

ON THE PROCEDURE OF GROWING LARGE MONOCRYSTALS

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IN modern science and engineering the growing of monocrystals and their application plays an important part. Although crystals have been in practical use since many years because of their ultra-violet and infra-red power of transmission for optical purposes and for piezoelectrical and photoelectrical processes, the problem of growing them synthetically has only become acute when the store of natural crystals no longer met the ever-increasing requirements with regard to quantity and quality. This development commenced approximately 20 to 30 years ago.

By crystal growing, we understand the production of larger monocrystals in laboratories under constant conditions of growth. Monocrystals are crystalline bodies, the crystallographic axes of which have the same orientation at every point. Such crystals can be produced from any pure substances as well as from mixtures of these substances. Only after one had succeeded to produce large monocrystals, was it possible to examine many physical properties of metallic and non-metallic substances and to produce constructional elements for optical, piezoelectrical and electronic purposes.

As the growing of crystals is a little known specialised field, I wish to describe here the fundamental methods and a few applications of synthetic crystals.

In the growing of crystals, two basic processes are applied:

1. Growing from a solution,
2. Growing from the molten stage.

The hydrothermal synthesis for which high pressures and high temperatures are used in thick-walled steel vessels which can be closed (the so-called autoclaves), is still considered as a growing process from the solution, whereas the Verneuil process (flame melting process) represents the growing process from the molten stage. We are commencing with the growing of crystals from the solution. As mostly water is used as a solvent it is, of course, presumed that the substance to be crystallized readily dissolves in water without decomposing. If the solubility of the substance—as usually happens—depends on the temperature, i.e., if it dissolves more at higher than at lower temperature, then a nucleus—a small monocrystal of the substance in question—can be placed in the solution which was saturated at a certain tem-

perature. By slowly and continually lowering the temperature of the solution, a controlled deposit of the substance on to the nucleus can be brought about. On the other hand, if the solubility of the substance diminishes with rising temperature,—which occurs less frequently—the temperature of the solution must be slowly increased to effect a growth.

A process using an apparatus consisting of three containers is another variation of the method of growing crystals utilizing a drop in temperature. Whilst crystallisation takes place in one container, the two others are used for the saturation and temperature adjustment of the solution. Between the individual containers is a slight temperature gradient which is required for maintaining the crystallisation.

This process is especially suited to the manufacture of large monocrystals. In addition to the abovementioned processes of production, growing of crystals at a constant temperature with adjusted evaporation is also possible. A nucleus placed in the saturated solution is forced to grow by an initially low and subsequently increasing evaporation of the solvent conditioned by the continuous growth of the crystal.

With these methods of growing the surfaces of a crystal, the quickest growth may be 1 to 2.5 mm. daily, so that it may take weeks or months to obtain a crystal of the required dimensions. If clear, homogeneous and optically pure crystals are required, the temperature of the solution must be perfectly regulated during this time by a thermostat and a steady even mixing of the solution ensured, otherwise flaws—in the shape of clouding, turbidity and cracks—may occur in the growing crystal. The ends of the crystal which do not grow on to the wall of the container show well developed and even surfaces (see Illustration 1).

Illustration 1 shows examples of synthetic crystals grown according to the temperature falling method.

Examples from the solution-growth method are: alum which is used in optics, sodium potassium tartrate (Seignette), ammonium-dihydrogen phosphate (ADP), ethylene diamine tartrate (EDP), dipotassium tartrate (DKT), lithium sulphate, etc., used for piezoelectrical and electro-optical purposes. The hydrothermal growing of crystals has become of special importance for the synthetic production of

quartz crystals during the last 15 years, when it was highly developed particularly regarding the production technology. Here also the two fundamental methods of crystallisation at constant temperature, or with a temperature gradient, are used. Growing by means of a drop in temperature where very long autoclaves are used to maintain the temperature difference offers considerable advantages, and is used nowadays almost exclusively for the synthesis of quartz. We therefore wish to explain this process briefly. The base of the autoclave is fed with broken up natural quartz as a nutrient preparation whilst the orientated and uniaxial quartz nuclei crystals are fixed in the other part of the autoclave. A sufficient solubility required for the quartz to grow is then effected with increased temperature and pressure by a weakly alkaline solution. (At a volumetric ratio of 75 to 80% approx. 400° C. pressures approaching 1000 atm.) By differently heating the two ends of the autoclave a temperature gradient and thus also a difference in the concentration of the solution is achieved, i.e., by higher heating of the base part a greater saturation occurs in the nutrient substance than in the nuclei. The solution which in respect of the nuclei solution being oversaturated deposits the surplus, and the quartz nuclei grow. The varying concentration causes differences in the density, effecting a strong convection of the solution to make a continuous movement of the substance from the nutrient preparation to the nuclei possible.

liquid. Even when a crystallisation from the solution as well as from the melt is possible, as for instance with rocksalt, the latter process is almost exclusively used because of the considerable saving of time.

