CRYSTAL GROWTH FROM MELTS IN 0-G ENVIRONMENT

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ABSTRACT

The value of highly perfect single crystals to technology is discussed. Many crystals used sell in the range $10,000 - $100,000 per pound. Many potentially useful crystals which cannot be grown on earth because the melt cannot be contained could be grown from containerless melts in 0-g. Very desirable increases in perfection of other crystals currently being used could probably be achieved in 0-g. The factors limiting perfection and their relation to gravity are discussed. Different techniques of growth in 0-g are discussed and a very versatile crystal pulling apparatus which combines the advantages of float zone refining and Czochralski growth is schematically described.

PROMISE

Of the many possibilities which have been suggested for space manufacturing it seems to us that crystal growing offers the most promise of rapid economic success. Many crystals now used in technology for such purposes as lasers, laser modulators, semiconducting devices, transducers, substrates for large scale integrated circuits, etc., sell for prices in the range of $10,000 - $100,000 per pound. The fact that these prices are paid gives a measure of the technological value of the crystals.

Many potentially useful crystals have not realized their promise because it has not proven possible so far to produce them of suitable size and perfection. In a number of cases this seems to be solely due to the unavailability of a crucible material that will hold a melt from which the crystal can be grown. Noteworthy examples of difficult to contain melts are transition metal oxides including rare earth iron garnets and compounds with high alkali and alkali earth content.

We believe crystals of this class can be grown relatively easily from containerless melts in space and that the economic rewards from such an accomplishment would clearly be great.

In many other cases the crystals currently used in technology are limited in perfection by fluctuations in composition and/or the accompanying strains. Semiconductors, for example, are very sensitive to dopant levels (carrier concentrations) and even small fluctuations can render the device useless. Ferroelectric crystals used for laser modulation, second harmonic generation, and other nonlinear effects are extremely sensitive to fluctuations in stoichiometry which induce domain structure and/or result in birefringence variations. This effect causes detrimental optical losses in the device.

There are at least three well recognized causes for these composition fluctuations in melt grown crystals[1] 1) Faceting results from the irregular nucleation of new growth along <u>low index planes</u> in a low temperature gradient. 2) Constitutional supercooling results from the instability of the growth front to a perturbation in the composition of the melt under conditions of high temperature gradient. In extreme cases this leads to the formation of trails of precipitated solute. 3) Temperature fluctuations leading to compositional fluctuations result from turbulent[2] or oscillatory[3] convection in the melt.

These convective thermal oscillations during growth have long been known to lead to oscillations in the carrier density of semiconductors.[4] Growth striations due to this cause have also recently been positively identified in[1,2] rare earth doped CaF_2, $Nd\text{-}CaWO_4$, $Ba_2NaNb_5O_{12}$, $Nd\text{-}Y_3Al_5O_{12}$, $Cr\text{-}Al_2O_3$, and $Cr\text{-}MgAl_2O_4$.

Convection and the associated oscillations would of course be absent in 0-g. Absence of convection and the constraints imposed by a melt container in 0-g also offer the possibility of arranging the heater and insulation geometries in such a way that the freezing isotherm is not near parallel to any low index crystal planes and at the same time the temperature gradients are small. This would minimize problems due to both faceting and constitutional supercooling. Therefore, there is real promise that better quality crystals of these materials can be grown in o-g.

Modest improvements in crystal quality resulting in devices with improved characteristics or higher yields of acceptable devices could again have a tremendous economic importance.

TECHNIQUES

Conceptually the simplest way of growing crystals in 0-g is from a seeded free floating melt. This possibility was mentioned by several speakers last year. Consideration of surface energies indicates that the seed and growing crystal would always stay inside the spherical melt until the maximum dimension of the crystal corresponded to the diameter of the melt. Perfection of crystals obtained by this technique would be limited by faceting and constitutional supercooling as are other melt grown crystals.

The cooling time necessary to grow high quality crystals would certainly be measured in hours. Clearly some method of keeping the melt centered in the furnace for this length of time would be needed. Magnetic induction and gas jets have been suggested as means for positioning such a melt. Both would probably lead to temperature fluctuations in the melt and hence imperfections in the crystal.

In addition the constant attention of an operator would be necessary to keep the melt centered. Alternatively, a servo system could possibly be devised but this would involve an additional development of sensors and control circuitry. It might be difficult to design sensors and positioning devices compatible with a furnace which will provide the necessary temperatures and temperature gradients.

All of this is not to say that good crystals could not be grown from a free floating melt. It is only to convince you that the modified Czochralski method which we propose is actually simpler as well as far more versatile.

A schematic drawing of our design is shown on slide 1. It can also be looked at as a modification of the floating zone principle to incorporate the advantages of the Czochralski method. These are the use of a well crystallized seed and the ability to neck down the crystal to prevent the propagation of twin boundaries, dislocations, etc.

The basic equipment would be two opposing crystal pullers with reversible and varying pull rates and a suitable heating arrangement with controls and programmer. The insulation would be designed and fabricated from suitable materials for the specific crystal pulled. A versatile puller would have interchangeable containers for a variety of atmospheres, i.e., reducing or oxidizing. This design would not require positioning of the melt.

