Journal of Crystal Growth **8** (1971) 304–306 © *North-Holland Publishing Co.*

FLUX GROWTH OF LARGE CRYSTALS BY ACCELERATED CRUCIBLE-ROTATION TECHNIQUE

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Received 19 October 1970

A novel stirring technique is described which, in conjunction with localized cooling, permits control of nucleation in closed crucibles for crystal growth from high-temperature solutions.

There seems to be general agreement that the growth of big single crystals from high-temperature solutions would be possible under the following conditions:

(1) Control of nucleation[1–3]);

(2) Maintenance of a sufficiently fast solution flow at the crystal interface[4,5]);

(3) Prevention of constitutional supercooling[4,6]);

(4) Prevention of dendritic growth after nucleation[7,8]).

In crystal growth from aqueous solution, these conditions are realized by the use of seed crystals and stirring. Unfortunately, both seed crystals and stirring are extremely difficult to employ under the conditions of high-temperature solution growth which require a sealed crucible for solvents of high vapor pressure (see for instance refs. 9–12).

In the following we wish to discuss a new crystal-growing method using accelerated crucible-rotation technique (ACRT) which, in conjunction with localized cooling, seems to solve problems (1)–(3) above.

Note that uniform crucible rotation[13]) does not lead to adequate mixing of the melt. The crucible and melt rotate at the same angular velocity. The main virtue of uniform rotation is the fact that it tends to diminish temperature differences due to a thermally asymmetric furnace.

On the other hand, accelerated rotation, for example, bringing a crucible from rest to rotation, leads to effective stirring of the liquid. Parts of the solution close to the crucible wall follow any changes in the motion with little delay. Parts further inside tend to continue in their previous motion due to inertia. The resulting pattern of motion is one of slippage and shear around the rotation axis. Now assume that there was a local variation in solute concentration (or temperature) before the accelerated rotation commenced. After

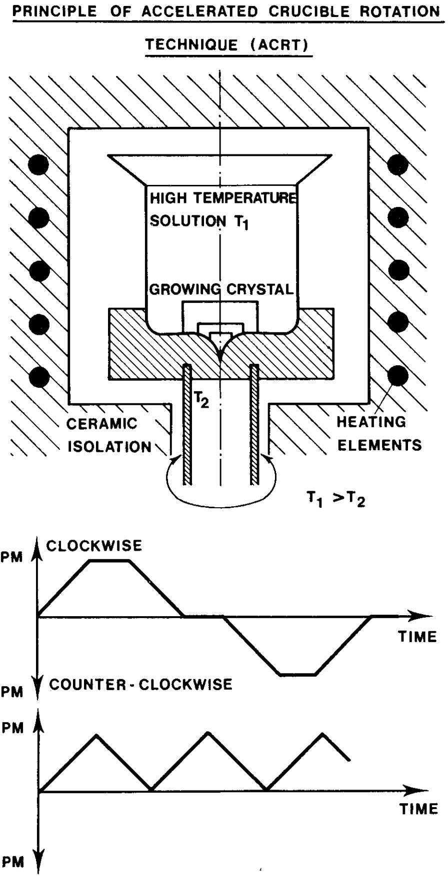

Fig. 1. The experimental setup with the platinum crucible on the ceramic tube whose rotation is accelerated and decelerated. The curves show sample cycles of accelerated rotation.

accelerated rotation, this inhomogeneity is still located at the same radial distance from the axis as before, but it is now distributed in the shape of a tightly coiled spiral. In this pattern, material of the deviating concentration is in close contact with other material. As a result, the ordinary diffusion (heat-conduction) process leads to a rapid equalization of the concentration (and temperature). Note that accelerated rotation mixes the liquid in much the same way as a uniformly rotating stirrer in the laminar regime.

The effectiveness of this stirring mechanism may be illustrated by the following example. A melt of density 6 g cm^{-3} and viscosity 5 cp in a crucible of radius 5 cm is brought to uniform rotation of 60 rpm. Then the spiral arms discussed above have a radial distance of 0.007 cm. With a typical solute diffusion constant of 10^{-5} cm^2 sec^{-1} the concentration difference disappears by diffusion in a time of about 0.1 sec. The equalization of temperature is even faster.

Only circular mixing has been explained by ACRT. As we found from simulation experiments, mixing in radial and vertical directions occurs by convection (which is always present with temperature gradients) and by the motion of the solution caused by centrifugal forces. Additional mixing is caused by the shape of the crucible, by baffles which may be fixed to the crucible wall, and of course by the growing crystal itself.

