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# Vacancy Precipitation and the Origin of Dislocations

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The precipitation of vacancies in crystals and the subsequent collapse of vacancy discs to form dislocation loops are considered for various conditions of cooling and supersaturation, with special reference to conditions prevailing during crystal growth from the melt. The vacancy supersaturation required for growth of a dislocation loop (a collapsed vacancy disc) of a given size to occur, is calculated. These results are compared with the theoretically evaluated vacancy supersaturation, reached in a crystal, as a function of condition prevailing during growth. The results of experimental studies of crystals grown from the melt, are compared with the theoretical predictions discussed above. It is observed, in particular, that crystals produced under conditions of insufficient supersaturation, for the growth of discs to occur, are found to be free of dislocations detectable by means of X-ray diffraction techniques suitable for observing individual dislocations. The results of this study are consistent with the hypothesis that the collapsing vacancy disc mechanism plays an important rôle in the creation of dislocations in crystals grown from the melt. The effects of impurities on the above mechanism, and particularly of impurity concentration gradients, are discussed.

## 1. Introduction

Dislocations do not exist in thermal equilibrium with respect to any conceivable sources or sinks in a crystal. Their origin must, therefore, be sought in kinetic mechanisms, whereby the dislocations are formed at the expense of some other configuration associated with a free energy higher than that of the crystal containing dislocations. Several such mechanisms have been considered to-date[1], but none were so far explored, theoretically or experimentally, in sufficient detail to allow definitive conclusions to be reached regarding their relative importance. In this paper the precipitation of vacancies and the subsequent collapse of vacancy discs to form dislocation loops are examined for various values of cooling rate and of supersaturation, with special reference to conditions prevailing during crystal growth from the melt.

In recent years, direct electron microscopic observation of collapsed vacancy discs (dislocation loops)* in rapidly cooled metal foils[2] has provided direct proof that dislocations can be generated by this mechanism under certain conditions. So far, however, the vacancy supersaturation required for nucleating discs of a given size has not been determined; in fact, experiments on the quenching of thin foils, for the purpose of determining this supersaturation, are beset with inherent difficulties. Some of these difficulties are as follows. When dislocation loops are observed in foils quenched to a sufficiently low temperature, so that vacancy mobility is small and the escape of vacancies to external surfaces or internal sinks may be neglected, the temperature at which vacancy discs have nucleated is not known*. If the quenching is done to successively increasing temperatures, in an attempt to determine the supersaturation (or temperature) at which nucleation of discs occurs, a temperature is eventually reached where the escape of vacancies to external surfaces may no longer be neglected**. In this case the experiment would be performed under conditions of rapidly decreasing supersaturation and, therefore, may be meaningless as far

* Throughout this paper the expression "dislocation loops" refers to loops formed by the collapse of vacancy discs.

* All that can be said, in this case, is that the discs have nucleated at some temperature above that of the quenching medium, hence at a supersaturation lower than that corresponding to the quenching medium.

** In all cases that the author is aware of, discs appear to nucleate at a temperature higher than that for which the escape of vacancies to external surfaces of thin foils becomes important.

as determining the vacancy supersaturation required for nucleating discs is concerned. Similar difficulties of interpretation are encountered in the observation of the disappearance of small dislocation loops in thin foils, as a function of increasing temperature.

## 2. Vacancy Supersaturation and Growth of Dislocation Loops

In this study attention is focussed on calculations of the vacancy supersaturation reached in a crystal, as a function of specimen dimensions and of diffusion conditions prevailing during crystal growth from the melt. These results are compared with the supersaturation required for growth of a dislocation loop of a given size to occur, which is also calculated. The above comparison yields the value of the critical cross-sectional dimensions of the crystal below which the supersaturation of vacancies is not sufficient for growth of dislocation loops. Different values of the cross-sectional dimensions are obtained for different sets of diffusion parameters, corresponding to the usual range of crystal growth conditions encountered in the laboratory.

In order to calculate the supersaturation of vacancies in a crystal, the following model is used:

1. The crystal is an infinitely long cylinder of radius $A$.
2. The vacancy concentration throughout the crystal, at the melting temperature $T_M$, corresponding to time $t=0$ is the equilibrium value $C_0 \cong \exp(-U_f/kT_M)$ where $U_f$ is the formation energy of a vacancy.
3. The external surface of the cylinder constitutes the only sink for vacancies.
4. The temperature of the crystal decreases exponentially with time, $T=T_M \exp(-\beta t)$, where $\beta$ is a constant.
5. The diffusion coefficient is a function of temperature only (and hence of time).
6. As the temperature decreases with time the concentration of vacancies at the surface of the crystal, $C_A(t)$, is the bulk equilibrium value for the particular instantaneous temperature prevailing (the surface is assumed to be an ideal sink).

