EFFECT ON GRAIN SIZE DUE TO PASSAGE OF ELECTRIC CURRENT DURING SOLIDIFICATION OF CADMIUM

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It has been observed that the grain size of cadmium is considerably reduced by the passage of direct electric current during the process of solidification. The observed effect has been attributed to the increased lattice vibrational frequency caused by electron-phonon interaction. The enhanced lattice vibrational frequency increases the rate of nucleation and hence reduces the grain size.

Considerable work has been done on the growth of metallic crystals from melts using various types of crystal seeds and employing different types of temperature gradient furnaces. The grain size of metals is very important because many of their properties such as tensile strength, hardness, etc. depend directly on it. Langenberg, *et. al.*[1] have succeeded in reducing the grain size of iron ignots using a moving magnetic field. Other investigators[2,3] have studied the process of solidification of melts under the influence of electric fields with a view to study the segregation and desulphurisation of iron. However, the effect of electric current on grain size during the process of solidification does not appear to have been studied so far. This has been investigated in this paper.

EXPERIMENTAL PROCEDURE

Cadmium metal was melted in nitrogen atmosphere in a Pyrex glass tube (Fig. 1) specially designed for this purpose. Two tungsten electrodes (2 cm. apart) were inserted in this tube. The main tube (length 5 cm., dia. 7 mm.) in which solidification takes place was connected to another tube (dia. 25 mm.) in which nitrogen atmosphere is maintained. The temperature of liquid cadmium was raised to 400°C by placing the tube in a furnace, without any temperature gradient. Direct current of 15 amperes was passed in the melt during the entire period of solidification. After solidification some samples were slowly cooled and others quenched. The samples thus prepared were hand polished, etched with chromium trioxide and studied under a Vicker's projection microscope.

Two representative microphotographs obtained by using yellow-green filter with magnification 40 are shown in Fig. 2 and Fig. 3. They show grains of a slowly cooled sample—Fig. 2 represents the region through which no current was passed and Fig. 3 the region through which current was passed. These figures show that the grain size is considerably reduced by the passage of electric current. Similar results were obtained with quenched samples also.

DISCUSSION

It is not possible to treat this problem in the light of any rigorous theory, since we are dealing with melts in rapidly changing solid-liquid phase. However, a qualitative explanation of observed experimental results is given below:

The rate of nucleation from a liquid metal is given by[4]

$$I = N^*_s \epsilon \nu_l \, n(1) \, e^{-(\triangle G^*_D + \triangle G^*)/KT} \quad (1)$$

where I=Rate of nucleation

N^*_s=Number of atoms of the liquid in contact with the solidifying nucleus

$n(1)$=Number of atoms in supersaturated phase

ν_l =Lattice vibrational frequency

ϵ =Probability of a given atom to join the solidifying nucleus

$\triangle G^*_D$ =Free energy of activation in diffusion which is usually of the order of KT

and $$\triangle G^* = \frac{16\pi\gamma^3_{mc}}{3\triangle G^2 v}$$

In the expression for $\triangle G^*$, γ_{mc} and $\triangle G_v$ stand for the interfacial free energy between melt and crystal, and the thermodynamical free energy respectively.

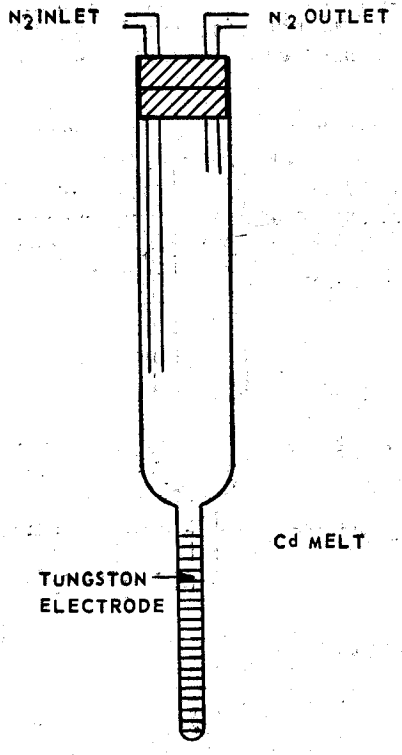

FIG. 1—Pyrex glass tube

Equation (1) shows that the rate of nucleation depends upon two factors (*a*) Lattice vibrational frequency ν and (*b*) The exponential term $e^{-(\triangle G^*_D + \triangle G^*)/KT}$

Lattice vibrational frequency

It is well known that there is a strong interaction between free electrons and phonons in metals. Considering the effect of electrons upon ionic motion in the Fermi-Thomas approximation, Staver & Bohm[5] have treated the phonons and electrons as a set of coupled

