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Growth of single crystals of copper and their thermal profile estimation

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Abstract. Copper crystals have been grown by Czochralski technique in a 6-bar argon gas environment. X-ray analysis shows that these are single crystals and are strain-free. A slight pressure environment that is truly hydrostatic seems to improve the quality of the crystals. Thermal profile estimation results show that the values of temperature which decrease upto the neck region are same in magnitude as those measured during the experiments and that necking improves the thermal profile and, consequently, the crystal quality. No facet formation has been observed in these crystals.

Keywords. Copper crystals; high pressure growth; Czochralski technique.

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1. Introduction

The melt growth methods, where crystallization takes place by a phase change from liquid to solid, have been in continuous use for several years (Gilman 1963; Brice 1965; Lal 1982) and are being extensively employed for the growth of a variety of single crystals including those of metals and their alloys. Renewed interest in these techniques is due to the importance of these crystals in industry and in the understanding of the basic mechanisms of crystal growth (Bennema 1984; Giling and Dam 1984). The crystal properties are critically dependent on the crystal perfection and there is great interest these days in the growth of highly perfect crystals (Rosenberger 1979). One of the imperfections which are incorporated during the crystal growth is the dislocation. There are several factors which lead to high dislocation density often observed in melt grown crystals. In Czochralski growth, the dislocations often result from the high thermal stresses present in the crystal during the growth. So, if one can monitor these thermal gradients in the growing crystal one can obtain highly perfect crystals.

Among the various metals, copper has been chosen for single crystal growth, as its physical parameters are well established. Single crystals of copper with low dislocation content (dislocations $< 10^3/cm^2$) have always been found difficult to grow because the yield stress of copper is low which makes it very sensitive to thermal stresses. Moreover, its surface gets contaminated very easily, thereby producing dislocations in the growing crystal. Different workers have studied the growth of copper crystals (Faust 1968; Savitskii and Novokhatskya 1968; Inoue 1974; Wantabe 1974; Van der Hart and Uelhoff 1981). Inoue has grown these in vacuum of $1–3 \times 10^{-5}$ torr by the Chalmers

method. The growth direction was ⟨111⟩ and dislocation density ranged from 10^5–10^6/cm^2. Their microstructural studies indicated the presence of a network of small angle boundaries in these crystals. Wantabe has grown copper crystals by the Bridgman method. The observed dislocation densities were of the order of 10^5/cm^2 and the crystals contained sub-boundaries. Low dislocation density copper crystals have been grown by a number of workers (Sworn and Brown 1972; Buckley-Golder 1977). Sworn and Brown observed small dislocation loops and did not detect screw dislocations as the topographic arrangement employed by them was not suitable for their detection. So the dislocation content of their crystals could be greater. Buckley-Golder succeeded in growing low dislocation density crystals but these were of small dimension (diameter ~ 1·2 mm). In the present paper, attempts to grow strain-free low dislocation density single crystals of copper employing high pressure growth and the thermal profile calculation performed for crystals of specific shape are reported. In §2 we shall briefly discuss the heat flow problem in Czochralski system. The experiments will be described in the following sections.

2. Heat flow in Czochralski system

Figure 1a shows the Czochralski system and figure 1b the heat flow in the sytem. The general heat flow equation may be written as (Van der Hart and Uelhoff 1981)

$$\nabla\cdot(\lambda\nabla T)=\rho c\frac{\partial T}{\partial t}, \tag{1}$$

where T is the temperature, λ the heat conductivity, ρ the density, c the specific heat and t the time. If the heat conductivity is independent of the temperature, then (1) can be written in cylindrical co-ordinates as

$$\left\{\lambda\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\partial^2}{\partial z^2}\right)-\rho vc\frac{\partial}{\partial z}-\rho c\frac{\partial}{\partial t}\right\}\ T=0, \tag{2}$$

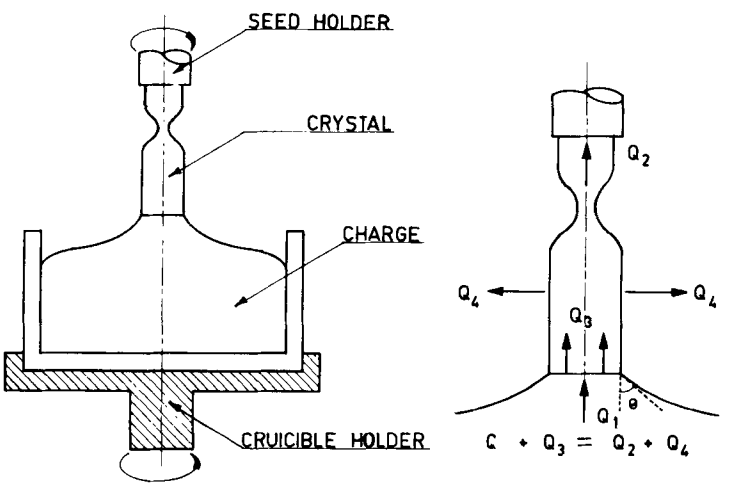

Figure 1. a. Principle of Czochralski crystal pulling process. **b.** Heat flow in a growing crystal.