The concentration of vacancies in the crystal, as a function of distance from the axis and of time, is obtained by solving the appropriate diffusion equation, subject to the above initial and boundary conditions. The equation to be solved in this case (Fick's second law, written in cylindrical coordinates) is:

$$\frac{\partial c(r,t)}{\partial t} = D(t)\left[\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c(r,t)}{\partial r}\right] \qquad (1)$$

subject to the conditions:

$$\begin{aligned} C(A,t) &= C_A(t) \qquad r=A \qquad t>0 \\ C(r,0) &= C_0 \qquad 0\leq r\leq A \qquad t=0 \end{aligned} \qquad (2)$$

$$T = T_M \exp(-\beta t)\,. \qquad (3)$$

Eq. (1) cannot be integrated in closed form when condition (3) is introduced. A set of numerical solutions was, therefore, obtained for various values of crystal radius $A$ and of diffusion parameters[3]. The results covering the range of interest for the experiments discussed below are shown in Fig. 1.

The vacancy supersaturation necessary to nucleate a disc can be calculated in principle. In practice, reliable values of the supersaturation are not known because of large uncertainties in the energy of such a vacan-

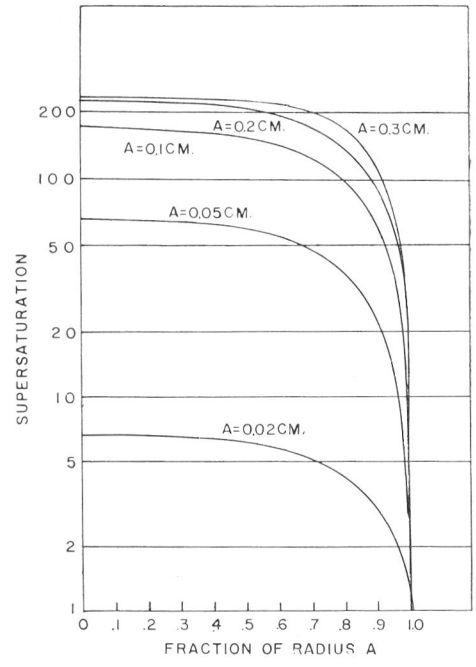


Fig. 1. Supersaturation of vacancies in a cylindrical crystal aluminum cooled from 933°K to 588°K *versus* fraction of radius (Radius of crystal in centimeters written beside each curve.)

cy configuration. Assuming that vacancy discs have formed and collapsed into dislocation loops, it is possible to calculate the supersaturation required for growth of a loop of a given radius. In this case one can calculate an upper limit of the supersaturation, by evaluating the energy of the dislocation loop from microscopic concepts; this leads to an overestimate of the energy of a loop, when the condition $r \gg b$ (where $r$ is the loop radius and $b$ the Burgers vector) is *not* fulfilled. In fact, the overestimate increases with the decreasing ratio $r/b$. Since, in the case of most metals, a vacancy disc is expected to collapse into a dislocation loop for $r \lesssim 2b$[4], it is clear that the supersaturation calculated from macroscopic considerations of the loop energy will be an overestimate.

For the purpose of the present study it is more convenient to determine the critical temperature, $T_C$, corresponding to the critical vacancy supersaturation. This temperature was calculated[5] and is given by:

$$T_C = \frac{1 - \dfrac{K(\mu b^3)_{T_0}}{U_f}[1+300(\beta+3\alpha)]}{\dfrac{1}{T_M} + \dfrac{(\mu b^3)_{T_0}}{U_f}(\beta+3\alpha)} \qquad (4)$$

where $K$ is a numerical factor that depends on the value chosen for $r$, and $(\mu b^3)_{T_0}$ (which varies approximately as the strain energy per atomic plane of a dislocation) is taken at $T_0 = 300°K$. $\mu$ is the appropriate shear modulus, $\beta$ is the temperature coefficient of the shear modulus (which is considered to decrease with increasing temperature and $\alpha$ is the linear coefficient of thermal expansion.

A comparison between the supersaturation corresonding to $T_C$ and the maximum supersaturation attained in a crystal, for given growth conditions (determined from supersaturation curves such as shown in Fig. 1) yields the crystal radius for which the supersaturation is not sufficient for generating dislocations by the above process.

## 3. Experimental Results

Results of experimental studies of aluminum single crystals grown from the melt were compared with the theoretical predictions discussed above. The experiments were carried out on crystals grown from the melt by the Czochralski method. In order to study the variation of dislocation density with crystal diameter, tapered specimens, in the shape of elongated cones ("carrot"—shaped), were grown under a wide range of variables which included the conditions corresponding to the critical supersaturation discussed above. It is observed, in particular, that the dislocation density found in these crystals, for a given set of growth conditions, is a rapidly varying function of crystal size, as expected on the basis of the theoretical considerations. Specifically, for a given set of diffusion parameters (determined by the growth conditions) the dislocation density decrease with decreasing diameter of the crystal*. Generally, a change of growth conditions which corresponds to a decrease of vacancy supersaturation is accompanied by a decrease in dislocation density. Crystals produced under conditions of insufficient supersaturation for growth of discs to occur are found to be free of dialocations detectable by means of an X-ray diffraction technique suitable for observing individual dislocations. Through an appropriate variation of the shape of the crystals it is demonstrated that the disappearance of the dislocations is not due to dislocations growing out of the crystal by reaching the external surfaces**.

