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ACCELERATED CRUCIBLE ROTATION: A NOVEL STIRRING TECHNIQUE IN HIGH-TEMPERATURE SOLUTION GROWTH

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The role of diffusion and convection in conventional flux growth is compared with the strong stirring effect of the accelerated crucible rotation technique (ACRT). ACRT allows fast solution flow rates at the growing crystal faces. By this and by homogenization of the solution many problems in flux growth are solved. Control of nucleation in a closed crucible is achieved by combination of ACRT with localized cooling. Large inclusion-free crystals with applications in solid state physics and technology have been grown.

1. Introduction

This paper describes a new technique of stirring and its application to crystal growth from high-temperature solutions[1]).

In crystal growth from melts and from solutions, stirring and, to a lesser extent, convection, reduce the thickness of the boundary layer in front of the growing crystal[2–7]). In a well-stirred system, surface diffusion and particle integration (including the desolvation processes) dominate as rate-limiting growth processes over volume diffusion through the unstirred layer if supersaturation is high enough. Also fast motion of melt or solution relative to the growing crystal surface prevents the adverse effect of constitutional supercooling on the interface stability[8–10]).

By stirring, the solution is homogenized with respect to temperature and concentration. Therefore further nucleation after the first nucleation or after insertion of a seed crystal can be minimized or prevented altogether.

For these reasons stirring is employed in crystal growth wherever possible. But in high-temperature solution growth stirring by seed crystals is extremely difficult because generally volatile solvents like PbO, PbF_2, Bi_2O_3, or mixtures of these with B_2O_3 are used. Rotating seed crystals were applied only in a few exceptional cases which are listed, with the obtained maximum stable growth rates in table 1.

In the following it will be shown that an adequate stirring effect and growth rates as listed in table 1 can be achieved in a closed crucible by accelerated crucible rotation.

Compared to diffusion and convection which are

TABLE 1

Maximum stable growth rates in high-temperature solution growth (from experiments)

Crystal	Solvent	Linear growth rate (Å/sec)	Remarks	Reference
$GdAlO_3$	$PbO–PbF_2–B_2O_3$	~200	ACRT	This work
$NiFe_2O_4$	$Na_2Fe_2O_4$	200	Pulling from solution	11
$NiFe_2O_4$	$BaO–B_2O_3$	~500	Pulling from solution	12
$NiFe_2O_4$	$PbO–PbF_2$	~260	Seeded growth from solution	13
YIG	$BaO–B_2O_3$	120	Seed crystal on stirrer	14
YIG	$BaO–B_2O_3$	150	Pulling from solution	15
YIG	$BaO–B_2O_3$	260	Garnet film growth in a temperature gradient	16
YIG	$BaO–B_2O_3$	~150	Pulling from solution	17
$Ba_2Zn_2Fe_{12}O_{22}$	$BaO–B_2O_3$	200	Pulling from solution	18

slow material transport mechanisms in conventional flux-growth experiments, the Accelerated Crucible Rotation Technique (ACRT) reduces the thickness of the stagnant boundary layer and therefore allows faster stable growth rates. In addition, homogenization of the solution by ACRT combined with localized cooling permits control of nucleation. These statements are supported by estimates of the boundary-layer thickness and the maximum stable growth rate, by simulation experiments, and by successful crystal-growth experiments.

2. The role of convection in high-temperature solution growth

In the conventional flux-growth practice by the slow-cooling technique one relies exclusively on natural convection as the mechanism for material transport and homogenization. By comparison, heat conductivity and diffusion are significant processes only if there are appreciable temperature or concentration gradients. Thus they contribute to heat and material transport at boundary layers, but only very little within the bulk of the solution where, by the crystallization process, by inhomogeneous heating and by flux evaporation, relatively small concentration and temperature gradients are constantly generated. Therefore convection is generally present in crystal-growth experiments*.

