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High temperature solution growth of yttrium aluminium garnet crystals using accelerated crucible rotation

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The value of ACRT† stirring has been confirmed in the case of $Y_3Al_5O_{12}$ crystal growth, its main advantage being to suppress nucleation in the bulk solution and increase the yield of crystals. Restriction of nucleation to 1 to 5 crystals has been achieved, particularly by close control of temperature stability and by the provision of an "anchor" to prevent crystals from becoming detached due to the stirring action.

1. Introduction

The beneficial effects of stirring in crystal growth from solutions are well established, and large crystals of several materials are grown industrially from stirred aqueous solutions. In the case of high-temperature solutions, the softness of platinum (which is normally the only inert constructional material) is a handicap in the use of immersed stirrers and the volatility of the solvents at the growth temperatures is also a problem. Scheel [1] introduced the accelerated crucible rotation technique (ACRT) by means of which stirring of high-temperature solutions in sealed platinum crucibles is possible through the use of a continuously changing crucible rotation rate. The stirring action occurs through a combination of spiral shearing flow in a horizontal plane and Ekman-layer flow across the crucible base as the solution loses or gains angular momentum. This mode of stirring will occur whenever the rotation rate is changed, for example when rotation is suddenly stopped, but for optimum application in crystal growth the rotation rate must be changed slowly and smoothly in order to avoid the nucleation of new crystals. Typically maximum rotation rates below 50 rpm and periods of 30 to 120 sec are used. ACRT has been successfully applied to the growth of yttrium iron garnet [2, 3] and crystals of excellent quality have been produced on an industrial pilot plant scale [4].

In spite of its successes, definitive studies of the effects of ACRT are sparse and the scarcity of control experiments may have been partially responsible for some reluctance to adopt ACRT stirring. In this paper, the conclusions are reported of a lengthy study of the growth of yttrium aluminium garnet, $Y_3Al_5O_{12}$ from a molten salt solution in which an attempt was made to assess the relative importance of the various factors affecting crystal size and quality, including ACRT stirring.

2. Furnace design

Early experiments were handicapped by a lack of reproducibility which was attributed to inadequate control of the furnace temperature. Precautions were taken, therefore, to protect the environment of the growing crystals from uncontrolled fluctuations arising from sudden draughts or from slow changes in the ambient temperature.

The furnace and crucible assembly is shown diagrammatically in Fig. 1, the crucible being 6 cm diameter and 7 cm high, with a welded lid. The furnace cavity of 23 cm × 23 cm × 23 cm was surrounded by 16 cm insulation and contained six "Crusilite" heating elements supplied by a Euro-

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[†] ACRT: accelerated crucible rotation technique.

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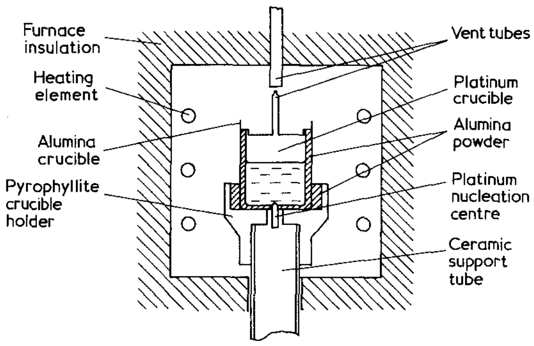

Figure 1 Schematic diagram of furnace and crucible.

therm 040 controller, with a Eurotherm 120 programmer to give the required heating and cooling rates. The sensor used to control the furnace temperature was a Pt–30% Rh/Pt–6% Rh thermocouple which did not require an accurately regulated reference junction [5]. The furnace was located in a hood which was connected to an extraction system operating at a constant flow rate. The temperature in the crucible, with alumina powder substituted for the solution, could be controlled to better than ±0.5° C over long periods and to ±0.05° C over periods of some hours.

Lead fluoride vapour can escape in small quantities from the solvent even from nominally sealed crucibles and can greatly reduce the life of the "Crusilite" heating elements. To prevent such attack, a platinum tube 2 mm diameter and 6 mm long was welded to the crucible lid, and the end partially sealed by crimping. This allowed the escape of air during the initial heating of the crucible and directed PbF_2 vapour to a ceramic vent tube so that it was removed from the furnace cavity by the air extraction system. Heating element life was typically 10 000 h and solvent loss by evaporation was only 1 to 2% over a 3 week experiment.

