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Zinc Single Crystals with Hexagonal Geometry Grown in Macrosonic Fields

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Application of macrosound (25 kc; 50 W.cm^{-2}) affects the growth of a cylindrical zinc single crystal whose c axis is almost perpendicular to its length axis so that its shape is changed into a uniform hexagonal geometry. This result is discussed on the basis of concepts that involve the influence of macrosound on the stability of forms of crystal faces through dislocation activation.

Introduction

It has been shown that macrosound (intense ultrasonic waves) may affect the surface roughness, crystallographic orientation and critical shear stress of zinc single crystals grown from the melt (Langenecker & Frandsen, 1962). The effects proved to be dependent upon the intensity of the applied field and they were discussed on the basis of concepts that involve the influence of sound on the conditions of vacancy supersaturation during cooling of the crystal, and the formation of dislocation networks during homogenization behind the solid–liquid interface.

The influence of 25 kc macrosound on the crystallographic orientation, *i.e.* the change in the angle χ_0 which is formed by the basal plane and the longitudinal axis of the crystal, amounted to as much as 10°. The initial orientation of the seed crystal usually was $30° < \chi_0 < 60°$. However, some attempts were made to study the influence of sound waves on χ_0 in the case of 'extreme oriented' crystals, where χ_0 is either close to 0° or 90°; but no constructive result was obtained at that time. This was essentially due to two facts, one of which was that the experimenters were mainly interested in the influence of sound on the critical shear stress of crystals rather than in effects on their crystallographic orientation. The discovery of the acoustic effect on the crystal orientation was therefore a by-product.

The other fact which hindered more detailed investigations on χ_0 was the difficulty in the control of the proper acoustic radiation; the ultrasonic equipment available at that time was not satisfactorily developed. Since then, the equipment for production and control of macrosound has been markedly improved. The form of waves, the power amplitudes, and the duration (*i.e.* the number of cycles) are now satisfactorily reproducible.

On the basis of our earlier work, and because of our considerable interest in the effects of macrosound on crystal orientation, we continued with experiments in that line, particularly with the use of specimens whose crystallographic orientation is close to $\chi_0 = 0°$. This paper presents results of such studies on zinc single crystals in which the angle $\chi_0 < 5°$, *i.e.* where the c axis is almost perpendicular to the longitudinal axis of the specimen.

Material and experimental equipment

The single crystals were grown either from a high purity melt of 99·999% zinc, or from a less pure melt containing 99·93% zinc. A modified Czochralski (1917) apparatus was used as shown in Fig. 1. The modifications of the Czochralski pulling device consisted essentially of an improved macrosonic equipment which generated and controlled the irradiation. The acoustic output of the piezoelectric transducer was measured through the use of a MASSA microphone which was placed on the tip of the transducer instead of the

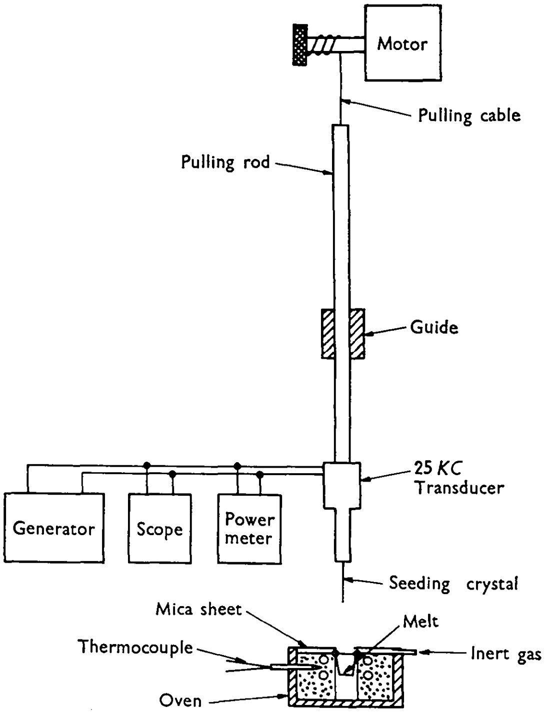

Fig. 1. Modified Czochralski crystal pulling apparatus.

seeding and growing crystal. With the MASSA pickup the power meter was calibrated in units of acoustic energy emitted from the tip of the transducer. The intensity (sound power level) of sound waves emitted from the transducer was adjustable within 0·1 and 100 W.cm^{-2}.

After the calibration, the MASSA microphone was replaced by a seed crystal which had previously been examined for uniform shape, diameter, and crystallographic orientation. Surface and diameter of the crystal were investigated through the use of a Reichert metallograph. Only uniform cylindrical crystals having a diameter of about 1 mm were used. The crystallographic orientation was determined by the X-ray crystal rotating method. The seed crystals had a χ_0 of almost 0°.

Zinc was molten in a conventional oven under the protection of inert gas (96% nitrogen, 4% hydrogen). Then the seed crystal was inserted into the melt and subsequently raised to a speed between 3×10^{-3} and 5×10^{-2} cm.sec^{-1}. After normal growth of about 2 cm of uniform cylindrical zinc single crystals, the macrosonic irradiation was turned on; after growth of another 2 cm, the sound was turned off. The portions that had been grown under the influence of macrosound were investigated in the microscope and examined by X-ray.

