate. This is achieved, for example, by stirring the solution. Under such conditions, a speed of 1 mm/h or more is possible (rapid growth). The cleaning of raw materials, stabilization of temperature and supercooling, and the creation of hydrodynamic flows ensuring uniform nutrition of faces are important.

Growing single crystals from a gaseous medium

It is carried out by sublimation of the substance and its condensation to a cooled seed. Chemical reactions are also used when transporting the substance to the growth zone, its decomposition or synthesis on the seed. Cultivation is carried out either in an airtight container along which a temperature gradient is created, or in a gas stream. To obtain whiskers, drops of solvent are applied to the seed surface, from which crystallization proceeds faster than from vapor. When growing single crystals from a polycrystalline sample, the latter is kept at high temperature to recrystallize small crystalline grains into coarse grains. If the substance has polymorphic modifications, then single crystals of the low-temperature phase can be obtained by cooling the crystals in a certain temperature field. Many substances are grown in the form of single crystals. The largest quantities are produced of Si, Ge (Czochralski method), quartz (hydrothermal method), alkali-galloid compounds (Kyropoulos method), corundum with various impurities (Verneuil, Czochralski methods and directed crystallization), $Y_3Al_5O_{12}$ with Nd admixture (Czochralski methods and directed crystallization), $LiNbO_3$, $LiTaO_3$ (Czochralski method), $K(H_5D)_2PO_4$ (lowering the temperature and "feeding"), $LiIO_3$ (evaporation of the solvent). Technical diamond in the form of small single-crystal grains (up to 0.2 mm) is obtained from graphite by pressing in a small volume at a pressure of about 4.4 bar and temperature 1100 °C.

The main methods for growing single crystals include the following methods.

Growing from a solution in a melt (spontaneous crystallization). PbO (886 °C), PbF_2 (824 °C), B_2O_3 (450 °C), Bi_2O_3 (817 °C), V_2O_5 (670 °C), etc., are usually used as low-melting fluxes. Crystallization occurs upon cooling below the saturation point.

The main advantage of the method is that crystallization can be carried out significantly below the melting point of the resulting material. Disadvantages can be listed as follows: contamination with flux elements, the need for very precise temperature control, the use of expensive platinum and other crucible materials. The following requirements are imposed on fluxes: they should not be volatile and toxic, if possible, be minimally included in single crystals (if they are not their

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components), there should be moderate viscosity of the melts.
For example, to grow crystals of a ferrogranate, a charge containing molar is taken. %, 10 Y_2O_3, 20.4 Fe_2O_3, 36.8 PbO, 27.1 PbF_2, 5.5 B_2O_3.The composition of the crystallizing target product $Y_3Fe_5O_{12}$ does not correspond to the melt composition in the ratio of the concentration of the main components, as in the case of crystallization of ferrite crystals. The processes of growth of single crystals in the implementation of their technology are subject, in fact, to the same basic thermodynamic and kinetic laws as the synthesis of powder and film materials.The most important factor is the high-temperature phase diagram of the charge components in the liquidus and solidus regions. Crystal growth occurs through the appearance of nuclei, which, depending on the temperature and chemical potentials of the components, can dissolve or grow further, i.e., they may have critical sizes, etc. According to this option, the melt holding temperature is 1250 ÷ 1300 °C (15 hours), the cooling rate after that before crystallization is 0.3 ÷ 0.5 deg/h. Crystallization is stopped at 950 ÷ 1000 ° C and the remaining melt is removed, the obtained crystals are purified by boiling in nitric acid. The crucible rotational speed during cultivation is 20 rpm, the rotation is carried out for 15 s in one direction and 15 s in the other with a 5-second pause.

Verneuil Method

The Verneuil method explained in Fig. 8.3, is implemented by pouring small portions of the powder mixture into a tubular furnace, where this mixture is melted during a fall in an oxygen-hydrogen flame and feeds a drop of melt on the seed surface. The seed is thus gradually pulled down, and the drop is at the same level along the height of the furnace.

