

Czochralski Growth of Oxide Single Crystals

IRIDIUM CRUCIBLES AND THEIR USE

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Iridium is used extensively as a material for crucibles containing oxide melts during single crystal growth because of good chemical compatibility with them in slightly oxidising atmospheres. With care, iridium crucibles can be used in this way for long periods.

During the past decade iridium has been used increasingly as a crucible material for the growth of high melting point oxide and mixed oxide single crystals. These crystals are required mainly as electronic materials and include the compounds listed in the Table.

Examples of uses for these compounds include solid state lasers, magnetic bubble device substrates, insulating substrates for semiconductors, and monolithic crystal filters. In these and similar applications a single crystal with a high degree of structural perfection is required, and device quality crystals are generally grown from the molten state by the Czochralski technique using an iridium crucible to contain the melt.

Crucible Use

The Czochralski technique, as applied to oxides, has been described fully elsewhere (1-3) but in outline the process consists of slowly withdrawing a rotating single crystal seed from a bath of molten oxide. Melt solidifies on to the seed, which is grown into a crystal of the required diameter by controlling the heat input into the crucible. Both radio-frequency (r.f.) and resistance heating of the iridium crucible are employed but the former is more common. A typical growth apparatus and growing crystal are shown in Figs. 1 and 2.

Iridium crucibles are available in a wide range of shapes and sizes but are usually cylindrical with capacities varying from around 30 cm³ to several litres. They are normally manufactured either from hot-rolled iridium sheet by welding or from iridium powder by hot pressing; the respective processes produce coarse- and fine-grained structures.

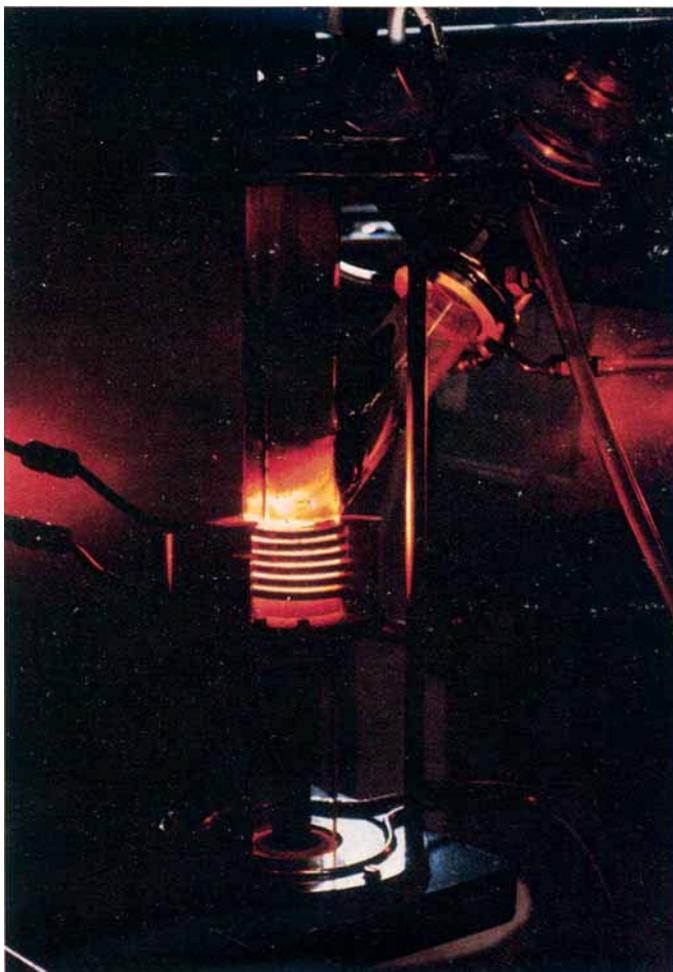
A typical cycle to which a crucible is subjected during crystal growth is:

- (i) charging;
- (ii) growing the crystal at the particular oxide melting point;
- (iii) cooling the crucible and residual charge after contact between the crystal and melt has been broken.

Single Crystal Materials		
Compound	Formula	Melting Point
spinel	MgAl ₂ O ₄	2105°C
sapphire	Al ₂ O ₃	2050°C
yttrium aluminium garnet	Y ₃ Al ₅ O ₁₂	1970°C
yttrium orthoaluminate	YAlO ₃	1875°C
gadolinium gallium garnet	Gd ₃ Ga ₅ O ₁₂	1725°C
lithium tantalate	LiTaO ₃	1650°C

Fig. 1 Typical apparatus for single crystal growth by the Czochralski technique includes this chamber, which contains within a refractory enclosure the iridium crucible heated by the r.f. coil.