Results

First of all, some of the earlier experiments were repeated; in fact, with crystals of 'medium' orientation (*i.e.* $30° < \chi_0 < 60°$) the earlier results reported (Langenecker & Frandsen, 1962) were confirmed.

Next, crystals were grown with orientations close to $\chi_0 = 0°$; this was achieved through the growth of crystals on medium oriented seeds the tip of which has been bent to a determined degree before inserting into the melt. The new 0°-crystals were then used as seed crystals in the subsequent experiments.

Physical shape

A typical result of five successful experiments is shown in Fig. 2. This high-purity zinc crystal has an orientation of $\chi_0 \simeq 3°$ and it was grown under the influence of a 25 kc macrosonic field having an intensity of about 50 W.cm^{-2}; the speed of pulling, $v = dx/dt = 1{\cdot}3\times10^{-2}$ cm.sec^{-1}; and the temperature gradient $G = dt/dx \simeq 35$ °C.cm^{-1}.

The external shape, *i.e.* the physical geometry of the specimen grown during irradiation, is of pronounced hexagonal geometry. The seed crystal used in this experiment, however, was a uniform cylindrical specimen. Upon application of macrosound (indicated in Fig. 3 by A) the circular uniformity of the adhering and growing crystal turned into a six-sided rod and continued to grow in this hexagonal geometry as long as macrosound was applied. At the position indicated in Fig. 3 by B, the sound intensity was reduced from about 55 W.cm^{-2} to about 50 W.cm^{-2} which caused a decrease in diameter of the specimen. But there was no change in its geometrical shape. At point C, the sound power amplitude was increased again (above 55 W.cm^{-2}) which caused a growth with increasing diameter. Still, the hexagonal geometry was continued. At D the sound field was turned off.

Fig. 2. Zinc single crystal with hexagonal geometry grown in a macrosonic field (25 kc).

After the macrosound was turned off, the crystal continued to grow in the uniform cylindrical manner as it did before the irradiation. Also its diameter returned to its previous value, *i.e.* about 1 mm as before irradiation. This is not surprising, since the diameters of portions not irradiated are determined by the temperature of the melt and the rate of pulling in the Czochralski (1917) device.

Two similar experiments in which the less pure zinc was used gave similar results; this indicates that the appearance of the hexagonal geometry does not depend on purity.

Intensity limits

It should be mentioned that in the case of medium oriented crystals macrosound having intensities of the order of 5 W.cm^{-2} is sufficient to cause detectable

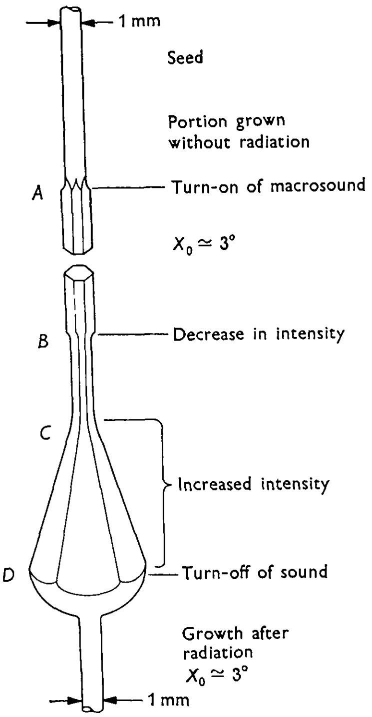

Fig. 3. Sketch of the zinc crystal shown in Fig. 2.

effects on crystal growth; at intensities greater than about 40 W.cm^{-2} medium oriented high purity zinc crystals deform plastically (Langenecker, Frandsen & Colberg, 1963) and thereby stop the growth. In the case of extreme oriented crystals, however, intensities up to 60 W.cm^{-2} may be applied. Such intensities are just below those at which deformation of the crystals occurs.

Rate of growth

Through variations in the speed $v = dx/dt$ within 3×10^{-3} and $1{\cdot}5 \times 10^{-2}$ cm.sec^{-1}, we found that the appearance of the hexagonal geometry was not confined to a distinct speed v. However, with increasing v, the edges of the hexagonal portions became less pronounced and above a speed of some 10^{-2} cm.sec^{-1} the crystals grew in the familiar cylindrical manner, but much less uniform in diameter than at low values of v.

Even at high speeds ($v > 2 \times 10^{-2}$ cm.sec^{-1}) at which no crystals with hexagonal geometry were obtained, the specimen grew as cylindrical single crystals up to speeds of the order of $v \simeq 5 \times 10^{-2}$ cm.sec^{-1}. This rate is about 1·6 to 1·8 times as great as the maximum rate at which zinc single crystals can be grown when no macrosound is applied. Measurements on zinc crystals of other orientations ($0° < \chi_0 < 60°$) indicate that macrosound increases the rate of growth by a factor of 1·6 to 1·8 for crystals of any orientation.