Advantages of this method are as follows: lack of fluxes and expensive crucible materials; no need for precise temperature control; the ability to control the growth of a single crystal. Disadvantages are following: due to the high growth temperature, the crystals have internal stresses; the stoichiometry of the composition may be impaired due to the recovery of components by hydrogen and the evaporation of volatile substances. Growing rate is a few millimeters per hour.

A working principle of a device for single crystals growing by the Stockaberg-Bridgman method is shown in Fig. 8.4. The single crystals emerging in the lower part of the melt crucible serve as a seed. The crucible descends into the colder zone of the furnace. The lower part of the crucible is conical. The cultivation speed is also a few mm/hour.

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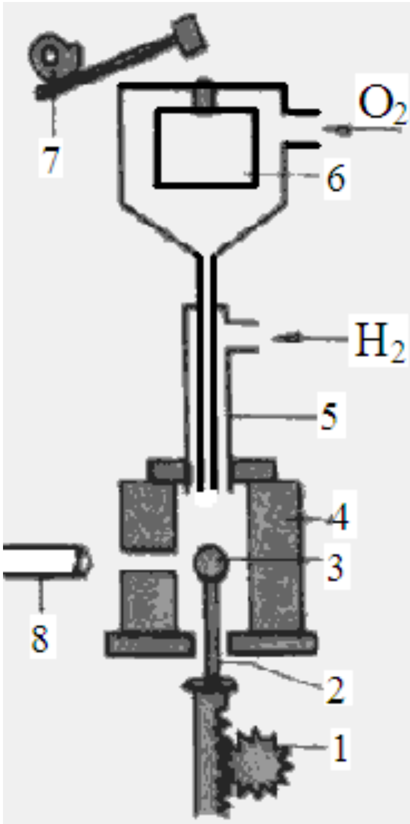

Fig. 8.3. Scheme of the installation for growing single crystals by the Verneuil method: 1 - the mechanism of lowering the crystal; 2 - crystal holder; 3 - growing crystal; 4 - muffle; 5 - burner; 6 - hopper; 7 - shaking mechanism; 8 - catheter

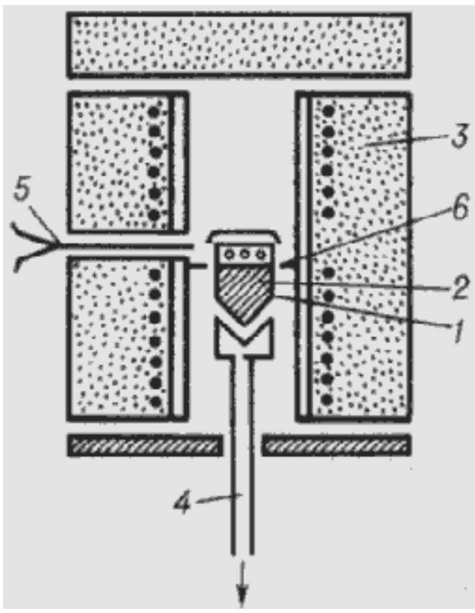

Fig. 8.4. Stockaberg-Bridgman method: 1 - a crucible with a melt; 2 - crystal; 3 - oven; 4 - refrigerator; 5 - thermocouple; 6 - heat shield

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The Czochralski method

According to the Czochralski method shown in Fig. 8.5, a single crystal is pulled up to the seed from a bath with a melt. Heating is usually carried out using microwave radiation. To relieve emerging stresses, an additional furnace is used, through which the grown crystal passes and is annealed.

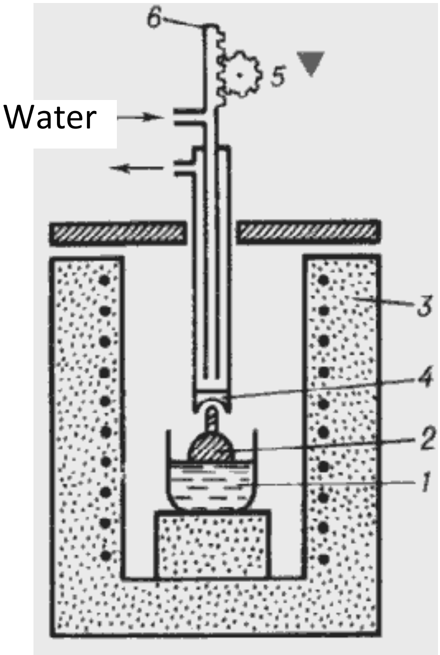

Fig. 8.5. Scheme of the installation for growing single crystals by the Czochralski method: 1 - a crucible with a melt; 2 - crystal; 3 - oven; 4 - refrigerator; 5, 6 - pulling mechanism