The flow velocity of thermal convection is low and amounts to the order of 1 to 5×10^{-2} cm sec^{-1} for typical flux-growth conditions[19]). Even for a low viscosity liquid of 1 centipoise and the high thermal expansion coefficient of 10^{-3} °C^{-1}, the flow velocity will reach only 10^{-1} cm sec^{-1} for a temperature difference $\Delta T = 10$ °C. The width of the metastable Ostwald–Miers region imposes a limit on the permitted temperature difference of roughly this order of magnitude. For these flow velocities the stable crystal growth rate is limited by volume diffusion through the relatively thick boundary layer of approximately 5×10^{-2} cm and lies in the order of 50 Å sec^{-1}. Because of constitutional supercooling only small inclusion-free crystals have been obtained so far.

By the presence of convection cells, pockets with high supersaturations are probably formed locally and cause nucleation of many crystals instead of one or two which then may grow to large sizes. Localized cooling and convection generated by asymmetric temperature distribution increased only slightly the size and quality of the flux-grown crystals. In their crystal-growth experiments with a 2 gallon crucible, Van Uitert et al.[20]) combined crucible rotation with localized cooling at the bottom. Despite the expected improvement in convection the authors reported multinucleation. The resulting YIG and YAG crystals were very large when compared to crystals obtained from smaller crucibles, while the ratio of crystal-to-crucible size seems to have been comparable for large and small crucibles.

3. The accelerated crucible rotation technique (ACRT) in high-temperature-solution growth

Convection alone or in combination with uniform rotation is far from optimum as a material transport mechanism. In high-temperature solution growth a mechanism is required which agitates the solution in much the same way as conventional mechanical stirring in crystal growth from aqueous solutions. Accelerated and decelerated crucible rotation is proposed to achieve such a stirring effect in flux growth. Consider a crucible which is initially at rest. Then constantly accelerate the crucible to rotation about its vertical axis. The outer region of the solution follows the change in crucible motion with little delay. The center of the melt, however, continues to remain at rest due to inertia. Thus a shearing of solution rings is produced. Slowly the center of the solution begins to move, too, until, after a considerable time, it rotates at the same rate as the crucible.

By the laminar slip of the solution around the rotation axis a spiral is formed which, for typical flux-growth conditions and acceleration to 60 rpm, has the order of a thousand arms. Therefore any local variation in solute concentration or in temperature is distributed along this spiral. Since the spiral arms have a radial distance of less than a tenth of a millimeter, the concentration and temperature differences disappear by diffusion and heat conduction in a time of less than a second. The hydrodynamics of convection and of ACRT will be presented in the paper by Schulz-DuBois[21]).

Alternating accelerated and decelerated crucible ro-

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* Convection flow rates due to thermal and concentration differences are believed to be of the same order of magnitude generally, depending on the material parameters and the growth conditions.

TABLE 2

Comparison of the influence of diffusion, convection, and ACRT on thickness of boundary layer and on maximum linear growth rate for volume-diffusion-limited growth

	Mean velocity of solution (or particles) at the crystal surface (cm sec^{-1})	Thickness of boundary layer[a] (cm)	Maximum linear growth rate (Å sec^{-1})
Diffusion	(5×10^{-5})	(1.7)	(0.5–3)
Convection[b]	4×10^{-2} [c]	6×10^{-2}	20–80
ACRT	1	1.2×10^{-2}	100–500
ACRT	10	4×10^{-3}	(300–1500)[d]
ACRT	100	1.2×10^{-3}	(1000–5000)[d]

[a] Calculated from formulas of Carlson[4]) and of Bennema[6]).

[b] For $T = 1400$ °K, $\Delta T = 10$ °C, $l = 5$ cm, $\eta = 2$ cp, $\rho = 7.5\ \text{g cm}^{-3}$, $c_p = 0.15\ \text{cal g}^{-1}\ \text{deg}^{-1}$, $\beta = 8\times10^{-4}\ \text{deg}^{-1}$, $K = 0.02\ \text{cal cm}^{-1}\ \text{sec}^{-1}\ \text{deg}^{-1}$.