3. Crystal growth

Van Uitert *et al.* [6] grew $Y_3Al_5O_{12}$ crystals from solutions containing an excess of Al_2O_3. In their large, unsealed crucibles, the Al_2O_3 formed a crust which reduced subsequent loss of solvent by evaporation; but alumina crystals are undesirable in stirred, sealed crucibles since they intergrow with the garnet phase. A stoichiometric $Y_2O_3:Al_2O_3$ ratio was therefore preferred, and no alumina crystals have been observed. The solute concentration was 18 wt% and the solvent consisted of 53.1% PbF_2, 43.4% PbO and 3.4% B_2O_3 by weight [6]. The melt volume was typically 70 cm^3. The solution had a liquidus temperature of 1260° C [7] and a viscosity of about 0.25 p [8] corresponding to a kinematic viscosity in the region of 0.045 St.

In a typical crystal growth experiment, the furnace was heated to 1315° C in 20 h using an ACRT stirring rate of up to 50 rpm, with 120 sec period to ensure a homogenous melt. The system used to produce the rotation programme has been described previously [9]. The furnace was then slow-cooled using a programme based on the principles outlined by Scheel and Elwell [10, 11]. The initial cooling rate was 0.3° C h^{-1} which was automatically increased to 1.6° C h^{-1} over a period of 200 h until the furnace reached 900° C. The cooling rate was then increased to 10° C h^{-1} and this relatively slow rate of cooling the grown crystals was maintained down to room temperature in order to avoid cracking the larger crystals.

It was considered of particular importance to restrict nucleation to the central region of the crucible base, since crystals grown on the base normally contained fewer defects than those grown at the surface of the solution. In attempts to restrict nucleation to a selected site, a crucial parameter is the temperature gradient at this site. Tolksdorf and Welz [2] have reported temperature measurements in the vicinity of their nucleation site and employed gradients of the order of 10° C cm^{-1} in the vertical direction with a much lower horizontal gradient. The vertical temperature profile at the site of the static crucible in our furnace is shown in Fig. 2. The measurement was obtained with the solution replaced with alumina powder but with conditions otherwise similar to those used during crystal growth. The vertical gradient at the nucleation site was slightly below 10° C cm^{-1} and was greater than that obtained by Tolksdorf and Welz [2] in the absence of a cooling air flow, although less steep than the maximum value they could achieve with a cooling air stream passing through a sealed ceramic tube located just below the base of the crucible. A similar cooling system was used in our early experiments but this arrangement suffered from the disadvantage that it introduced additional temperature fluctuations which arose through changes either in the temperature or in the rate of flow of the air, and was therefore abandoned in the interests of precise temperature control. The ACRT stirring resulted in regular

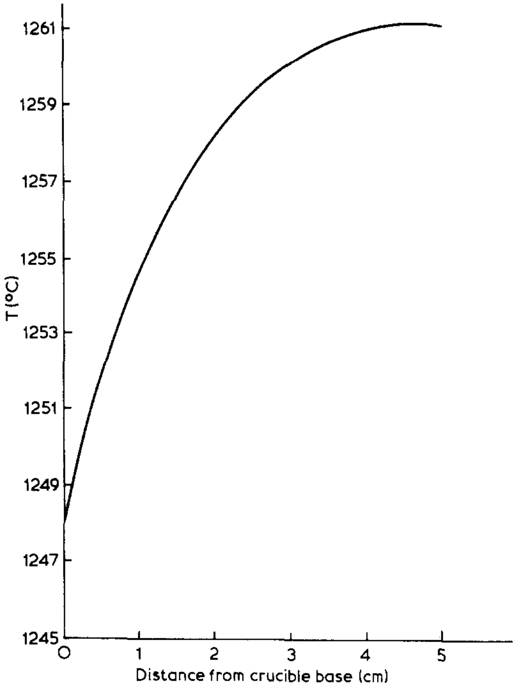

Figure 2 Temperature gradient measured in crucible containing Al_2O_3.

temperature oscillations of about 1° C amplitude in the furnace cavity with the period of the rotation cycle, but these do not appear to have a detrimental effect on crystal quality. Similar oscillations were reported by Tolksdorf [4].

A more serious adverse effect of ACRT was found in the first experiments, since the stirring action caused the crystals to become detached from the crucible base and to float to the surface of the liquid after attaining a size several mm in diameter. Evidence of this effect was provided by the observation of planes of inclusions which formed in regions previously in contact with the crucible base, since the resulting irregular surface grew very rapidly following detachment of the crystal.

This problem was solved by the introduction of a platinum rod welded to the crucible base to act as a nucleation centre. The rod projected 2 mm into the crucible and was tapered to a point. Below the crucible the rod projected downwards for a distance of 14 mm through a 10 mm diameter hole in the crucible holder, so that the nucleation site was cooled both by conduction along the rod and by radiation through the aperture. This arrangement is shown in Fig. 1.