The method of zone melting

Zone melting presented in Fig. 8.6, consists in driving the melt zone along the length of the single crystal preform, while impurities are concentrated in the melt zone. The crystal is cleaned, its final part is then removed. Heating is carried out by induction, radiation-optical or other method. The growth rate for methods 4 and 5 is close to that for methods 2 and 3. The implementation of the last three methods requires the regulation of the growing gas environment.

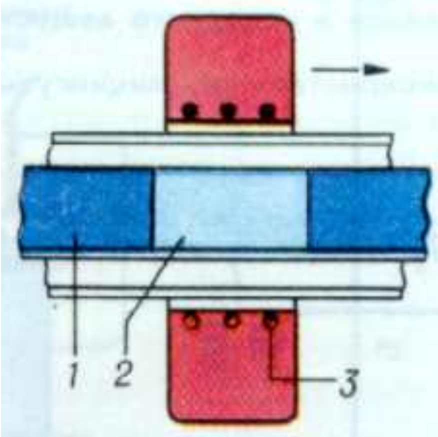

Fig. 8.6 Scheme of the device for zone melting:
1 - solid phase; 2 - melt; 3 - heater
(the arrow shows the direction of movement of the heater)

Hydrothermal cultivation

The starting oxides or the finished complex oxide are dissolved in aqueous solutions of acids or alkalis to implement the hydrothermal growth method. The apparatus is showed in Fig. 8.7.

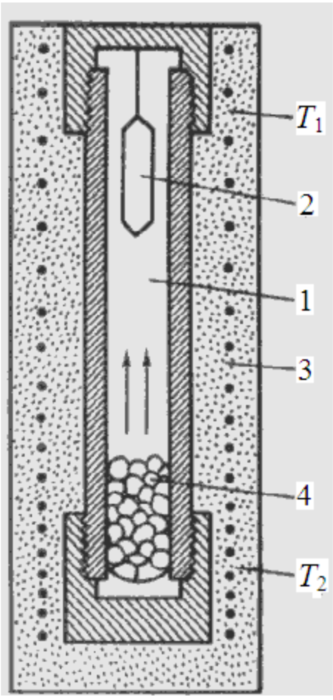

Fig. 8.7. Scheme of an autoclave for hydrothermal synthesis: 1 - solution; 2 - crystal; 3 - oven; 4 - substance for crystallization ($T_1 < T_2$)

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Cultivation is carried out in autoclaves with protective corrosion-resistant liners, for example for ferrites at 375 ÷ 725 °C and a pressure of 1800 ÷ 2000 atm. Due to the temperature difference in the upper and lower zones of the autoclave, a crystal is released at the top. The cultivation speed is from fractions of millimeters to several millimeters per day. The grown single crystals are usually of high quality and characteristic crystallographic faceting, since they grow under conditions more or less close to equilibrium. After receiving single crystals, they are precisely oriented in space and subjected to mechanical processing like cutting, grinding, or polishing. For example, single-crystal IR optics such as cattle (thallium halides) are processed due to their low hardness on lathes in special protective boxes. The single crystals are coated with protective coatings and, if necessary, layers of materials for various functional purposes

The method of solid-phase recrystallization

To grow crystals by solid-phase recrystallization, a ceramic preform and a single-crystal seed are brought into contact, sometimes a substance initiating the recrystallization process is placed between them, in particular, when producing ferrite crystals, or thin layer iron oxide. If the recrystallization rate exceeds the rate of pore exit to the surface, the resulting crystal can be quite porous.