The Platinum Metals in the Production of Laser Crystals

By B. Cockayne, B.Sc., Ph.D., A.Inst.P.

Royal Radar Establishment, Great Malvern

Because of their high melting points and lack of chemical reactivity with oxide materials at high temperatures, several of the platinum metals are very useful as container materials for molten oxides. This article describes the use of platinum, rhodium and iridium in the vertical pulling of oxide crystals from the melt. Such crystals form the basis of many solid state lasers and other electronic devices.

Platinum has been used for many years as a crucible material in the solution growth of oxide crystals from solvents such as motlen PbF_2/PbO mixtures in the temperature range 900° to 1400°C. These crystals are often small (maximum dimension < 1 cm) and contain trapped solvent which makes them impure and optically imperfect. With the advent of the solid state laser, the requirement arose for larger oxide crystals (typically 5 cm long by 1 cm diameter) with a very high degree of optical perfection and chemical purity. As a consequence, considerable effort has been devoted to the vertical pulling of oxide crystals from their own melts, because this technique had been used successfully to grow large perfect crystals of semiconducting materials such as silicon, germanium and indium antimonide. The development of the vertical pulling technique for oxides has

demanded solutions to the problems of growing at temperatures in the region of 2000°C under oxidising conditions, and the platinum metals have played a substantial role in the success achieved.

An illustration of the apparatus used for oxide single crystal growth is given in Fig. 1 and the actual growth of a calcium tungstate

Fig. 1 Schematic representation of the apparatus used for the vertical pulling of oxide single crystals:

    A   iridium crucible
    B   iridium heat shield
    C   rhodium-platinum heat shield
    D   r.f. coil
    E   melt
    F   refractories
    G   direction of gas flow
    H   direction of pull
    I   direction of rotation
    J   silica envelope
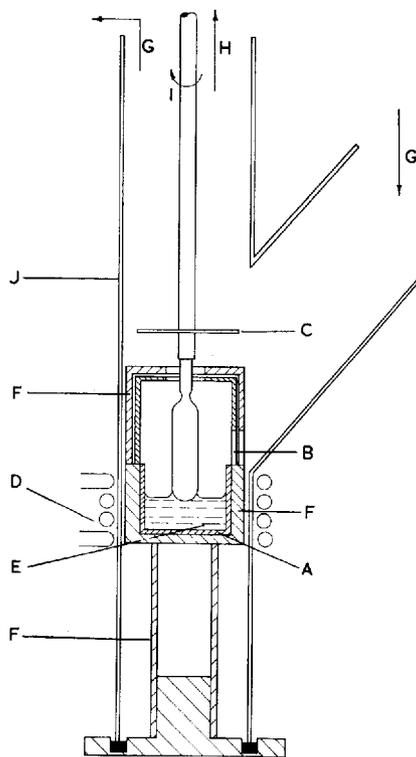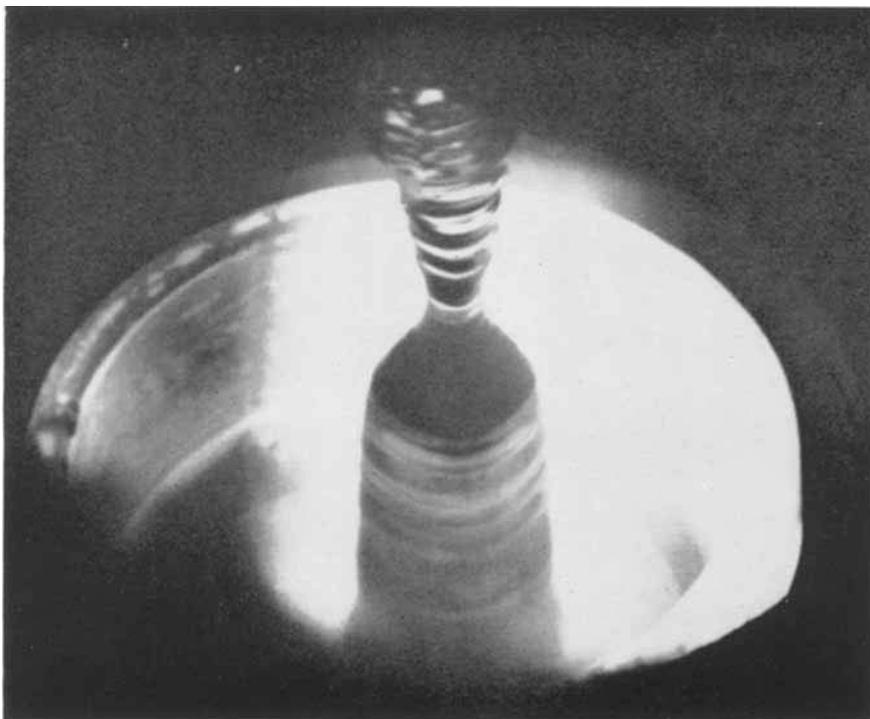
Fig. 2. A single crystal of calcium tungstate being vertically pulled from an iridium crucible at approximately 1600°C