[c] After Cobb and Wallis[19]), we get the same value for our conditions.

[d] Surface reactions are rate-limiting processes.

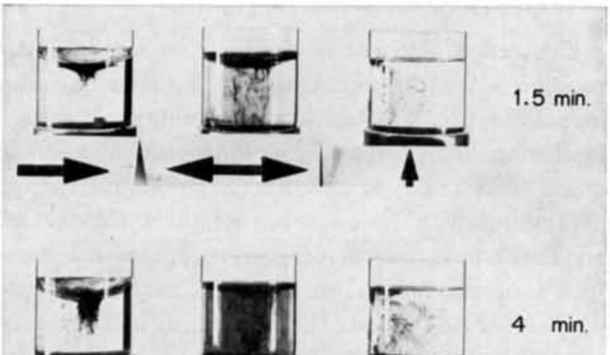

Fig. 1. Simulation experiment demonstrating the strong mixing effect of ACRT.

tation acts much the same way as a stirrer acting in the laminar regime. In addition to this rotational stirring effect, mixing in vertical and radial directions is provided by the Ekman flow and by the deformation of the liquid due to centrifugal forces, which is demonstrated by the parabolic surface at high rotation rates and the nearly flat surface of the liquid at rest. And, of course, there will be the relatively small mixing effect of the superimposed natural convection.

If the ACRT stirring technique is combined with localized cooling, control of nucleation is possible and only one or two nuclei are formed. Similarly, if a seed crystal is arranged in the crucible and all conditions are properly controlled, there is no additional spontaneous nucleation.

A forced flow of solution is produced along the crystal surface. The flow rate is determined by the properties of the solute-solvent system, by the crucible (and crystal) geometry and dimensions, and by acceleration and rotation rates. Flow velocities of 1 or even 100 cm sec^{-1} relative to the crystal are not difficult to

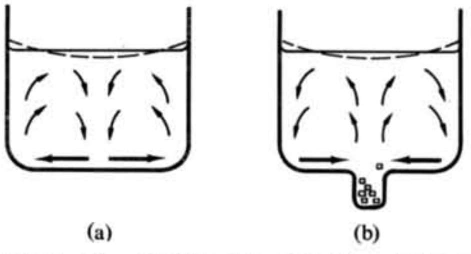
(a) (b)

Fig. 2. (a) Direction of radial and vertical flow during acceleration due to centrifugal forces (Ekman flow). (b) Trap of crystallites during deceleration.

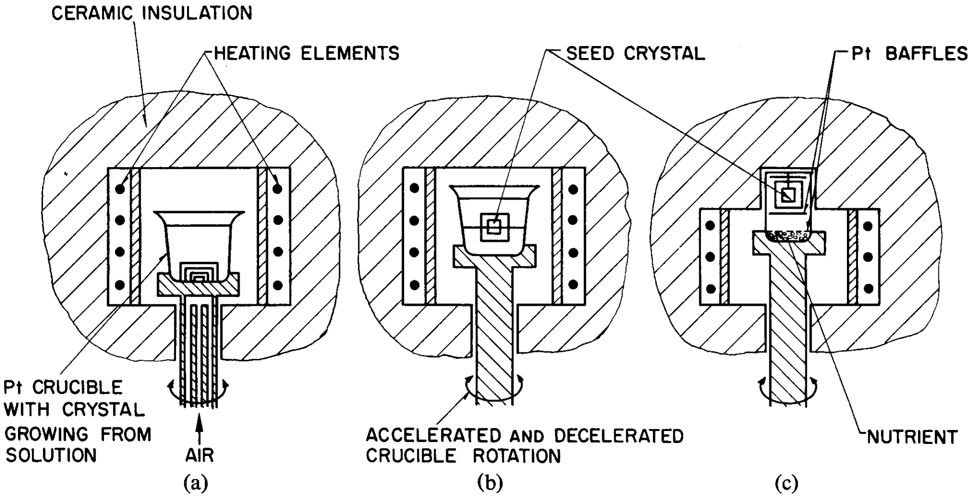

Fig. 3. (a) ACRT with localized cooling for nucleation control (slow cooling technique). (b) ACRT with a seed crystal under iothermal conditions (slow cooling technique). (c) ARCT with as seed crystal in constant temperature gradient.