Even with the nucleation projection, crystals could become detached from the crucible base if the rotation rate exceeded 20 rpm. This rate was well below the maximum rate for optimum mixing which was determined from simulation studies to be around 50 rpm. These simulations, using a liquid of similar kinematic viscosity to the high-temperature solution, showed that rapid mixing can be achieved if the rotation cycle is varied from zero to 50 rpm and back to zero over a period of 1 min. Such high rotation rates were used only for stirring the solution prior to slow cooling.

With the maximum rotation rate set at 20 rpm and a gradual acceleration and deceleration it has been found possible to nucleate reproducibly 1 to 5 crystals on the crucible base. A selection of crystals, silver-coated to reveal the external morphology, is shown in Fig. 3. The largest crystal grown to date weighs 33 g (centre crystal of Fig. 3) and was grown using a maximum stirring rate of 20 rpm with a period of 120 sec, and the conditions used in the growth of this crystal (run no 5) and in a range of other typical experiments, are listed in Table I.

In order to confirm the value of ACRT stirring, control experiments were performed using identical conditions (including the use of ACRT to ensure solute dissolution prior to cooling) but with the crucible stationary during growth. The first control experiment resulted in a cluster of five crystals, inclusion-free and of combined weight 22 g, grown on the crucible base. Repetition of this experiment gave a cluster of five crystals weighing only 4 g. In each case a large number of smaller crystals grew on the surface of the solution, and it was this nucleation away from the cooled site that provided the main difference between growth without and with ACRT stirring. The yield of usable crystals is increased from 32% in unstirred solutions to 53% with stirring.

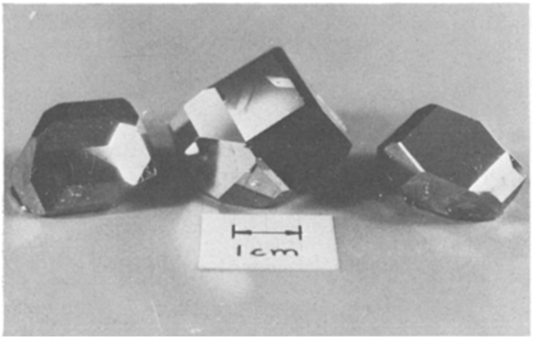

Figure 3 Typical yttrium-aluminium-garnet crystals (silver coated).

TABLE I

Run no	Melt size (g)	Slow cool range (°C)	Slow cool rate ($°C h^{-1}$)	Stirring				Yield of macroscopic crystals (%)	Largest crystal (g)	Comments	
				Soak		Slow-cool					
				Period (sec)	Max. revs (rpm)	Period (sec)	Max. revs (rpm)				
1	399.08	1289 936	0.3–1.5	120	50	180	40	46	6.5	1 crystal on base	
2	399.08	1307 907	0.3–1.4	120	50	180	30	45	15.67	1 crystal on base	
3	399.08	1312 906	0.3–1.6	120	50	180	30	46	31.5	5 crystal cluster	
4	399.08	1315 922	0.3–1.5	120	50	120	20	45	29.1	1 crystal on base	
5	399.08	1300 866	0.3–1.6	120	50	120	20	63	32.8	1 crystal on base	
6	399.08	1305 913	0.3–1.5	120	50	–	–	31	22.4	5 crystal cluster	Control runs
7	399.08	1295 912	0.3–1.5	120	50	–	–	33	4.7	5 crystal cluster	

4. Conclusions

Stirring the solution during crystal growth by slow cooling has the advantage that spontaneous nucleation in the bulk solution can be eliminated, so that crystals nucleate only in a cooled region. The major disadvantage of the application of ACRT to the growth of relatively low-density crystals was the tendency for the crystals to become detached from the nucleation site by acceleration of the crucible. This problem was avoided by the introduction of a fine platinum rod to anchor the crystals, but even with this precaution it was necessary to restrict the rotation rate to 20 rpm.

Crystals over 30 g weight were produced from only 70 ml of solution. Although $Y_3Al_5O_{12}$ crystals of 150 g were produced earlier [12], these required solution volumes of several litres and the central region of these large crystals contained very high concentrations of solvent inclusions. The crystals grown in this investigation were normally of very good optical quality and were often free from inclusions. The dislocation density, as revealed by X-ray diffraction topography was less than 10 cm^{-2}. The crystals are being used in an investigation of the relationship between surface features and internal defect strucutre.

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