The Platinum Metals in Crystal Pulling

CRUCIBLES AND OTHER APPARATUS

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The platinum metals do not react with most molten oxides and halides and therefore they have many applications in crystal pulling. They can be used not only for crucibles but also for heat shields and baffles to control both the spatial and temporal temperature distributions. The construction and use of these components is described in this article.

Single crystals of oxides and halides have an ever increasing number of uses. For example, gramophone styli, watch bearings, lasers, piezo-electric filters, and electro-optic devices are often made from oxide crystals and some optical components are manufactured from halide crystals. In many cases the most satisfactory crystals can be pulled from the melt by the method first used by Czochralski (1). One of the major difficulties with this technique is finding materials to make the necessary parts of the growth system. For oxides and halides the platinum group metals are often a good choice since they do not react with the molten charge or the atmosphere which must be maintained over it.

TABLE I

Conditions for the Growth of Some Crystals

Crystal†	Melting Point °C	Crucible Material	Atmosphere	Pulling Rate mm/h	Rotation Rate rev/min
$Y_3Al_5O_{12}$	1950	Iridium	Nitrogen	2	60
$LiTaO_3$	1650	Iridium	Nitrogen	10	30
$CaWO_4$	1650	Rhodium	Air	10	100
$MnFe_2O_4$	1500	Iridium	Nitrogen	5	10
$NaBa_2Nb_5O_{15}$	1450	Platinum	Oxygen	5	30
$Sr_{0\cdot5}Ba_{0\cdot5}Nb_2O_6$	1406	Platinum	Oxygen	5	10
$LiNbO_3$	1250	Platinum	Oxygen	5	30
$ZnWO_4$	1200	Platinum	Air	10	100
BaClF	1008	Platinum	Nitrogen/ Hydrogen	8	85
$Bi_{12}GeO_{20}$	930	Platinum	Oxygen	10	50
$NaNO_2$	271	Platinum	Vacuum	*	70

† The crystals of $Y_3Al_5O_{12}$ were for use in lasers. $LiTaO_3$, $NaBa_2Nb_5O_{15}$, $Sr_{0\cdot5}Ba_{0\cdot5}Nb_2O_6$, $LiNbO_3$, and $Bi_{12}GeO_{20}$ were for electro-optic devices. $CaWO_4$ and $ZnWO_4$ were for maser studies. $MnFe_2O_4$ was for tape recorder heads. BaClF was for a quantum counting device. $NaNO_2$ crystals were for pyroelectric devices

* Kyropoulos method crucible cooled at 4 deg C/h

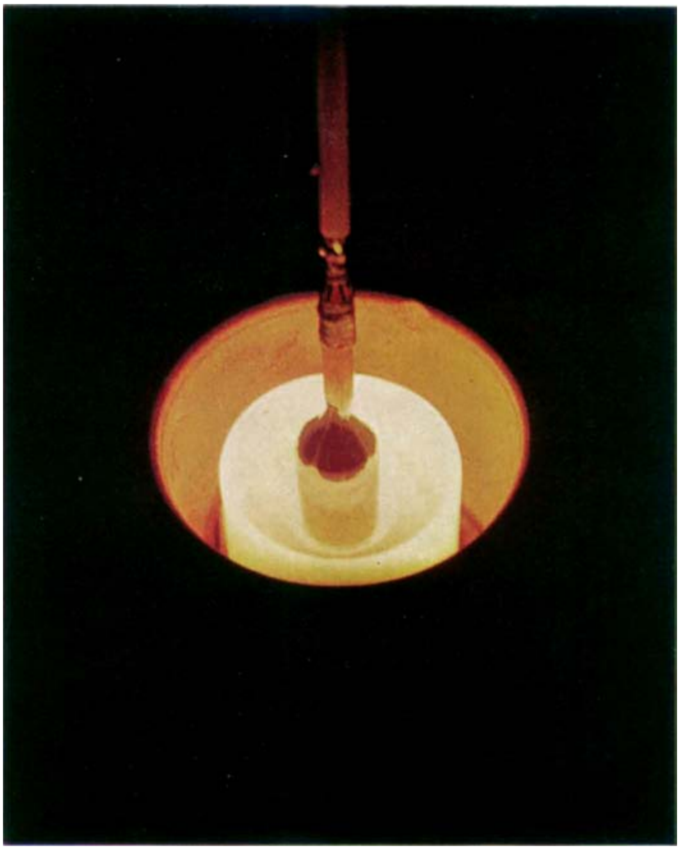

Fig. 1 A simple crystal pulling system. The melt is contained in a platinum crucible heated inductively. A seed crystal is lowered to touch the melt surface, is held there for a few minutes and then is raised slowly. The diameter of the growing crystal can be changed by varying the temperature of the crucible. The growing crystal is rotated to eliminate radial asymmetry. Both the lifting and rotary movements must be smooth if homogeneous crystals are to be grown; in this case both movements were provided by a hydraulic system (2)

