Crystal Growing from Oxide Melts

THE CHOICE OF CRUCIBLE MATERIALS

By J. G. Day

Research Laboratories, Johnson Matthey & Co Limited

The technique of growing single crystals from a melt either by directional solidification, by crystal pulling, or by crystallisation out of a flux melt has, in recent years, been applied to such high-melting materials as ferrites, alkali earth tungstates, titanates, and many refractory oxides, including rutile and magnetite. Relatively large crystals of all these materials are being produced in many laboratories and have proved invaluable for studying such characteristics as microwave resonance and emission in ferrites and other compounds, as well as for producing crystals for maser application.

With these materials, the success of the operation depends primarily on finding a crucible material that will withstand attack by the molten oxide at temperatures up to 2000°C and one, moreover, that will behave satisfactorily in the oxidising atmosphere usually maintained during crystal growth.

Refractory ceramic oxide crucibles, such as are normally used for melting metals are, in general, unsuitable since they are all liable to be fluxed severely by the molten oxides. The so-called 'refractory' metals, molybdenum and tungsten, are generally unsuitable since they are all attacked rapidly by oxygen at high temperatures and can only be used in reducing or neutral atmospheres.

Platinum Crucibles

The only materials that have been found to withstand these severe conditions are the platinum group of metals and their alloys. In a few instances unalloyed platinum crucibles have been found satisfactory, but generally it is necessary to choose materials of higher melting point, such as the rhodium-platinum alloys, or the metals rhodium or iridium.

One of the earliest workers in this field was J. Smiltens (1), and in 1952 he succeeded in growing single crystals of magnetite by directional solidification (frequently referred to as the Bridgman-Stockberger method), of a melt contained in a platinum crucible in an atmosphere consisting of a mixture of CO and CO_2. The crucibles were lowered at a rate of 5.5 mm/hr through a furnace, the hot zone of which was kept at 1575°C. By this technique single crystals which were reported to contain less than 0.002 per cent of platinum were obtained.

Many later workers have had more difficulty in keeping the temperature sufficiently low to avoid damage to the crucible and have preferred to use crucible materials of higher melting point, although Harrison (2) has been successful in growing single crystals of aluminium garnet ferrites in crucibles of the alloy of platinum with only 2 per cent of rhodium, which would not be expected to be noticeably different from pure platinum. Generally, the relatively low melting point of platinum crucibles imposes a serious limit to their use for crystal growing by directional solidification or crystal pulling, but platinum crucibles can be used safely for growing crystals by the Bell Telephone Laboratories method, which was particularly developed for growing garnet ferrites.

For these materials it was necessary to take steps to keep the temperature as low as possible, since the melting points of garnet ferrites, and indeed of all crystals containing ferric oxide as a constituent, are higher than the dissociation temperature of Fe_2O_3 at atmospheric pressure. In the Bell Laboratories method (3, 4), the garnet is mixed with 30 to 40 per cent lead oxide and 30 to 40 per cent of lead fluoride, and is heated in a platinum crucible for 4 to 5 hours at about 1250°C, at which temperature the garnet completely dissolves in the flux as a consequence of the formation of a eutectic between the lead oxide and the garnet. The mass is then slowly cooled at the rate of 1.2 to 1.3°C per hour to 980°C. During this operation crystals of the garnet are precipitated and grow in the molten mixture of lead fluoride and lead oxide. When the temperature has fallen to about 980°C the melt is quenched and the crystals of garnet, which may be several millimetres in length, are leached out of the solidified matrix. This technique has been successfully used for the growth of yttrium gallium, yttrium aluminium (5, 6) and various other rare earth iron oxides.

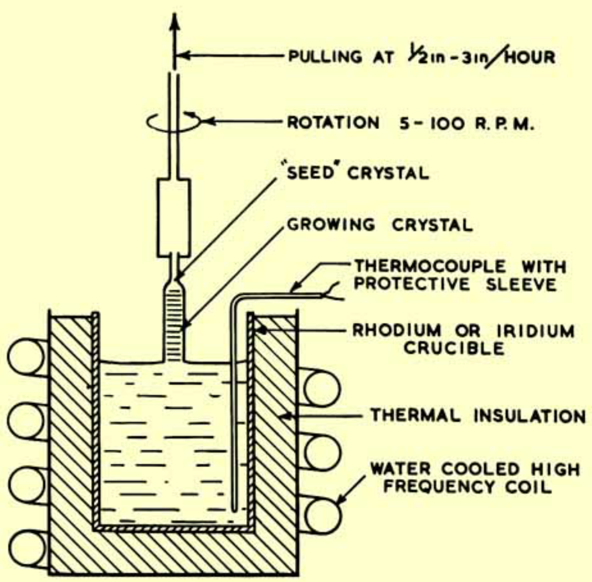
Other solvents than the lead oxide-lead fluoride mixture have been used when growing crystals by this technique, including borax, halides, and vanadium pentoxide. Remeika (7) used a mixture of Bi_2O_3 and B_2O_3 as a solvent for the preparation of the ferromagnetic piezoelectric compound $GaFeO_3$.