crystal from an iridium crucible is shown in Fig. 2. Essentially, a seed crystal of the same composition as the melt, or an inert material such as an iridium rod, is dipped into the melt. At the optimum temperature, solidification can be made to occur by slowly withdrawing and rotating the seed under carefully controlled conditions, thereby growing a crystal. If an inert rod is used, polycrystalline growth generally occurs, but single crystal growth can be achieved by reducing the diameter of the polycrystalline aggregate until only one crystal is growing. The process of reducing the crystal diameter is also often employed when a single crystal seed is used in order to minimise the propagation of defects from the seed into the crystal. The crystal diameter is controlled mainly by adjusting the heat input to the melt, and the seed crystal can be made to grow out to the required diameter after the necking procedure by reducing the power supplied to the crucible.

As radio-frequency heating is the most commonly used source of power and since oxide materials are generally insulators, the crucible used to contain the melt must also act as a susceptor. Because of the insulating nature of the melt, steep radial temperature gradients exist and the crucible wall is therefore at a higher temperature than the melt centre, which is required to be at or slightly above the melting point of the oxide material. The crucible material chosen for a particular oxide must therefore have a considerably higher melting point than the oxide. The oxides of major optical interest are listed in the table together with their uses and the most suitable crucible materials.

With the higher melting point materials such as sapphire and spinel, the radial temperature gradients can reach 300°C cm⁻¹, and radiation shields or afterheater assemblies are therefore required to minimise the gradients so as to avoid crucible failure before the oxide

is fully molten. These shields are also made of iridium and are shown in the general photograph of platinum metal ware used in the growth of oxide crystals, Fig. 3. The reduction in temperature gradients achieved with the shields and with afterheaters also reduces the thermal stresses to which the growing crystals are subjected, thereby minimising strain (1). This is particularly important in the growth of anisotropic materials such as calcium tungstate and sapphire because dislocation generation readily occurs if the thermal stresses are allowed to exceed the yield stress of the material. Subsequent polygonisation leads to the formation of low angle boundaries, which impair the optical perfection of the crystal by presenting small changes in refractive index to a light beam passing through the crystal.

In the growth of oxides the oxidation resistant properties of the platinum metals are particularly useful. For instance, lithium niobate must be grown in an atmosphere of 100 per cent O_2 to avoid decomposition and platinum is therefore the only suitable crucible material. For the same reason, calcium tungstate and sapphire require small concentrations of oxygen (0.1 to 4 vol. per cent) in an otherwise inert atmosphere. In these cases the iridium crucible is slightly oxidised but the gas flow can be arranged so as to sweep any iridium oxide formed away from the melt surface. If no such precaution is taken, iridium platelets become entrapped within the crystal and act as light scattering centres.

Float Zoning

Oxide single crystals can also be grown by a modified floating zone recrystallisation technique (2). In this method growth is achieved by moving a resistance heated strip, made of the platinum metal appropriate to the melting temperature of the crystal required, in a controlled manner up into a sintered charge rod. The melt thus formed flows through a hole in the strip on to the seed crystal below, where solidification takes place. The seed crystal is maintained at a temperature slightly lower than that of the strip by either a rhodium-platinum or an iridium wound resistance furnace, according to the temperature required. Crystals with melting points up to and including that of sapphire have been grown by this method (3).