realize. These reduce the thickness of the stationary boundary layer[4,6]) surrounding the crystal to the order of 10^{-2} to 10^{-3} cm, which, in turn, permits greater stable growth rates. In table 2 a comparison of the boundary layer thicknesses and the corresponding stable growth rates calculated for volume-diffusion-controlled growth are shown for the flow rates of convection and of ACRT, respectively. The data for pure diffusion are also shown and are somewhat hypothetical since one would expect convection to be present generally in flux-growth experiments. Crystal growth by convection requires an extremely low cooling rate in order to maintain a stable crystal growth rate of approximately 50 Å $\sec^{-1}$ only. In ACRT a flow rate of 1 cm $\sec^{-1}$ is adequate for a stable growth rate of 100 to 500 Å $\sec^{-1}$. From table 1 it appears that no growth rates higher than this order of magnitude have ever been observed experimentally. This evidence suggests that by application of ACRT the diffusion through the boundary layer is no longer the main growth-rate limiting process.

4. Simulation experiments and crystal-growth results

The ACRT stirring effect can be easily demonstrated by a simulation experiment. Three glass beakers containing a liquid of a viscosity of 2 centipoise ($H_2O+H_2SO_4$) are heated from below in order to establish convection. Equal amounts of $KMnO_4$ as a coloring agent are placed at the center of the liquid surface where they float due to surface tension. The left beaker is continuously rotated, the right one remains at rest, while the center one is subjected to accelerated and decelerated rotation by a motor which is switched on and off for about a minute at a time. Fig. 1 shows the situation at times of 1.5, 4, 15, and 66 min, respectively, after the beginning of the experiment. In the center beaker the $KMnO_4$, as far as it is dissolved, is distributed homogeneously over the entire beaker volume in a time of one or two cycles of acceleration. After 15 min all the $KMnO_4$ is completely dissolved and a homogeneous solution is obtained.

In the uniformly rotated beaker there are stable unmixed regions with no coloration at all. This agrees with the observations by Carruthers and Nassau[22]). Due to Taylor–Proudman cells in the uniformly rotated beaker there seems to be even less mixing than in the stationary one.

In fig. 2 the directions of Ekman flow and the deformation of the liquid body due to centrifugal force are shown. The most simple experiment for demonstration of the Ekman flow is a cup of tea containing tea leaves. These tea leaves float to the circumference, when the tea is stirred, and back to the center when the stirring action is stopped.

Figs. 3a–3c show examples of experimental arrangements for flux growth by ACRT. To date, the greater part of our experience is with the method of fig. 3a. The 500 cm^3 platinum crucible with its special mechan-

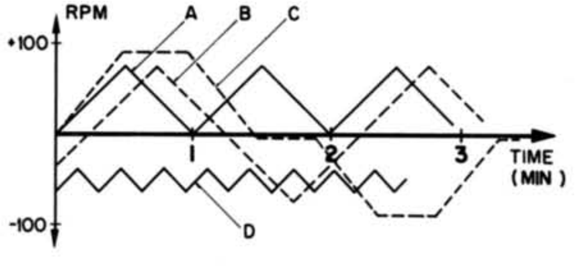

Fig. 4. Examples of cycles of accelerated crucible rotation.

ical stable shape is sealed by argon-arc welding, and is supported by a suitably shaped ceramic disk which in turn is placed on a ceramic tube. The latter is rotated about its vertical axis with periodically alternating acceleration and deceleration. Several useful cycles are illustrated in fig. 4. For flux growth, cycles A, B, C are appropriate. Cycle D may be useful in the Czochralski technique, when corresponding accelerated counter rotation of the crystal is used additionally.