It is a known fact that a melt cooling under normal circumstances solidifies in polycrystals. To achieve a monocrystalline growth there are two possibilities; in both cases, crystallisation commencing in one place and continuing through the whole melt. According to the first method evolved by Nacken and Kyropoulos, a cooled down nucleus is planted into the overheated melt. For this purpose the melt is in a jar made of a suitable material standing in an electric oven. The growth commences from the nucleus acting as a cooling centre. The growing is controlled by slowly removing the crystal and by continuous lowering of the temperature of the melt up to the solidifying point. Thus, monocrystals of salt-like compounds the melting points of which range from 500 to 1,000° C. of approx. 15 kilo weight can be produced within a few days. It is characteristic of this method that the crystals have a rounded shape contrary to those grown from a solution (see Illustration 2).

In the process developed by Bridgman and Stockbarger, a cylindrical jar with a conical-shaped point is slowly lowered through two superimposed ovens. The temperature of the upper oven is kept constantly above the melting point of the substance, whilst the tempera-



Illustration 1: Synthetic crystal of ADP, sodium potassium tartrate and potash alum.



Illustration 2: Sodium chloride (crystal on the left) and lithium fluoride monocrystals grown according to the Kyropoulos method.

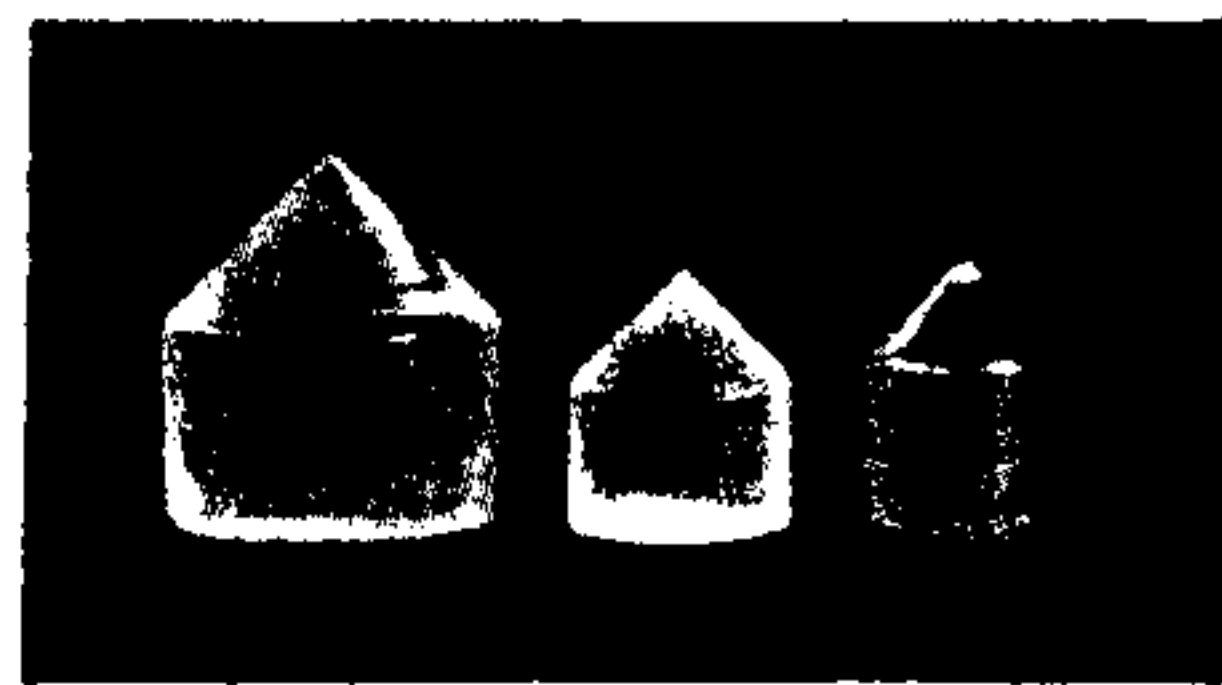


Illustration 3: Sodium chloride (crystal on the left, lithium fluoride and KRS 5 crystal on the right) monocrystals grown according to the Stockbarger method.