Ancillary Uses

In addition to their direct use in crystal growth, the platinum metals also play an important role in ancillary studies leading to the growth of either new or more perfect

Oxides of Major Optical Interest and their Most Suitable Crucible Materials			
Material	M.P. (°C)	Crucible	Material Use
Lithium Niobate ($LiNbO_3$)	1250	Platinum or rhodium-platinum	Electro-optics
Calcium Tungstate ($CaWO_4$)	1566	Rhodium or iridium	Laser host for Nd^{3+}
Yttrium Aluminium Garnet ($Y_3Al_5O_{12}$)	1970	Iridium	Laser host for Nd^{3+}
Sapphire (Al_2O_3)	2050	Iridium	Laser host for Cr^{3+}
Spinel ($MgAl_2O_4$)	2105	Iridium	Possible laser host

Sapphire and spinel are also used as insulating substrates for the epitaxial deposition of silicon
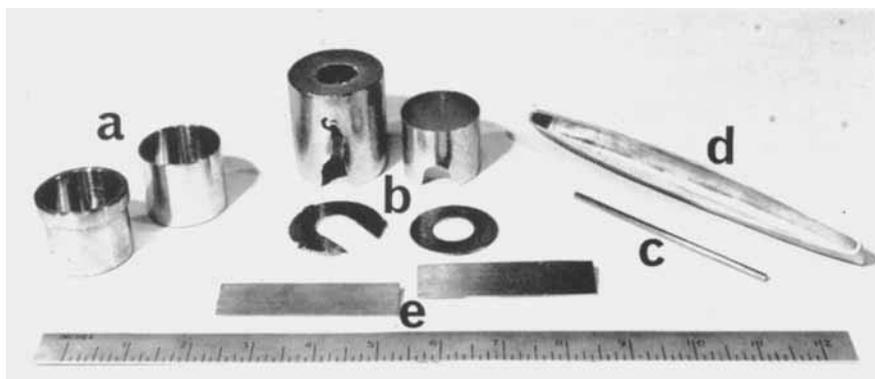
Fig. 3. Platinum metal ware used in the growth of oxide single crystals

a) Iridium and platinum crucibles   *b) Iridium heat shields*
c) Iridium rod   *d) Iridium boat*   *e) Iridium strips for float zoning*

single crystals. For example, certain impurities in calcium tungstate can be removed by zone-refining this compound in an iridium boat, again using radio-frequency heating as the source of power. The high temperature thermocouple materials such as iridium: iridium-rhodium have also been useful in determining the phase relationships in mixed garnet systems such as $Y_3Al_5O_{12} - Gd_3Al_5O_{12}$ and $Y_3Al_5O_{12} - Dy_3Al_5O_{12}$, where the melting points lie within the temperature range $1850°$ to $1970°C$.

The metals platinum, rhodium and iridium thus play an important part in the major growth techniques now used for forming single crystals of high melting point oxides, many of which act as host lattices for laser ions.

References

1 W. Bardsley and B. Cockayne, Conf. Proc. I.C.C.G. Boston (1966) Published as Suppl. to *J. Phys. Chem. Sol.*, 1967, p. 109
2 D. B. Gasson, *J. Sci. Instrum.*, 1965, 42, 114
3 B. Cockayne, M. Chesswas and D. B. Gasson, *J. Mater. Sci.*, 1967, 2, 7

Ruthenium as a Methanation Catalyst

The value of natural gas for domestic heating and for industrial power has long been recognised, but in areas of the world not endowed with a convenient supply some alternative economic source of methane is required. The steam-reforming of higher hydrocarbons (for example, "light petroleum distillate" obtained from mineral oil), or the reaction of steam with carbon, yields a mixture of carbon monoxide and hydrogen from which methane may be produced by catalytic hydrogenation. What is then required is a catalyst that will perform this hydrogenation economically, and this must be a catalyst which is not particularly susceptible to poisoning by carbon monoxide.

A recent report from the United States Bureau of Mines (J. F. Shultz, F. S. Karn and R. B. Anderson, U.S. Dept of the Interior, Bureau of Mines, R.I. 6974, July 1967) has re-emphasised the outstanding catalytic

properties of ruthenium for carbon monoxide hydrogenation. The authors compare catalysts containing ruthenium, rhodium, platinum, palladium and osmium, but of all the catalysts examined only the ruthenium on alumina catalyst was adequately active. It achieved complete reaction at 220 to 240°C, whereas palladium and platinum failed to do this even at 500°C. The kinetics of the reaction using the ruthenium catalysts were examined in some detail: the rate increases with increasing hydrogen pressure and is slightly decreased by increasing carbon monoxide pressure. High molecular weight products appeared only when the H_2/CO ratio in the feed gas fell below two; catalyst poisoning only became important when this ratio fell below unity. The authors concluded that the use of ruthenium for carbon monoxide methanation was economically feasible.

G. C. B.