Initial experience with the ACRT was gained by growing gadolinium aluminate, $GdAlO_3$, an orthorhombic perovskite-type compound, from PbO-PbF_2-B_2O_3 solution. Many experiments without ACRT in crucibles of 30 to 1000 cm^3 yielded crystals of $GdAlO_3$ up to 20 g weight with flux inclusions and inclusion-free crystals up to 8 mm in size (approx. 4 g). For ACRT experiments the mixture of the starting materials of highest purity was premelted in the 500 cm^3 platinum crucible, which was sealed and heated to 1300 °C for 15 hr. Then it was cooled to 900 °C at a rate which increased from 0.3 to 0.5 $°C\ hr^{-1}$. Faster cooling rates than these caused interface instability (flux inclusions) by stronger constitutional supercooling (large faces, higher viscosities, decreasing diffusion coefficients). At the end of the run the crucible with the one or two crystals formed was allowed to cool slowly to room temperature.

The first two runs yielded just one crystal of $GdAlO_3$ each, of 210 g and 104 g weight, respectively. Another run in a small 140 cm^3 crucible yielded just two crystals with a total weight of 44 g. Fig. 5 shows the above-mentioned crystal of 210 g weight in the interior of which the light from behind is reflected. The overall dimensions of the crystal are $3.5 \times 3 \times 2.5\ cm^3$. Like other spontaneously nucleated crystals, this crystal shows a central region of dendritic growth. However the outer portions of these crystals of about 1 cm thickness are optically clear and free of inclusions. In crystal growth from aqueous solutions dendritic growth can be prevented by use of seed crystals. First experiments with seed crystals and ACRT in crystal growth from high-temperature solutions are promising. Other work is directed to magnetic materials, and large inclusion-free garnets have been grown.

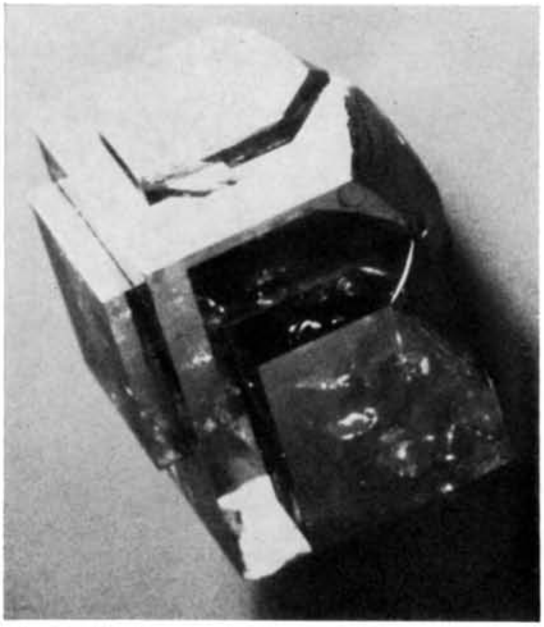

Fig. 5. Gadolinium aluminate crystal of 210 g weight showing internal light reflection through clear portion.

Subsequent to our preliminary description of ACRT at national crystal growth conferences[23]), other laboratories had similar success with crystal growth of magnetic garnets and of manganese telluride by ACRT[24]).

5. Conclusions

The accelerated crucible rotation technique (ACRT) has been demonstrated to have a strong stirring effect in crystal growth from high-temperature solutions by successful crystal-growth runs and by simulation experiments. Specifically, ACRT accomplishes control of nucleation, it suppresses the adverse effects of constitutional supercooling and convection, and it permits the realization of stable crystal-growth velocities in the range of several hundred Å sec^{-1}. The method is believed to be especially useful in the growth of large crystals for the magnetic bubble domain technology, for laser rods, and for electrooptic or nonlinear optical materials. Simulation and preliminary crystal-growth experiments indicate that ACRT is a valuable aid also for crystal growth from melts, from the vapor phase, and from hydrothermal solutions.

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