where v is the speed at which the crystal is pulled. Now the heat diffusion length $\lambda/\rho c$ for copper is 500 cm which is very large compared to the length of the crystal; so we can neglect the time dependence and (2) then reduces to

$$\left(\frac{\partial^2}{\partial r^2}+\frac{1}{r}\frac{\partial}{\partial r}+\frac{\partial}{\partial z^2}-\frac{v\rho c}{\lambda}\frac{\partial}{\partial z}\right) T=0. \tag{3}$$

One can assume that the temperature inside the crystal is independent of radius R_c and so we write (3) as

$$\frac{\partial^2 T}{\partial z^2}-v\rho c\frac{\partial T}{\partial z}-\frac{\dot{Q}}{V}=0,$$

where $\dot{Q}$ is the heat loss to the wall and V is the volume of radiating object ($V=\pi R_c^2\Delta z$) and is expressed as

$$\dot{Q}=2\pi R_c\Delta z h[T(z)-T_0(z)].$$

Now (3) becomes,

$$\lambda\frac{\partial^2 T}{\partial z^2}-v\rho c\frac{\partial T}{\partial z}-\frac{2h}{R_c}(T-T_0).$$

This equation will have exact solution if the material constants, R_c and T_0 are independent of z

$$T(z)=A\exp[p_1(z)]+B\exp[p_2(z)]+T_0$$

$$p_{1,2}=\frac{v\rho c}{2\lambda}\pm\left[\left(\frac{v\rho c}{2\lambda}\right)^2+\frac{2h}{\lambda R_c}\right]^{1/2}.$$

The boundary conditions chosen are

(i) $T=T_m$ at the interface, where T_m is the melting point of copper.
(ii) $T=T_p$ at the seed holder where T_p is the temperature of the water-cooled seed holder.
(iii) Radiation loss is $-\lambda(\partial T/\partial r)=\dot{q}_{\text{rad}}$ at $r=R_c$, $0<z<z_c$ which in linearized form is

$$\dot{q}_{\text{rad}}=\Gamma\varepsilon\sigma[T(r,z)^4-T_0(z)^4]$$
$$=h[T(R_c,z)-T_0(z)],$$

where Γ is the view factor, h is the heat transfer coefficient which is computed by iteration. The temperature field is thus calculated by an iteration method in the following way. The geometrical dimensions and the shape of the crystal are fixed. The temperature field is computed with a set of initial values of the thermal field. The new temperature profile is obtained by iteration procedure using the previous temperature profile. If the difference between temperatures in successive iterations is $< 0{\cdot}1$°C the iteration process is stopped.

In reality the material constants are temperature-dependent. Since the temperatures in the growing crystal vary largely, one has to consider this dependence. For this we employ the slice model (figure 2). The crystal is divided into N-slices of thickness Δz.

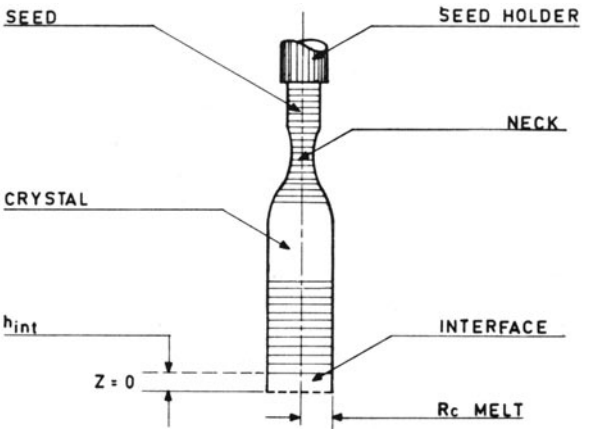

Figure 2. The mathematical slice model.

