figure. The strain in the film results from the electron beam bombardment and the simultaneous formation of a contamination layer on the film. The wide traces, such as the one at P are due to {101} slip. {121} slip occurs at Q. An example of {101}-{121} cross-slip occurs at R.

Dislocations may also move in a cooperative manner. Small angle grain boundaries, again under the influence of electron beam bombardment, have been observed to move through the lattice and decompose into single dislocations. Deformation twins may be formed by impact outside the microscope or as a result of electron beam bombardment in the microscope. Under the influenue of the electron beam these twins may grow in length and width or decay in a similar manner. The rate of lengthening is considerably faster than widening. Similar observations on twins have been made by Fourie *et al.* with thinned bulk samples[3]. One of the more interesting problems that has arisen is the origin of the dislocations in the twin boundaries. The twinning plane is the (301) plane. It is not a normal slip plane. It has been shown that at least some of the dislocations in the twinning plane were {121} dislocations which moved on their own slip plane until they intersected a (301) twinning plane. This plane then acted as a barrier for further motion, thereby effectively trapping the dislocations in the (301) plane[4].

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The Origin of Substructures Formed during the Growth of Crystals from the Melt

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The origin of optically visible imperfections in metallic crystals grown from the melt is discussed; these imperfections are classified as the dendritic, cellular and lineage structures. Dendritic structures and cellular structures are attributed to the instability of linear heat flow and solute diffusion, respectively, in the liquid; the origin of lineage structures, still somewhat obscure, is discussed in terms of vacancy mechanisms and other possible ways in which dislocations may be generated.

Introduction

Metallic crystals that have been grown by the solidification of molten "pure" materials, usually contain imperfections that are readily observed optically. The imperfections to be discussed occur in crystals which, because all parts derive from the same nucleus, are properly described as single crystals. The existence of a sub-structure indicates that different parts of the crystal differ from each other, either in orientation or in composition. The purpose of this paper is to discuss why these heterogeneities occur under conditions in which the imposed physical variables (temperature gradient, rate of change of temperature) are uniform.

There are three distinct types of optically visible substructure, namely, dendritic, cellular and lineage structures. Dendritic solidification in a pure melt is caused by the instability of a smooth solid-liquid interface in contact with an undercooled melt, if the growth rate is controlled mainly by heat flow but also varies with crystallographic direction. Dendritic freezing occurs only in those substances, and under those conditions, in which dislocations are not required to form a perpetual growth step; this mode of solidi-

fication is therefore not related to lattice defects, and will not be considered further here.

Cellular growth occurs in impure liquids and is caused by the rejection of solute at the freezing interface and its subsequent redistribution by transverse diffusion. The cellular substructure is delineated by a relatively high concentration of solute at the cell walls, and it is probable that this structure is stabilized by arrays of dislocations which relieve the lattice strain due to the solute atoms. Point defects do not appear to play any part in the formation of this structure, although there is evidence, to be discussed below, that the cell walls provide very effective sinks for vacancies. The cellular substructure, as such, is therefore not relevant to the subject of this conference, and will not be discussed further.

Lineage Structure

The lineage structure, as usually understood, is an array of small angle boundaries that are, in general, nearly parallel to the direction of growth of the crystal; when the crystal has a cellular structure, the lineage boundaries follow cell walls and are straight and regular if the growth conditions are uniform; typically, the boundaries are of about 1° angle, tilted about the growth axis, and are one to two millimeters apart. If the crystal does not have a cellular structure, the boundaries are less regular, but still of about the same angle and separation.

Earlier studies[1),2),3)] showed that the lineage structure develops gradually over a distance of a centimeter or so; recent work[4)] has indicated in some detail how this takes place. The final boundaries, of angle 1°—3°, are formed by the agglomeration of boundaries of much smaller angle (see Fig. 1). It is interesting that the very small angle boundaries converge for substantial distances. The sign of a tilt boundary can be defined in terms of the direction of rotation, or of the sign of the edge dislocations of which it may be composed. The lineage boundaries in a crystal are always of both signs, and the total rotation in one sense is always nearly equal to that in the opposite sense. Since the angles are small, and the boundaries are nealy pure tilt boundaries, it is reasonable to suppose that they consist of arrays of edge dislocations.

The main purpose of this paper is to discuss the origin of the dislocations from which the lineage structure is built up; it will be assumed, without conclusive evidence, that the structure is formed by the agglomeration of individual dislocations that are generated during the growth of the crystal. The structure reaches a steady state in about 1 cm, and at this stage it contains about 20 cm of boundary per square centimeter of cross section; the average tilt angle is about 1°; that is, about one dislocation for every 60 atom planes, or about 1 dislocation for each 10^{-6} cm of boundary. Thus the boundaries that exist after 1 centimeter of growth contain about $20/10^{-6}=2\times10^{7}$ dislocations, of which one-half are of one sign, and one half of the other. It follows that dislocation pairs (one of each sign) are produced at the rate of at least 10^{7} per cubic centimeter during the early stages of growth; the rate is probably higher because some must be lost by mutual annihilation, and some are likely to emerge at the surface of the crystal. In order to account for the observed structure, each dislocation pair must form a "half loop", the two ends intersecting the growth interface, since the propagation of the lineage structure depends on the dislocations remaining in existence, and increasing in length, as the crystal grows.