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Charging can take several heating and cooling cycles depending upon the form of the charge, e.g. whether crystalline and compact, or powdered and low density; a reasonable time span for a heating/cooling cycle is 2 to 6 hours. The time taken for growing the crystal is very dependent upon crystal growth rate and upon the length of crystal required, and can vary from a few hours for a small research-type crystal to a few days or even weeks for commercial-size crystals. Cooling occupies less time than growing the crystal and is typically 5 to 50 hours.

Crucible Failure and Its Avoidance

When a crucible fails, the failure is generally catastrophic and occurs by melting, brittle fracture, reaction between the crucible and oxidising atmosphere/melt, or any combination of these effects. Some new and failed crucibles are compared in Fig. 3. Particular types of failure are often related to particular materials. For instance, it is relatively easy to melt a crucible during the growth of

materials with melting points close to that of iridium, e.g. sapphire and spinel; to fracture a crucible containing materials that cause distortion, e.g. garnets; and to oxidise the crucible when oxygen is required in the gaseous ambient, e.g. lithium tantalate, or when a reactive component forms part of the melt, e.g. gallium oxide in gadolinium gallium garnet. However, considerable interaction occurs between these effects. For example, localised melting can cause cracking on subsequent cooling and preferential oxidation at grain boundaries can lead to intergranular fracture.

With care, failure by melting should only occur in extensively used crucibles that have

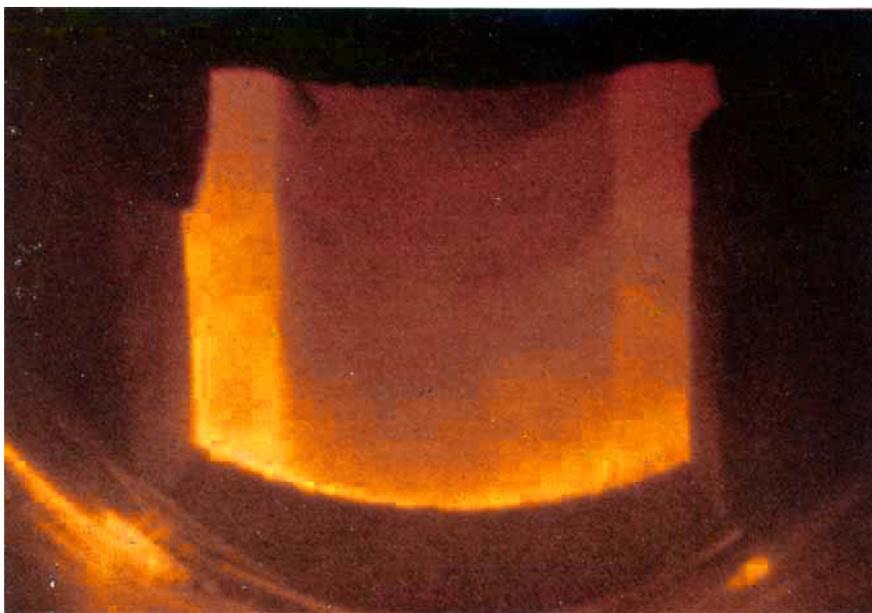


Fig. 2 Looking down the side arm of the chamber shown in Fig. 1, the growing crystal can be observed through an aperture in the refractory enclosure. The brilliant line just inside the refractory is the near side of the iridium crucible, the far edge of which, together with the melt level, can just be distinguished beyond the crystal

acquired in-service defects. In a new crucible, melting is frequently a result of making increases in temperature too rapidly in an effort to melt the charge quickly, instead of allowing an approximate equilibrium to be established and maintained between the thermal masses of the crucible, the melt and the surrounding refractory environment. The choice of refractory is, however, also important. Alumina, magnesia, zirconia, and thoria have all been employed but of necessity the melting point of the refractory must exceed that of the crystal being grown, thus excluding the use of alumina at the highest temperatures. Some refractories, such as zirconia, also tend to couple into the r.f. field at high temperatures, producing localised hot spots and crucible melting. Even pure zirconia will act in this way if properties become modified by spillages of the components into the refractory surround during crucible charging.

Failure of crucibles by distortion is a much greater problem, and occurs principally with materials of the garnet type. Several reasons

have been suggested for the distortion. The principal possibilities are:

- (i) that the iridium tends to sag under its own weight at high temperatures;
- (ii) that garnet materials expand on freezing;
- (iii) that relative expansion occurs between the crucible and solidified material.