The material constants and the temperature of each slice are then assumed to be constant. The temperature of each slice will be

$$T_i(z) = A_i \exp[p_1(i)z] + B_i \exp[p_2(i)z] + T_0^i,$$

where A_i, B_i are constants which depend on the boundary conditions and the geometry of the slice.

$$p_{1,2}(i) = \frac{v\rho_i c_i}{2\lambda_i} \pm \left[\left(\frac{v\rho_i c_i}{2\lambda_i}\right)^2 + \left(\frac{2h}{\lambda_i R_i}\right)\right]^{1/2}$$

with $z_i = i\Delta z \qquad i = 1, N$

$$T_i(z_i) = T_{i+1}(z_i) = T_i.$$

Using this procedure we performed thermal profile calculations for copper single crystals of specific shape including the neck region on top of the crystals. Results will be discussed later.

3. Equipment used

Figure 3 shows the Czochralski crystal growth equipment that was used in the present experiments. The pressure vessel is double-walled for efficient water cooling. The growth process is observed with the help of a video camera and a TV monitor. For this a sapphire rod has been fixed at the upper socket. The video camera pictures the solid–liquid interface through this rod and projects the same on to the TV monitor. Adjustable d.c. motors with tacho generators are provided for rotation and translation of the crucible and the seed crystal holder. The translation speeds can be controlled to within $\pm$ 0·01 mm/min and the rotation speeds to within $\pm$ 0·1 rpm. The starting material is melted by RF power conducted through a coaxial cable to a water-cooled induction coil. The pressure chamber is charged with inert gas by repeated evacuation

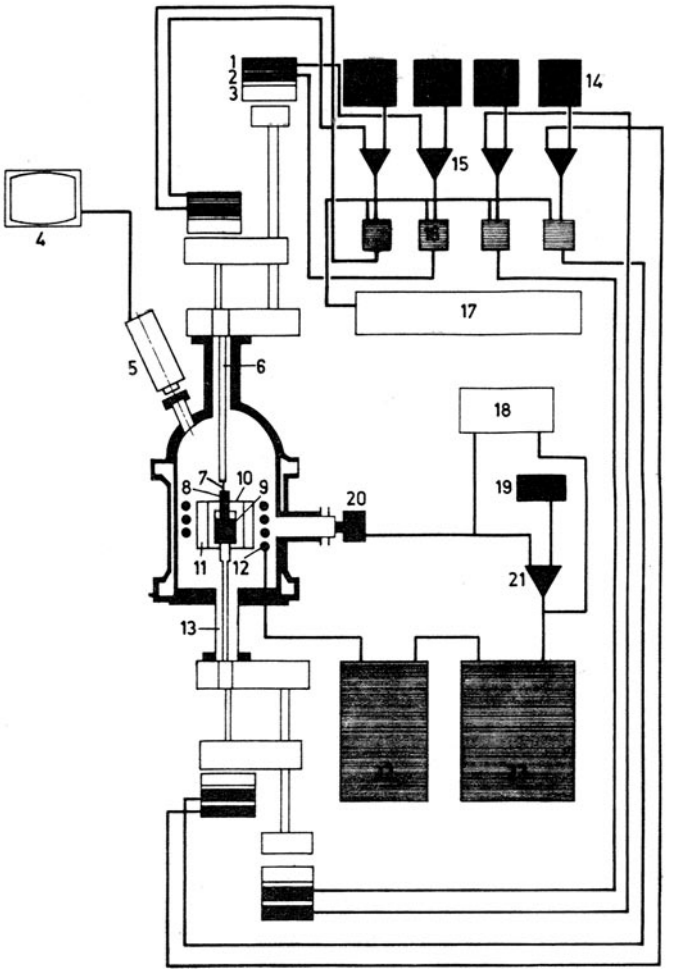

Figure 3. Layout of crystal puller. 1. Tacho-generator; 2. motor; 3. reduction drive; 4. TV monitor; 5. TV camera; 6. upper spindle; 7. seed holder; 8. crystal; 9. melt; 10. crucible; 11. radiation shield; 12. induction coil; 13. lower spindle; 14. speed reference; 15. comparison; 16. SCR control; 17. DC power supply; 18. recorder; 19. temperature reference; 20. optical pyrometer; 21. comparison; 22. HF unit; 23. HF generator.

and purging of the vessel by means of a vacuum pumping station and a gas handling system.