Experience with crystal growth from aqueous solutions indicates that excessive agitation is not favorable for growing high-quality crystals[14]). Therefore, instead of switching from zero to full rotation and vice versa we decided to accelerate and decelerate the crucible rotation smoothly for a more continuous flow of the solution relative to the growing crystal. Two pro-

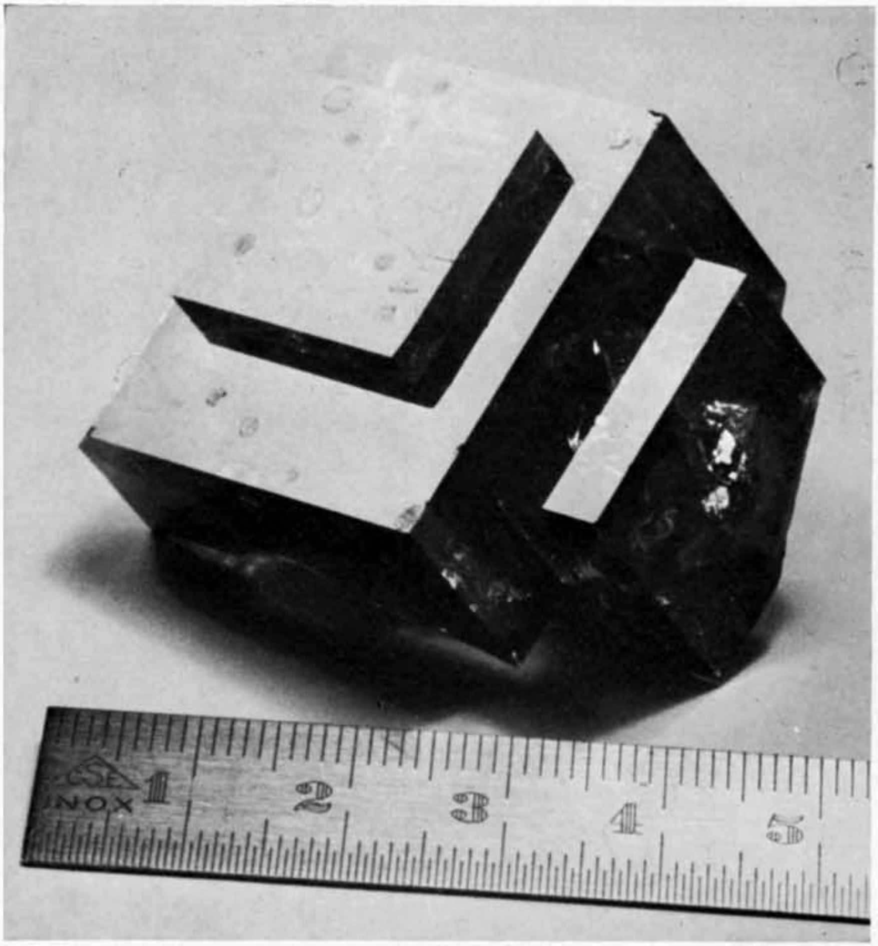

Fig. 2. A 210 g $GdAlO_3$ crystal grown from $PbO–PbF_2–B_2O_3$ solution by accelerated crucible rotation technique.

grams of accelerated rotation are illustrated in fig. 1. The optimum values of the cycling time and of the maximum rotational rate can be estimated by approximate analysis or from experience. The figure also shows the experimental setup. We have used platinum crucibles of 140 to 500 cm^3 with a cooled tip at the center of the bottom. Cooling is provided by thermal radiation through the supporting ceramic tube, occasionally enhanced by forced air flow. The arrows indicate the direction of accelerated crucible rotation.

Fig. 2 illustrates one example of the successful application of this method. The picture shows a 210 g crystal of $GdAlO_3$, an orthorhombic perovskite compound. It was grown from $PbO-PbF_2-B_2O_3$ solution in a 500 cm^3 crucible by cooling from 1300 to 900 °C with cooling rates of 0.3 °C/hr at the beginning to 0.6 °C/hr at the end of the run. This crystal grew from the only nucleus formed and it represents 66 per cent of the starting material. The center of the crystal shows dendritic growth, whereas the outer region of 1 cm thickness has good optical quality. Prior to this work, the largest clear $GdAlO_3$ crystals grown had a maximum size of a few millimeters[15-18]).

Future use of large seed crystals should make it possible to avoid the initial dendritic growth.

We feel that crystal growth under accelerated crucible rotation has considerable potential, not only with high-temperature solution growth, for example, of laser and bubble domain materials, but also in conjunction with the Czochralski technique. A more detailed description of ACRT is in preparation.

The authors thank Mr. H. Schmid for designing the apparatus.

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