Little experimental evidence exists to support the two first possibilities as major effects. In fact, possibility (i) is unlikely because for a given size and shape of crucible the sag should be greatest for the high melting point materials, such as sapphire and spinel, rather than for the garnets. For possibility (ii) to apply the solid material must have a lower density than the melt, something negated completely by automated crystal growth procedures using crystal weighing. These have shown conclusively that the buoyancy term is normal for garnets, i.e. the crystal is denser than the melt (4). Possibility (iii) is the most likely explanation but, unfortunately, thermal expansion data are not available for all the relevant materials



Fig. 3 New and used crucibles of 30 cm³ capacity. From the left are shown: a crucible slightly distorted by yttrium aluminium garnet; a crucible which has failed by melting; a new crucible made from welded sheet; a crucible heavily distorted and oxidised by gadolinium gallium garnet

over the whole temperature range from room temperature to melting point.

The thermal expansion coefficient of iridium increases from $6.24 \times 10^{-6}/^{\circ}\text{C}$ at room temperature to $15.19 \times 10^{-6}/^{\circ}\text{C}$ at 2225°C (5), whereas a typical garnet such as yttrium aluminium garnet (YAG) has an approximately constant coefficient of $8.9 \times 10^{-6}/^{\circ}\text{C}$ from room temperature to 1400°C (6).

Hence, two sources of stress for producing distortion are possible. The crucible can either contract around the solidified charge at high temperatures on cooling or be expanded at low temperature by the charge on heating. Both these mechanisms require the formation of a strong and continuous solidified crust upon solidification and very effective wetting of iridium by the melt; garnet melts fulfil both these criteria. Both high and low temperature distortion have been observed; Fig. 3 shows some of the effects induced.

As distortion occurs during heating and cooling rather than during growth, it can obviously be reduced by minimising the number of heating/cooling cycles during crucible charging, either by using densified material as the charge or by charging at a temperature slightly in excess of the melting point of the material required. Both these procedures raise difficulties due to possible contamination or preferential loss of a component so a choice must be made between

control of purity/composition and crucible lifetime. There is no unique method for avoiding distortion, although preferential freezing of the melt by crucible base cooling (7, 8) can limit the continuity of the surface crust and the associated distortion at surface level. However, this can sometimes transfer distortion problems to the crucible base. General distortion can be minimised by using slow heating and cooling rates, i.e. hours rather than minutes, so that equilibrium rather than forced distortion occurs. For garnet melts the relatively coarse-grained welded crucibles accommodate distortion better than the fine-grained pressed type by permitting some grain boundary sliding; pressed crucibles initially show little distortion but can fail suddenly by brittle fracture. However, for most materials there is little to choose between the two types of crucible.

Frequent inspection of crucibles after use is advisable. Cracks can easily be detected with a $\times 10$ eyepiece before they lead to catastrophic failure. At this stage, crucible life can be prolonged by 50 to 100 per cent if the surface is melted in a controlled manner using an argon arc welding procedure (see Fig. 4). This process also slightly refines the grain size, thereby increasing the crucible strength for a few growth cycles; it does, however, require a very experienced welder to perform the task successfully.

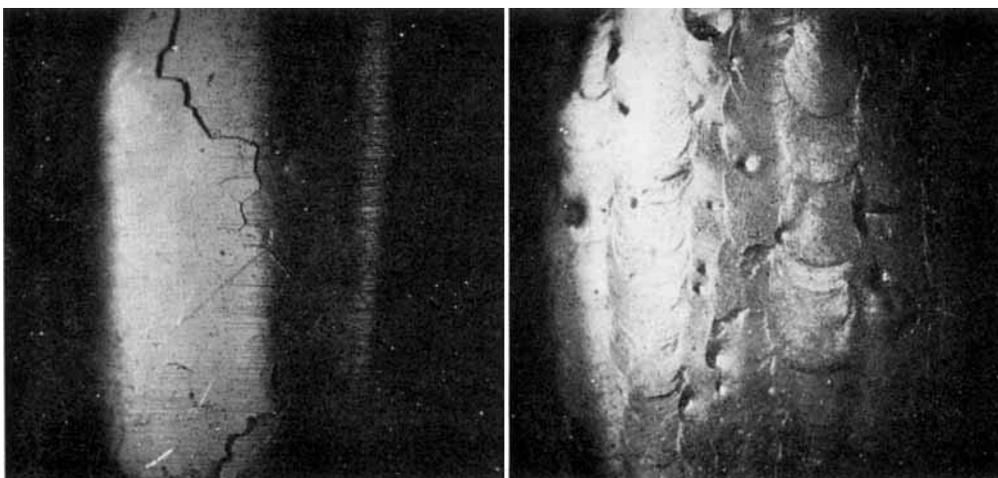


Fig. 4 (a) Typical intergranular fracture in an iridium crucible; (b) the surface of an iridium crucible after localised melting in an argon-arc welding apparatus