4. Experimental details

Graphite crucible was charged with 99·999% pure copper. Graphite material was chosen as it was found to be non-reactive to copper upto its melting point and it was easy to retrieve copper out of it after the growth run is completed. A 99·999% pure copper in the polycrystalline form was used as a seed crystal. Before loading, the seed crystal was etched in dilute HNO_3. The system was filled with pure argon upto a

Table 1. Growth conditions

Crystal pulling rate	0·2 mm/min
Crystal rotation rate	10 rpm clockwise
Crucible lifting rate	0·02 mm/min
Crucible rotation rate	10 rpm anticlockwise
Atmosphere	Argon
Gas pressure	6 bar
Pulling direction	⟨100⟩

pressure of 6 bars. After melting the charge the seed crystal was submerged in it. After complete wetting it was withdrawn at a very low speed. The crystal and the crucible were rotated in opposite directions. A neck was grown on top of the crystal. The necking involved gradually reducing the diameter of the growing crystal until a thin neck had been grown. The crystal diameter was then gradually increased to the required size and was subsequently maintained constant. The diameter was held uniform by monitoring the melt temperature only. The shape of the crystal is controlled by the angle of contact of the meniscus θ. If $\theta > 0°$ the crystal will narrow out and if $\theta < 0°$ it will grow out. When the melt temperature is increased the solid-liquid interface rises above the melt and the surface tension forces waist-in the liquid column under the crystal making θ negative. In the reverse situation the solid-liquid interface moves the surface of the liquid, θ increases beyond 90° and under extreme conditions the whole surface of the melt can be crystallized. A good visibility of the interface and a precise control of the power to the melt were, therefore, maintained. The growth conditions are summarized in table 1.

5. Results and discussion

By employing the high pressure Czochralski technique, we have grown copper crystals of varying sizes. Some of these are shown in figure 4. The crystal diameter was controlled by monitoring both the growth rate and (more usually) the melt temperature. The single crystallinity of the crystals was ascertained by taking Laue back reflection pictures. For this the crystal was cut normal to the growth axis and polished to 3 μm surface finish. The crystal was subsequently etched. A typical Laue picture taken of these crystals is shown in figure 5. The picture is spotty indicating that the grown crystal is a single crystal. It shows clearly a four-fold symmetry. The growth direction is therefore ⟨100⟩. This has been further confirmed by indexing the various reflections. The dislocation density was determined from the etch pits. Only those etch pits were counted which showed continuity after removal of subsequent surface layers. This gave an estimate of $< 10^3$ dislocations/cm^2. The microstructure showed no subgrain boundaries which were observed in the earlier works (Inoue 1974; Wantabe 1974). This indicates that the dislocation content of our crystals is sufficiently low to prevent the formation of subgrain boundaries. The order of dislocation density found in our crystals is very low. There seems to be some influence of the gas pressure which in our case is hydrostatic. This could be due to the fact that the crystal is mechanically extremely soft at T_m and that a slight ambient pressure prevents the dislocation generation by reducing the thermal stresses at the solid-liquid interface. The good

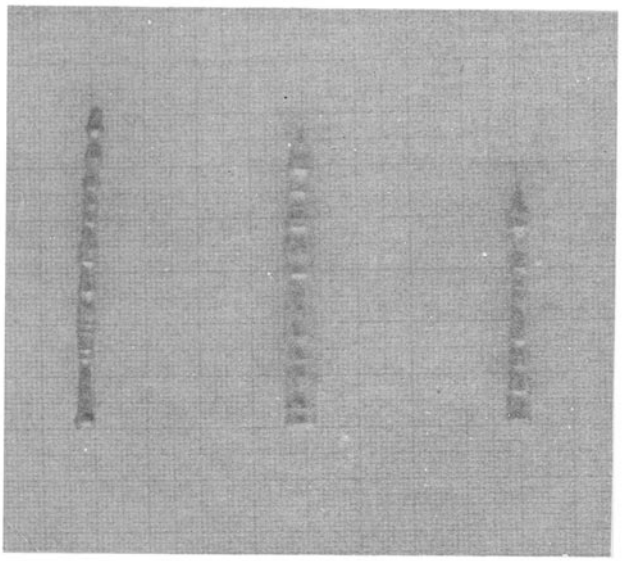

Figure 4. As grown single crystals of copper.

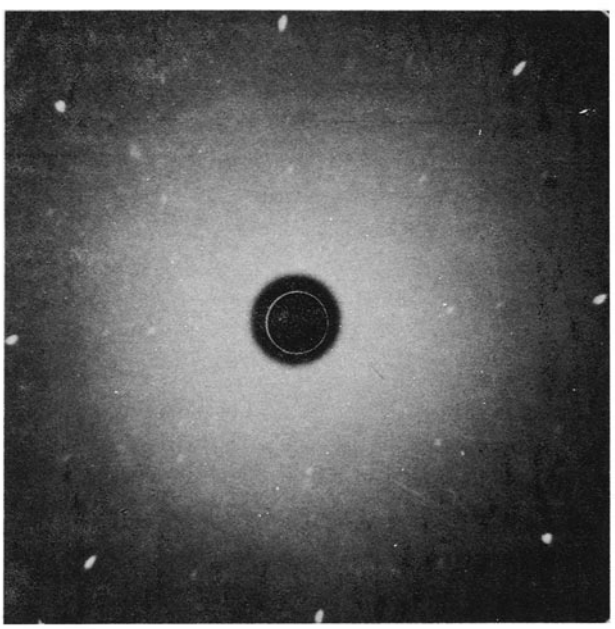

Figure 5. Laüe x-ray diffraction pattern.