The explanation originally advanced for the origin of the dislocations was that the supersaturation of vacancies, caused by the fall in temperature of the crystal, led to their

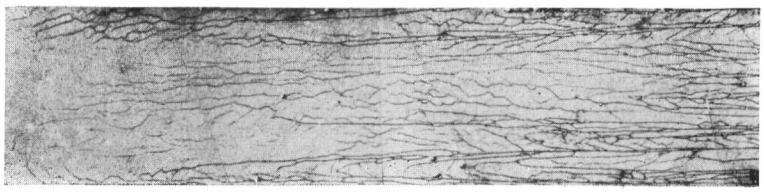

Fig. 1

condensation as "vacancy discs" which, on collapsing, produce edge dislocation loops (prismatic dislocations). If these loops formed at the interface, they would satisfy the conditions for contributing to the formation of the lineage structure; if formed away from the interface, they might grow towards it by climb.

It has recently been shown by Jackson[5] that the concentration of vacancies produced purely by the drop in temperature cannot be sufficient to cause homogeneous nucleation of vacancy discs near enough to the interface to be able to reach it by climb; the lineage structure is, in fact, formed even if the temperature of the crystal is maintained above the temperature at which vacancy discs should nucleate.

If the conclusion is accepted that the dislocations cannot be formed as a result of the supersaturation of vacancies by fall of temperature, it becomes necessary to consider other possible causes; these can be divided into a) other vacancy mechanisms and b) mechanisms not related to vacancies. Two mechanisms that depend on vacancies have been proposed: one is that the non-equilibrium process of solidification produces a vacancy concentration in excess of that which is in thermal equilibrium in the crystal. This would occur if some of the crystal sites, normally filled, during solidification, by atoms from the melt, were instead filled by the diffusive jump of neighboring atoms in the crystal. It is possible that as many as one per cent of the sites are filled by atoms that were already in the crystal; however, it seems certain that the subsequent "random walk" of these excess vacancies must lead to practically all of them returning to the solid liquid interface in a very short time, and therefore not being available for a dislocation forming mechanism[4]. In order to "trap" appreciable numbers of vacancies it would be necessary for the interface to advance at a much higher speed than is required for the formation of the lineage structure. The other vacancy mechanism that has been proposed is that the excess vacancies cause climb of existing screw dislocations into helical form. Intersection of the helix with the interface would give the required "half loops". This mechanism is ruled out on the grounds that there is no driving force to account for the diffusion of vacancies to dislocations rather than to the solid-liquid interface.

The arguments presented above suggest very strongly that vacancies cannot be responsible for the formation of the dislocations. However, there is some experimental evidence which conflicts with this conclusion. Elbaum[6),7] has shown that crystals of aluminum grown by the Czochralski method do not contain dislocations if their radius is less than a reasonable diffusion distance for vacancies in the time available; and Doherty[8] has demonstrated that when a cellular structure is present the lineage structure often fails to develop. This is attributed to the action of the cell walls, or of the pores sometimes found in them, as vacancy sinks. Doherty also finds evidence of high vacancy concentration near solid-liquid interfaces during growth. None of these observations is conclusive, since the absence of dislocations could be due to their ability to migrate laterally to the surface of the cell wall by slip, and Doherty's evidence on vacancy supersaturation may be reinterpreted in terms of the nucleation of vacancy pits rather than their growth.

If vacancy mechanisms are ruled out, it is necessary to conclude that dislocations are formed as such; four possible causes have been discussed, a) growth by the addition of misaligned crystal fragments, b) nucleation of dislocations to relieve stresses resulting from concentration gradients of impurities c) nucleation of dislocations by stresses of thermal origin d) nucleation (or multiplication) of dislocations by mechanically applied stresses.

Misalignment could arise from 1) growth around foreign particles trapped by the growing crystal; 2) joining on of "crystallites" and 3) formation of stacking faults at the growth interface. Of these, the first, suggested by Fisher[9] and tentatively identified by Jackson[10] as being caused by the same particles that act as nucleation catalysts in solidification, cannot be ruled out by any existing evidence. Jackson[11] is studying the growth of crystals in "catalytically clean" metal, but this experiment has not yet been completed. The existing theory of liquids would not predict the existence of crystallites

of sufficient size to form stable dislocation loops, and the frequency of occurrence of stacking faults should be far too low to account for the formation of 10^7 dislocation loops per cubic centimeter.