Discussion

At first, one may attempt to correlate the faces of zinc single crystals with the described hexagonal geometry to low order lattice planes. The c axis of these crystals proved, however, to be perpendicular to the length axis of the specimens, which precludes such attempts from plausible interpretations. Still, the hexagonal geometry exclusively appeared on crystals whose c axes are perpendicular to the length axis. Thus, crystal structure has something to do with the formation of the faces. The underlying correlation in structure and geometry is assumed however to be an indirect one; namely it is due to imperfections introduced in certain planes by acoustic effects.

From this point of view, the free surface energy (Gibbs, 1928)

$$V_0 = \sum_i \sigma_i F_i = \text{minimum} \qquad (1)$$

(where σ_i is the specific free surface energy of a plane i, and F_i is the area of the plane i) is different for perfect planes and for those which incorporate dislocated atoms. This difference appears in the deposition of atoms so that the deposition is increased in faces parallel to imperfect planes (Frank, 1949; Knacke & Stranski, 1952).

Without going into details we may state that the density of imperfections ending in planes parallel to the solid–liquid interface (in our case, the $(10\bar{1}0)$ plane) is augmented through activation of dislocations by macrosound. Langenecker (1957) and Langenecker *et al.* (1963) have shown that high strain amplitude ultrasonic stress waves — although alternating in sign — are capable of producing a 'forward' migration of dislocations. Accordingly, macrosound drives dislocations from the seed to the solid liquid interface.

Since the resolved shear stress required to move a dislocations (= dislocations confined to basal planes) is known to be much lower than those required for dislocations in any other planes, a dislocations are primarily moved by macrosound. The influence of these dislocations (which are assumed to be randomly distributed) will be most regular and symmetric when the defects enter the solid–liquid interface perpendicularly (for any other 'angle of incidence', asymmetric growth will result owing to an accumulation of dislocations on one side of the crystal as determined by the glide elements). This prerequisite for symmetric growth is fulfilled in crystals where the c axes are perpendicular to the length (or in other words, the $(10\bar{1}0)$ planes are parallel to the interface), which is in good agreement with the present observations.

The size and symmetry of faces to which the acoustically increased deposition of atoms may lead are assumed to be determined by an equilibrium in forces that result from imperfections (the strain energy of which enhances the growth) and in forces which result from the tension created by the drag of the melt on the seed.

We may also consider the idea that deposition of atoms around ending dislocation lines may initially occur as circular, and then may become polygonal, and in particular hexagonal as is known from many cases of crystal growth (Smakula, 1962). Superposition of all of these 'unit cells' around dislocations may then give the observed hexagonal geometry. However, it is quite unlikely that polygonal spirals grow around dislocations while the crystal is pulled from the melt. Thus, all that remains is to believe in the tendency of equilibrium to form hexagonal geometry, of which nature is known to give many examples. Several types of single crystal grown from the melt were shown to exhibit a hexagonal network the size and regularity of which were found to depend upon speed of growth, temperature gradient, and impurity content, but have nothing to do with crystal structure. Rutter & Chalmers (1952) have shown that these hexagonal cells of that network essentially consist of a particular distribution of impurities resulting from non-equilibrium during solidification. The hexagonal geometry reported in this paper, however, was found not to depend on impurities; thus, Rutter & Chalmer's concept does not apply to the present case.

The interpretation above of the acoustically formed hexagonal geometry implies that an increase in the rate of growth is expected to accompany the increase in the density of defects at the solid-liquid interface. It was quite gratifying that an increase in rate of growth, v, actually occurred during acoustic irradiation (this increase as mentioned in the preceding section amounted to as much as a factor of 1·6 to 1·8). It is still necessary to show that such an increase in v can not be achieved by much simpler effects than dislocation activation *etc.*, for instance by acoustically affected cooling of the solid phase.

For 'conventional' growth (when no sound is applied), Andrade & Roscoe (1937) correlate the rate of growth, v, with the temperature gradient G, in the form

$$v = \frac{(1+K_1/K_2)K_1}{L} \cdot G \qquad (2)$$

where K_1 and K_2 represent the thermal conductivity of the crystal and the melt, respectively, and L is the heat of crystallization per unit volume. This correlation is known to be a qualitative description rather than a quantitative one. However, an increase in v by as much as 1·6 to 1·8 requires a decrease in the temperature of the solidifying crystal by some 20° C. However, no changes greater than 8 °C were measured, and thus acoustic cooling can not account for the observed increase in v.

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The Determination of Axial Ratios from Powder Diffraction Patterns

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Accurate axial ratios of anisotropic crystalline phases can be obtained from precision powder data by computing exhaustively the axial ratios from pairs of closely spaced, non-overlapping reflections. The method has been applied successfully to the tetragonal, hexagonal, orthorhombic, and monoclinic systems.

The determination of axial ratios with the reflecting goniometer was developed into a precise technique by mineralogists of the nineteenth century. Compendia such as Dana's *System of Mineralogy* or Groth's *Chemische Krystallographie* are replete with this type of morphological information which has been of