Figure 1 shows a crystal being pulled from the melt. The caption explains the process and Table I enumerates conditions which have been found suitable for the growth of a number of crystals. There is an alternative process due to Kyropoulos (3) in which the crystal is not raised during growth but is allowed to grow into the melt as the crucible temperature is lowered. This process is widely used for halide crystals and requires essentially the same apparatus.

Both these processes need a crucible which does not react with the melt. For the crystals with lower melting points platinum is often satisfactory but, as Table I indicates, higher melting point materials necessitate the use of rhodium or iridium. Platinum has the advantages that it is the least reactive of these materials and is relatively easily worked. It has the disadvantage that in the pure state it is very soft at high temperatures so that it distorts in use, particularly if the melt expands on freezing. (It is unusual to remove all the melt during growth.) This problem can be overcome by alloying but some alloying elements can be leached from the crucible. Thus Whiffin and Orton (4) found that it was necessary to use high purity platinum for the growth of zinc tungstate if contamination by rhodium was to be avoided. (See Table II.) Melts containing alkali metal or bismuth ions also frequently leach impurities from platinum.

Elimination of Distortion

Problems with the distortion of pure platinum crucibles can be overcome in a number of ways. With some materials it is possible to supercool the melt by say 30°C before freezing is initiated and then rapidly raise the crucible temperature to a few degrees above the melting point before continuing to cool slowly. This results in the solid growing from the centre of the crucible rather than forming a solid skin locked to the crucible

Fig. 2 Some platinum components used in crystal growth. At the top of the photograph is a seed holder, in the centre is a silica ring from which is suspended a platinum baffle for suppressing thermal oscillations, and at the bottom is a crucible with a reinforced rim

walls and trapping some unfrozen melt below it. An obvious but expensive alternative is to use a thicker crucible. However in practice it is only necessary to reinforce the rim as shown in Figure 2. A thick rim is in any case desirable in all crucibles heated inductively because small distortions can cause local hot spots producing local melting which spreads progressively. (Iridium crucibles are particularly prone to this type of failure.) Another method for preventing distortion is to hold the crucible in a rigid support; a tightly packed powder as shown in Fig. 3 is usually adequate or a casing of a castable ceramic can be used. Van Uitert (5) has described the use of an iridium crucible sealed between two platinum ones to achieve the rigidity of iridium combined with the corrosion resistance of platinum.

Clearly, in a crystal pulling system it is necessary to hold the seed crystal. Figure 2 shows one method and some alternatives are given in Fig. 4.

TABLE II
Rhodium in Zinc Tungstate

Crucible	Rhodium in crystals mol. %
Rh	0.075*
Pt+10% Rh	up to 0.03
Pt+0.1% Rh	0.009

* This is sufficient to turn the normally colourless crystal black.

High Quality Crystals

So far, only the basic process has been discussed. However, the growth of high

Fig. 3 Various heat shields to decrease the temperature gradient in growing crystals. The beehive shape is fabricated from iridium and the others from platinum. These shields couple to the radio frequency field and act as additional heat sources above the melt

quality crystals often demands considerable refinement. The first improvement is to control (usually decrease*) the temperature gradient in the growing crystal (7). This can be done by placing a furnace over the crucible. However, a simpler and more reliable method is to use heat shields; Figure 3 gives some examples. If the most uniform possible crystals are required, it is necessary to eliminate the unsteady convection which can occur in melts heated from the side or from below. This convection produces a modulation of the growth rate which results in the presence of "growth striae" in the crystal. The effect can be eliminated by placing baffles in the melt (8, 9). In an unbaffled melt the temperature at a fixed point can oscillate several degrees with a period of a few seconds. A correctly located baffle can eliminate all measurable oscillations and so allow the production of extremely homogeneous crystals. Figure 2 shows the type of baffle used. This is lowered into the crucible after the charge has been melted. The baffle and two of the support wires are made of platinum, the third wire is 13 per cent rhodium-platinum. This wire with one of the others forms a thermocouple. The correct position for the baffle is the one which gives no variation in the output of this couple.