Stresses due to impurity gradients do not appear to provide an explanation, since Doherty[4] reports that the lineage structure was found in zone refined aluminum, and Aust and Rutter[12] have found similar imperfections in lead of very high purity. It appears unlikely that stresses of thermal origin should be far too small to nucleate, or even multiply, dislocations, and mechanically originated stresses, imposed accidentally, could not be consistent enough to cause the very regular and predictable structures that are observed.

The conclusion is that the origin of dislocations in single crystals of metals grown from the melt is not understood, and further experimental work must be completed before it is certain whether they form as an intrinsic feature of the process of solidification, or whether they occur as a result of impurities, either in solution or not, or of stresses imposed by the physical conditions under which growth takes place.

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DISCUSSION

Schoeck, G.: A couple of years ago, Tiller and myself (Schoeck and Tiller: Phil. Mag. (1960)) made some similar calculations and observations. We were especially interested in the formation of the striation structure which was at that time supposed to be due to the condensation of vacancies, which cause dislocation to climb into the liquid solid interface. After calculating the necessary vacancy supersaturation for this process we grew some crystals which were held at temperatures close to the melting point so that the necessary vacancy supersaturation never was obtained. Since these crystals showed the same dislocation structure we concluded that although vacancy condensation may contribute to the establishment of the dislocation network the most important factor for dislocation formation in crystals grown from the melt was probably microsegregation of impurities.

Elbaum, C.: Dr. Schoeck's experiment is concerned with a situation which appears to be quite different from the conditions of our experiments.

Young, F. W., Jr: I would like to report some of our results on the growth of copper crystals which pertain to the papers of Drs. Elbaum and Chalmers. First, it should be recognized that, since dislocations in copper climb only at temperatures near the melting point, the observation of sub-boundaries in as-grown copper crystals must mean that the dislocations were introduced at temperatures very near the melting point. We have grown 1 inch diameter $\times 6$ inch crystals, using a Bridgman technique, which had dislocation densities $5 \times 10^3/\text{cm}^2$ and with no sub-boundaries. We have found that the number of sub-boundaries is always small if the growth direction is [111] or [100], while the number of sub-boundaries is large if the growth direction is such as to have a (111) plane parallel to the growth direction. Thus, it is possible to grow large single crystals of copper with no lineage structure. We have sliced these crystals with an acid saw so as to obtain slices 1 inch in diameter $\times \frac{1}{3}$ inch thick. These slices were annealed at 1075°C for one week, and then furnace-cooled.

It was found that the dislocation density was reduced markedly by this annealing. For example, slices with an as-grown dislocation density of $5\times10^4/cm^2$ were found to have $5\times10^2/cm^2$ dislocations after the anneal. This observation would suggest that the collapse of vacancy clusters into dislocation loops, and subsequent expansion of such loops, is not an important mechanism for the formation of dislocations in copper. There is some indirect evidence, which can not be presented here, that there are some small dislocation loops in these slices. Perhaps these experiments may serve to better define the limits for calculations such as Dr. Elbaum's.

Elbaum, C.: Dr. Young's experiments are very instructive, but I think that they are not necessarily inconsistent with the results that I presented, since Dr. Young apparently observes a limiting dislocation density in his crystals.

Kuhlmann-Wilsdorf, D.: One of my graduate students, Mr. R. Fabiniak, has been able to construct a furnace and temperature control apparatus which allows to grow single crystals of pure aluminum at an ambient temperature within a very few degrees of the melting point. According to x-ray evidence, these crystals are free of sub-boundaries. This is, of course, in support of the theory of Chalmers and Teghtsoonian that sub-boundaries are due to vacancy condensation.

Chalmers, B.: I agree that this experimental result does not conflict with the vacancy condensation theory. However, our own experimental results show that, under some conditions, the sub-boundaries are formed in the immediate vicinity of the solid-liquid interface.

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Hexagonal Networks of Linear Imperfections in Single Crystals of Cadmium

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A new type of hexagonal network of dislocations has been observed in thin crystals of cadmium grown by sublimation. The vacancy-type loops, observed by Price, which are introduced by bombarding the crystals with negative ions in the electron microscope disappear when they reach a certain size. After a very short delay, hexagonal networks begin to develop in the area previously occupied by the loops. These networks lie in the basal planes. The directions of the three sets of linear imperfections which form them are parallel to the $\langle\bar{1}100\rangle$ directions in the basal planes. Mobile specks which are attributed to clusters of interstitial atoms have also been observed and seen to interact with the vacancy-type dislocation loops.

Price[1),2)] first observed vacancy-type dislocation loops in thin crystals of cadmium grown by the slow distillation of cadmium in an atmosphere of argon (Coleman and Sears[3)]). We have observed the formation and growth of dislocation loops of the same kind in similarly grown thin crystals of cadmium. Our crystals which were mounted either on copper grids or between copper grids were examined in the Philips EM 100B electron microscope operated at 100KV. Fig. 1a shows a compound vacancy-type loops of this kind.

In addition we have discovered and studied a new phenomenon which was apparently not observed by Price[1),2)]. After the vacancy-