quality of the crystal can also be attributed to the amount of thermal gradients which were present during its growth. Using the heat transfer equation and the slice model outlined in §2, we have estimated the thermal profile of the crystal surface. In figure 6 we have plotted the axial temperature distribution of the copper crystal of 7 mm diameter with the neck of 1 mm diameter. It is clear from the thermal profile that the

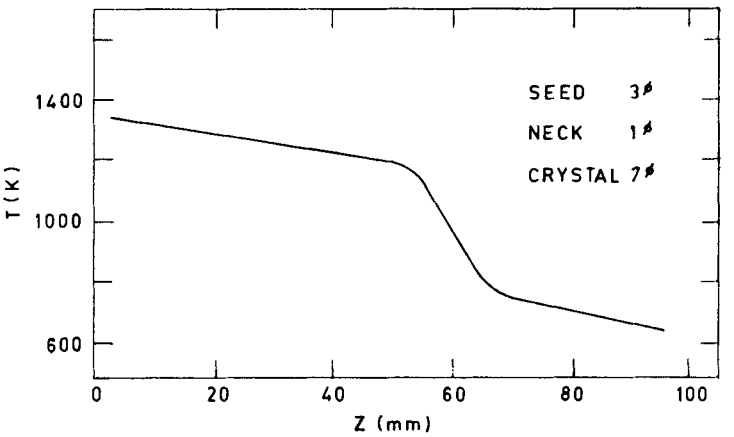

Figure 6. The axial temperature distribution as a function of the distance to the melt.

temperature falls very rapidly in the neck region. The calculations show that the surface temperature in this crystal falls by 165°C as we go away from the solid-liquid interface and reach the neck region i.e., during the first 5 cm growth of the crystal. This is in agreement with the magnitude of the temperature drop that was measured by using an optical pyrometer within an accuracy of $\pm$ 10°C. The measured fall was 175°C during the first 5 cm growth of copper crystal of the same dimensions upto the neck region. Such a temperature gradient is sufficiently low to prevent the generation of significant amount of thermal stresses and therefore could be one of the reasons for the observed low dislocation density. The measured low temperature gradients are the effects of the necking which is performed on top of the crystal. We have also found that these temperature gradients will be considerably high if the necking stage is omitted during the crystal growth. This indicates that the necking procedure establishes an optimum amount of temperature gradients within the crystal that will yield low thermal stresses and consequently lead to low dislocation densities.

We have not observed facet formation in our crystals. This could be attributed to the fact that the parameter $\alpha = \Delta S\eta/Rv$ (where S is the entropy of fusion, R is the gas constant η/v is the bonding parameter dependent on the surface orientation) is less than 2 for copper and the materials with $\alpha < 2$ crystallize with rough surfaces.

6. Conclusions

Strain-free single crystals of copper have been grown at 6-bar inert gas pressure. The slight hydrostatic pressure environment and the necking are found to improve the crystal quality. The dislocation density of these crystals was found to be less than 10^3 dislocations/cm^2.

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References

Bennema P 1984 *J. Cryst. Growth* **69** 182
Brice J C 1965 *The growth of crystals from the melt* (New York: Interscience)
Buckley-Golder I 1977 *J. Cryst. Growth* **40** 189
Faust J W 1968 *J. Cryst. Growth* **3/4** 433
Giling L J and Dam B 1984 *J. Cryst. Growth* **67** 400
Gilman J J 1963 *The art and science of growing crystals* (New York: John Wiley)
Inoue T 1974 *J. Cryst. Growth* **24/25** 418
Lal K 1982 *Synthesis, crystal growth and characterization* (Amsterdam: North Holland)
Rosenberger F 1979 *Fundamentals of crystals—Macroscopic equilibrium and transport concepts* (Berlin: Springer Verlag)
Savitskii E M and Novokhatskaya N I 1968 Growth and imperfections of metallic crystals (ed) D E Ovsienko (New York: Consultants Bureau)
Sworn C W and Brown T E 1972 *J. Cryst. Growth* **12** 196
Van der Hart A and Uelhoff W 1981 *J. Cryst. Growth* **51** 251
Wantabe J 1974 *J. Cryst. Growth* **24/25** 414