FIG. 2—Region through which no current was passed.

plasmons. The frequency of lattice vibration in this theory is given by[6]

$$\nu_l = \sqrt{\frac{m}{3M}} Z.\ v\,K \tag{2}$$

where ν_l = Lattice vibrational frequency

M = Ionic mass

m = Mass of electron

v = Velocity of electrons

and K = Wave vector

With the application of the electric field the velocity of free electrons increases thereby increasing the lattice vibrational frequency. However, the change in velocity of free electrons cannot be calculated accurately as the energy states are not normalizable in electric field and thus are not stationary[7]. As an approximation we can apply the free electron theory of metals to determine the velocity of electrons. This theory[8] gives the velocity of electrons at the Fermi surface as

$$v = \frac{\hbar K_o}{m} \tag{3}$$

where K_o is the wave vector at the Fermi surface. Under the influence of the electric field, the wave vector in the direction of the field increases. To calculate this increase, we take recourse to the concept of Brillouin zones in metals.

In the case of cadmium the first Brillouin zone is completely full while the second is partly full and partly empty. It may be assumed, as a first approximation, that by the application of the electric field the wave vector changes from π/a to $2\pi/a$ and hence the average velocity of free electrons can be expected to increase from v to v' (approximately upto $2v$). This increase in the velocity of electrons will increase the lattice vibrational frequency from ν_l to ν'_l (approximately upto $4\nu_l$) as can be seen from (2) and (3).

The exponential function

In the exponential term $\triangle G^*_D$ is constant and is of the order of KT while $\triangle G^*$ is proportional to $1/\triangle G_v{}^2$ which is a function of lattice vibrational frequency as shown below :

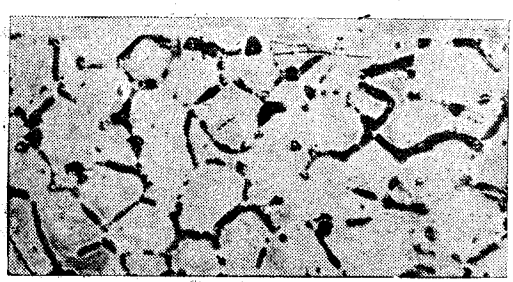

FIG. 3—Region through which current was passed.

The Helmholzt free energy is written as[9]

$$A = \tfrac{3}{4}Nh\nu_l - \frac{3Nh\nu_l}{e^{h\nu_l/KT} - 1} - 3\,NKT\,log\,\frac{e^{h\nu_l/KT}}{e^{h\nu_l/KT} - 1} \tag{4}$$

In the above equation N is the number of atoms per gm. Other symbols have their usual meaning.

Calculation shows that free energy is about $-4 \cdot 151 \times 10^9$ ergs/gm in cadmium near the melting point. As shown earlier the effect of electric current is to increase the lattice vibrational frequency. Substituting its increased approximate value in (4), we get free energy of the order of $-3 \cdot 229 \times 10^9$ ergs/gm. Thus by passing the current the height of the free energy barrier is reduced.

It has, therefore, been seen that both these factors, which determine the rate of nucleation, increase when electric current is passed during the solidification of the liquid melt. With the increase in the rate of nucleation it is possible to explain the reduction of the grain size observed experimentally.

CONCLUSION

Similar work on some other metals such as tin and bismuth is being done. Preliminary results show that by the passage of electric current grain size is reduced in these metals also. It may be possible to increase the hardness and strength of metals by reducing the grain size by this method.

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REFERENCES

1. LANGENBERG, P. & HONEYCUTT., *Trans. AIME*, (1961), 993.
2. ANGUS J., RAGONE D. V. & HUCKE E. E., "Physical Chemistry of Process of Metallurgy" (Interscience Publishers, Inc., New York), 1959.
3. OHTANI M. & GOKCEN, N. A., "Physical Chemistry of Process of Metallurgy" (Interscience Publishers Inc. New York), 1959.
4. TILLER W. A., "The Art and Science of Growing Crystals" (John Wiley and Sons Inc., New York), 1963.
5. BOHM D. & STAVER T., *Phy. Rev.*, 84 (1951), 836.
6. PINES D., "Solid State Physics," Vol. I (Academic Press Inc., New York), 1955.
7. WANNIER W. H., *Phy. Rev.*, 117 (1960), 437.
8. MOTT & JONES, "THEORY of the Properties of Metals and Alloys" (Dover Publication Inc., New York), 1958.
9. SEITZ F., "Modern Theory of Solids" (McGraw Hill Books Co., Inc., New York), 1940.