Slide 2 shows the operation of the puller. The end of a large, prepared ingot or crystal would be positioned and melted in the furnace. The ingot could be prepared by pressing and/or sintering a combination of materials yielding the right chemical composition. After the melt is obtained and thermally stabilized, the opposite puller would introduce a seed into the melt. The melt and seed could be simultaneously moved within the furnace to establish the proper gradients, etc. The seed puller would then "pull" the crystal as in the Czochralski technique. As the material is removed from the melt, the feed rod puller could replenish the supply at a steady rate. We believe a crystal puller of the type described here could be engineered, built, and tested within a year, and hence could easily be ready to go on a 1973 flight. Space Manufacturing Process Chamber #2 appears to have enough room for equipment designed along fairly conventional lines.

One final subject must be discussed. That is the source of heat which will be used. This has two aspects, the type of heating element in the furnace and the ultimate power source. Each useful crystal produced by melt growth will require from several kilowatt-hours to several tens of kilowatt-hours of energy. The only ultimate sources of power which appear practical are solar power and nuclear power. If nuclear power is used, the heating elements could be of any conventional type, i.e., resistance, electron beam, glow discharge, induction, etc. This has obvious advantages.

If solar power is to be used, it seems that high priority should be given to design of such a furnace and a Space Manufacturing Process Chamber compatible with it. A polar orbit would probably be required for the successful use of solar power. Solar power might have advantages for certain refractory insulating materials, but glow discharge heating should also be considered.

Since in the 1973 tests only battery pack power will be available, experimental runs should be made with a relatively low melting point material to limit power consumption. The material should also have been thoroughly studied on earth so that the results can be interpreted unambiguously. Many materials qualify, for example, KCl.

Production of say 100 crystals with a value of several million dollars would require of the order of 1000 kilowatt-hours of energy. Assuming this power is available, quantity production could begin in the 1975 space station.

A real evaluation of the cost effectiveness of crystal growth from melts in space depends on a realistic assessment of the power cost.

References

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3. D. T. J. Hurle, J. Gillman, and E. J. Harp, Phil. Mag. 14, 205 (1966).
4. D. T. J. Hurle, Phil. Mag. 13, 305 (1966), and references therein.

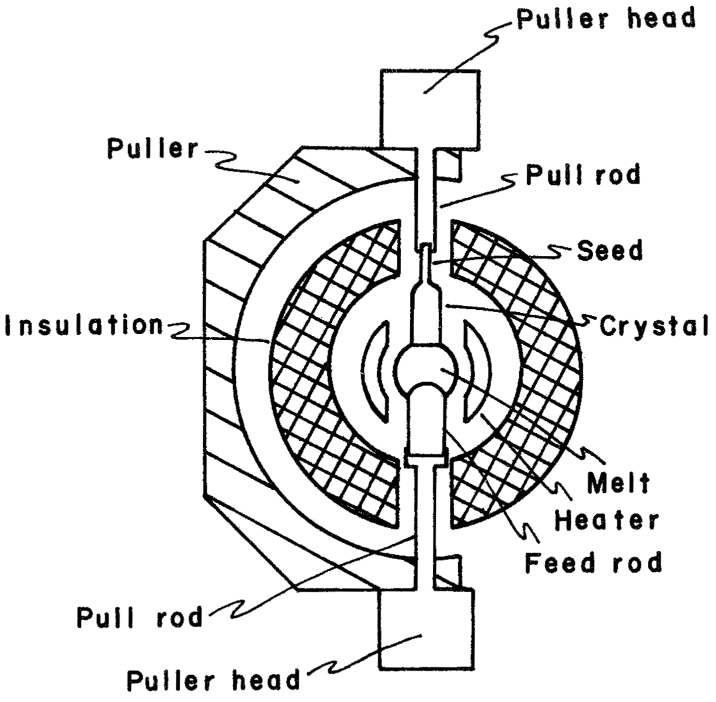

Fig. 1 Pull for 0-Gravity Environment

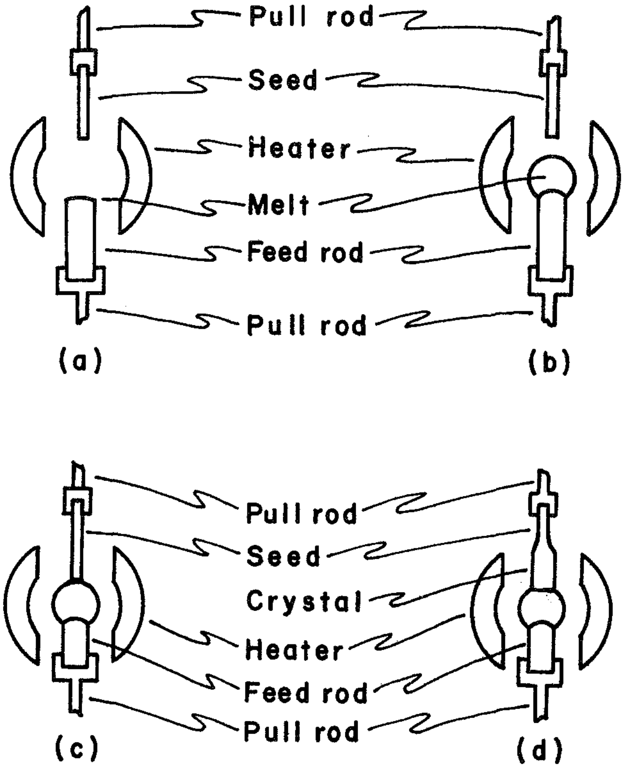

Fig. 2 Procedure for Crystal Growth in 0-Gravity Puller