Crucible oxidation can be reduced to a minimum by the use of inert atmospheres but, when oxygen is essential for the maintenance of melt stoichiometry, flame-spraying the outside of the crucible with zirconia can increase crucible life by a factor of 1.5 to 2.0, although if distortion occurs the coating is correspondingly less effective. Reaction of the crucible with particularly reactive components, e.g. Ga_2O_3 in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, can be reduced by presintering to form the required compound prior to charging rather than by using the component oxides directly. Oxidation and reactivity need careful control. Under particularly adverse conditions, e.g. the growth of $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ at 1725°C using 10 vol. per cent oxygen in the gas ambient, iridium losses of 0.5 to 1.0 g/h have been recorded.

Because many oxide materials are hard, the method used for removing residual unwanted charge from the crucible can have a considerable effect upon lifetime. The simplest method is to convert all the charge into crystal but in this case the last part of the crystal to solidify is usually full of defects caused by segregation phenomena; these defects can cause the whole crystal to crack. Inverting the crucible in the r.f. coil to melt out the charge is an alternative and better solution to the problem. Some oxides are

sufficiently brittle to respond to a few blows with a vibrating percussion instrument, after which the residual charge can be tapped out. However, residual solidified droplets do not respond well to any of these treatments but they can be removed either by chemical etching procedures (phosphoric acid at 300°C is a general oxide solvent) or by grinding with a dental drill assembly using diamond-impregnated drill bits. It must be emphasised that unwarranted use of percussion techniques during crucible cleaning can lead to severe distortion and to premature fracture.

Crucible Lifetime

In conclusion some typical crucible lifetimes are quoted. They represent a general trend rather than a guarantee, as crucible lifetime depends markedly upon the experience of the user. For materials such as sapphire, spinel and yttrium orthoaluminate, which do not cause distortion and which require little or no oxygen in the gas ambient, some 30 to 50 crystal growth cycles can be obtained with a typical 30 cm^3 crucible made from welded sheet. For the growth of an undoped crystal some 5 cm long by 1 cm diameter, this represents some 500 hours containment of molten oxide with a probable

further 200 to 300 hours of heating and cooling. The lifetime is considerably less for materials that cause distortion; 10 to 15 growth cycles could be considered good for yttrium aluminium garnet and a much greater number would be exceptional without some form of repair. Durability does not necessarily decrease with increasing crucible size but increases in wall and base thicknesses are beneficial for large crucibles, e.g. those of more than 100 cm³.

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The Detection of Breath Alcohol

PLATINUM ELECTRODES IN FUEL CELL SENSOR

The development of a fuel cell detector sensitive to alcohol in the breath has led to the production of a small portable instrument as a preliminary screening test for traffic law enforcement. A similar sensor is incorporated into a more accurate analytical instrument now in use in some countries for final evidence in place of blood and urine analysis.

These instruments are produced by Lion Laboratories Limited of Cardiff following extensive research at Innsbruck University under Professor Gruber and more recently by Dr T. P. Jones at the University of Wales Institute of Science and Technology, Cardiff.

The fuel cell sensor incorporates a phosphoric acid electrolyte and electrodeposited platinum on its electrodes. Breath instruments

with this sensor aspirate alveolar breath directly on to one fuel cell electrode where, as a fuel, it is oxidised catalytically on the platinum. The small current which is generated is amplified and displayed on an analogue or a digital meter or as a printout.

Fuel cell output has been found to vary linearly with blood alcohol concentration over the range of forensic interest. Sensor activity diminishes slowly with time but by occasional calibration checks a sensor can remain in operation for up to 12 months irrespective of the number of samples analysed. The sensor is specific only to alcohol in expired breath but it will respond in other locations to certain other fuels, e.g. alcohols, acetaldehyde and hydrogen.

The pocket size Alcolmeter produced by Lion Laboratories incorporates a fuel cell sensor with platinum electrodes for the detection of breath alcohol. The more accurate analytical instrument can be seen in the background