Although platinum crucibles have usually been found satisfactory in this work, Hoselitz (8) used rhodium-platinum crucibles for the preparation of various ferrites containing cobalt and manganese.

A feature of the Bell Laboratories method in which crystals are grown by precipitation from a molten flux, is that it is generally necessary to use much slower rates of growth than when growing crystals by direct solidification from a melt, and in some instances growth is continued for several days. Usually the crystals are numerous and small.

Rhodium-Platinum Alloys

Reference has already been made above to the production of magnetite crystals in a $CO\text{-}CO_2$ atmosphere by directional solidification by the Bridgman-Stockberger method at 1575°C. When this method is applied to such materials as cobalt ferrite, platinum was found unsatisfactory and Ferretti, Delaney, Arnott and Wold (9) found it necessary to use crucibles of 20 per cent rhodium-platinum alloy. In this work partial oxygen pressures of up to 1200 lb per square inch were employed. When Horn (10), however, attempted to use the same technique for preparing magnetite single crystals in a CO_2 atmosphere he was not so successful as Smiltens and found that his crystals were contaminated with platinum. Even when he employed rhodium-platinum alloys containing up to



Arrangement of the Czochralski crystal growing apparatus

40 per cent of rhodium, he still found trouble from contamination from platinum and rhodium. It is evident, therefore, that there is need for crucible materials with even higher melting points.

Rhodium and Iridium Crucibles

In the past there has been some hesitation in the use of rhodium and iridium crucibles in oxidising atmospheres at high temperatures through fear of high losses from the formation of volatile rhodium and iridium oxides. These difficulties appear to have been exaggerated. In particular, K. Nassau and his collaborators (3, 4), working at the Bell Telephone Laboratories, have shown that they may be used with remarkable success for producing large single crystals of high melting point oxides by the crystal pulling or Czochralski technique (11). The general arrangement of the equipment is illustrated in the diagram. The oxide or other compound is melted in a crucible conveniently heated by radio frequency and a seed crystal at the end of a rotating holder is dipped below the surface of the melt and then withdrawn slowly and steadily. The crystals produced in this manner are not constrained, as in the Bridgman technique, by the sides of the crucible, and the crystal is under full observation by the operator during the whole of its growing period.

In this equipment Nassau and his colleagues (4) have used rhodium and iridium crucibles successfully for growing single crystals of the following high melting compounds:

Calcium tungstate ..	$CaWO_4$
Strontium tungstate ..	$SrWO_4$
Barium tungstate ..	$BaWO_4$
Barium titanate	$BaTiO_3$
Barium strontium titanate	$Ba_{0.97}Sr_{0.03}TiO_3$
Rutile	TiO_2

In making the above materials some interesting minor variations in the performance of the crucibles were observed. In making calcium tungstate, Nassau and Broyer found that rhodium crucibles ¼ to 1¼ inch diameter with 1.5 mm wall thickness were the most durable. Crystal growth was initiated on a platinum wire and growth was carried out in air between 1610° and 1620°C. Crystals as large as 1 inch in diameter and up to 18 inches long have been pulled. Single crystals of barium titanate were grown at about 1650°C from rhodium crucibles, when 0.36 weight per cent of rhodium was detected in the crystals, and from iridium crucibles when 0.02 weight per cent of iridium was detected. To minimise loss of iridium by the formation of IrO_3 and to ensure a more quiescent melt some crystals were grown under an atmosphere of nitrogen.

For growing rutile a melt temperature of about 1900°C was necessary and for this iridium crucibles were used. When operating in air the melt boiled violently, but quiescent melts were secured in an atmosphere of nitrogen. The single crystals contained only 0.05 weight per cent of iridium.

It seems likely that increasing use may be expected in future of iridium and rhodium as crucible materials for melts which need to be maintained at very high temperatures, around 2000°C. Experience of such workers as those at the Bell Telephone Laboratories indicates that oxidation of these massive metals at these temperatures is not necessarily severe and can be controlled by simple blanketing with an inert gas.

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