The 2-chamber autoclaves are based on the same growing principle, but the dissolving and growing process is carried out in two different chambers, which are connected with each other.

Today it is already possible to produce quartz crystals of approx. 1 kilo weight in 2 to 3 months.

With substances which melt without decomposing or which are not water-soluble, the crystallisation is effected from the molten

ture of the lower oven is below the melting point. The oven combination thus has a vertical temperature gradient so that when continually lowering the jar in a certain place between the ovens, the crystallisation will commence on the top of the cone and expand from there. This method of growing has the advantage that substances with a high vapour pressure, or substances affected in the molten stage by the atmosphere, or the vapours of which are poisonous, all of which can be crystallised by working

in closed vessels or in a vacuum. (Illustration 3 shows crystals produced according to the Stockbarger method.)

Other processes (Stoeber) utilize the heat difference in such a way that initially the temperature on the lowest point of the vessel is below the melting point so that the first nuclei form there. By means of "nuclei selection" it is then possible to grow monocrystals by progressively lowering the temperature. These methods also allow for the production of large monocrystals, within a relatively short time. It is obvious that high demands must be placed on the temperature regulation, the course of the mechanical processes and the purity of the raw material.

The crystals produced from molten solutions—predominantly halides of alkali and alkaline earth metals—are used in infrared and ultraviolet spectroscopy as prisms, windows and bulbs. In infrared spectroscopy, *e.g.*, the crystals are used in a range where glass is not sufficiently transparent for testing rotation vibration spectra, and thus serve for ascertaining the structure of molecules. The methods of growing monocrystals of metal have become of immense technical importance, as their properties considerably deviate from those usually existing as polycrystalline aggregates. Similarly to the Nacken-Krypoules method, a cooled rod is dipped into the metal solution kept at a constant temperature. When this rod is slowly and evenly pulled out, monocrystalline coats of the solidifying metal are formed on it. With-

out going into details of its principles, mention should be made of the zonal melting process which was developed a few years ago and is used mainly for the purification of semiconductor substances, but can also be used in a modified way for the growing of monocrystals. It offers the special advantage of melting without a jar.

The crystallisation of substances with melting points above 1,500° C. is limited in the above-mentioned processes by the problem of ovens and jars. Verneuil published in 1891 a process according to which, except for minor changes, monocrystals are manufactured even today. The heating source is an oxyhydrogen flame. The substance is introduced into the oxygen current as a fine powder and falls on a clay stick on which it melts. Initially, a cluster of crystals forms from which by collective crystallisation a favoured nucleus grows to a pear-shaped monocrystal of approx. 5 cm. Corundum and spinel (melting points in the region of 2,000° C.) are examples of crystals produced in such a manner. Their use as precious stones and jewel bearings is well known. Production has so far advanced that thin orientated rods can be grown which can also be bent into loops for textile thread guides.

This process has also been successfully applied for growing silicone, but the flame melting heating was replaced by radiation or induction heating to make crystallisation in a vacuum or neutral gaseous atmosphere possible.—(Courtesy : *Jena Review*, No. 1, pp. 24-26.)

CONGRESS AND EXHIBITION AT FRANKFURT, 1958

THE European Congress of Chemical Engineering and theACHEMA Congress, 1958, have been scheduled to take place at Frankfurt am Main from 31st May to 8th June 1958.

The scope and size of the forthcoming Congress will be considerably larger than the last meeting held in 1955 since the Congresses of the European Federation of Chemical Engineering and the European Federation of Corrosion which will take place within the framework of the European Congress of Chemical Engineering, will be organised with the co-operation of 58 technical and scientific societies from 17

different countries. During the same period the Gesellschaft Deutscher Chemiker is arranging a special meeting with a series of lectures and the DECHEMA will hold its Thirty-Second Annual Meeting.

Hundreds of firms from different countries are expected to take part in the Exhibition arranged at the Congress, with their exhibits on the latest developments in science and technology.

Further details can be had from : DECHEMA, Frankfurt am Main-7, Postfach (Germany).