Precious metal thermocouples have other uses in crystal growth. With oxide and halide melts, for example, they may be used unsheathed to determine the temperature distribution in the melt, which is vital in the control of perfection (7). They can also be used to monitor the crucible temperature to ensure that the temperature control system

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* It is sometimes necessary to increase the temperature gradient in order to maintain a constant diameter (6).

Fig. 4 Seed holders constructed from strip and wire. Their materials are selected to suit atmosphere and temperature. That on the left was made from platinum and was used for $Ba_xSr_{1-x}Nb_2O_6$, that in the centre was for melts giving off corrosive vapours and that on the right in 40 per cent rhodium-platinum was for $Y_3Al_5O_{12}$

is working, or even to activate it. Such couples should be welded to the crucible. Platinum: rhodium-platinum couples can conveniently be welded to platinum crucibles by heating both the couple and the crucible and then tapping the couple on to the crucible with a polished steel hammer. (This technique can also be used to fasten wires to other platinum components.) In inductively heated systems thermocouples can act as pick-up loops. This problem can be overcome by using a filter of the type shown in Fig. 5.

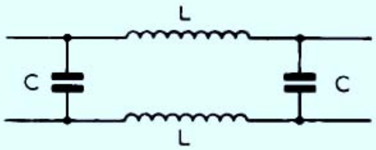

Fig. 5 An electrical filter for use on thermocouple circuits. The inductors L are radio frequency chokes with low self capacity and an inductance of either 13 or 23 mH. The capacitors are not critical but exceed about 2 μF. (Electrolytic capacitors may be used but have a life of only a few months)

Maintenance of Components

Obviously, great care must be taken to ensure that the apparatus used in crystal growth is clean. Most melts are very reactive and will readily dissolve any contamination on surfaces which they touch. Some melts, e.g. ones containing bismuth oxide, are readily reduced by organic matter and a reduced melt will usually attack the platinum metals, so that care must be taken to remove lint and grease. The authors' colleagues soak new components in hydrochloric acid and remove traces of old melts with a fusion mixture composed of two parts of sodium carbonate and one part of disodium tetraborate. After washing away the fusion mixture with water a further soak is given usually in hydrochloric acid but for some melts (e.g.

ones containing lead ions) nitric acid is used. Large amounts of old melts are more easily removed with a trepanning drill before the use of the fusion mixture.

Apart from cleaning, precious metal components require little maintenance. Platinum parts which distort can be annealed and bent or hammered back into shape, although too much working is not desirable, and if much work must be done the material should be annealed several times. Annealing and welding are conveniently done with a gas torch but care must be taken to maintain an oxidising rather than a reducing flame.

This article discusses the main uses of the platinum group metals in crystal pulling. The ideas behind the use of the various components are given in the references so far cited and a comprehensive review is given in reference 10.

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Platinum in Crystal Growing and Optical Fibre Production

Since the advent of solid state lasers in 1960 the optical and electronic industries have made significant developments in the preparation of novel oxide single crystal materials for devices such as light modulators, second harmonic generators and bubble domain memories. A further advance in materials technology is the development of optical fibre waveguides for communications. One factor common to these devices is that they are all produced with platinum apparatus.

Several grades of platinum are available for the fabrication of crucibles. The selection of a suitable grade of platinum is determined by the degree to which the optical or electrical characteristics of the end-product are influenced by specific trace impurities, and the physical and chemical properties of the crystal melt.

Where mechanical strength and thermal stability are important, as in general analytical work, platinum selectively doped with rhodium and iridium is used, although rhodium is slowly leached from the crucible by corrosive fluxes and highly reactive melts.

Platinum used for both melt and flux-melted crystal growing should be as free as possible from these and other metals, which may be detrimental to certain optical and magnetic devices. In the case of barium titanate, the ferroelectric Curie temperature may be lowered, whereas in lithium niobate the susceptibility of the crystals to laser damage may be increased. Rhodium also substitutes in the lithium niobate lattice, causing absorption in the visible region of the spectrum.

In order to reduce to an absolute minimum trace metal contamination of the crystals, it is advisable to employ crucibles fabricated from a thermocouple grade of platinum known as Thermopure. This material is, however, comparatively soft and if a thin wall is used the crucible may need to be reinforced at the rim or to be supported in a ceramic sheath.

In optical transmission fibres, absorption in the near and infra-red spectral region is controlled largely by sub-p.p.m. levels of the first row transition metal ions. Since the purity of the bulk glass is so critical it has been necessary to introduce an ultra-high purity Fibre-optic grade of platinum to meet the stringent requirements of this comparatively new technology. This Johnson Matthey material has a total metallic impurity level of less than 10 p.p.m. (total iron plus copper content less than 5 p.p.m.). P. M. W.