The results of this study are consistent with the hypothesis that the collapsing vacancy disc mechanism plays an important rôle in the creation of dislocations in crystals grown from the melt.

## 4. Effects of Impurities

Some effects of impurities and of impurity concentration gradients on the nucleation of loops will now be examined.

In the presence of an impurity concentration gradient*** there is usually a flow of

* This applies only in the range where the vacancy supersaturation varies rapidly with crystal diameter (see Fig. 1).

** Crystals of a diameter 1.5 to 2 times the critical value for the disappearance of dislocations, were grown to a length forty times the diameter. No variation was observed in the dislocation deusity, over the entire length of the crystal.

*** For the purpose of the present discussion it will be assumed that only two atomic species, $A$ and $B$,are present.

atoms of one kind in one direction, $I_A$, and a numerically different flow of atoms of the other kind, $I_B$, in the opposite direction. If the total number of atomic sites in the solid is conserved, the difference between the net rates of flow of the two atomic species must be compensated by a flow of vacancies, $I_V$ in a direction determined by the condition that the vector sum of the three flows vanish:

$$I_A+I_B+I_V=0\ . \qquad (5)$$

The existence of the vacancy flow $I_V$ gives rise to the well-known Kirkendall effect[6].

Configurations similar to conventional Kirkendall diffusion couples frequently arise in crystals grown from the melt. More specifically, over a wide range of growth parameters, of experimental interest, the presence of small amounts of impurity in the liquid leads to the formation of a characteristic substructure during solidification[1]. The substructure consists of narrow regions (approximately 50 microns wide) where the impurity content is alternatingly higher and lower than the average*. These regions are approximately parallel to the direction of growth; they are, of course, separated by large concentration gradients. Each pair of such regions, having respectively a low and a high concentration of impurities, constitutes a Kirkendall-type diffusion couple. At temperatures near the melting point (immediately after solidification) rapid diffusion must be associated with these concentration gradients. A flow of vacancies must, in general, accompany the diffusion process.

In conventional Kirkendall-type diffusion couples the flow of vacancies, due to the pumping action of the chemical gradient, leads to a supersaturation of these imperfections on the side of the diffusion interface which contains a higher concentration of the faster diffusing constituent. Frequently, this supersaturation results in the formation of pores visible by optical means. Experimental results[7] available to-date seem to support the view that these pores nucleate (heterogeneously) on large extraneous particles, introduced accidentally during preparation of the couples.

* The differences in concentration may be as high as a factor of ten.

In the absence of such heterogeneous nuclei (as is normally the case in crystals grown from the melt) it may be expected that the vacancy supersaturation due to the unequal diffusion flows will reach values substantially higher than those observed or inferred in the case of conventional Kirkendall couples.

It is proposed that this extra supersaturation of vacancies (added to the supersaturation resulting from the drop in temperature) will lead to preferential nucleation of dislocation loops in the diffusion zone.

The diffusion process discussed above can be expressed more formally in terms of the vacancy current $I_v$ associated with a chemical (impurity) concentration gradient:[6]

$$I_v=-D_v \operatorname{grad} C_v+KC_v \operatorname{grad} C_i \qquad (6)$$

where $D_v$ is the diffusion coefficient for vacancies (which is a function of composition), $C_v$ is the concentration of vacancies, $C_i$ is the concentration of impurity atoms, $K$ is a coefficient which gives a measure of the pumping action for vacancies arising from the concentration gradient.

The first term on the right side of Eq. (6) is the usual Fick current of vacancies. The second term represents the vacancy current which gives rise to the Kirkendall effect. The two terms have opposite signs; when the Kirkendall effect occurs the second term is larger than the first and the vacancies flow from the side of the couple where their density is low to the side where their density is high. This flow is responsible for the local increase in supersaturation to be added to the supersatution that arises from a drop in temperature. Further work on the quantitative aspects of this supersaturation, especially in connection with crystal growth, is in progress.

The process proposed above should occur whenever a gradient of impurity concentration arises during crystal growth. The occurence of this process in connection with the specific impurity substructure, discussed above, is however, more amenable to quantitative treatment than the case of an arbitrary concentration gradient.

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## COMMENT

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### Crystal Defects in Evaporated Single Crystal Tin Films*

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Electron microscope studies of imperfections in crystals have been limited primarily to thinned bulk samples. Few studies using evaporated films have been made, owing to the experimental difficulties encountered in making satisfactory specimens. Recently it was shown that single crystals of white tin with a remarkably high degree of crystalline perfection could be made by evaporation under ultra high vacuum conditions[1) 2)]. These films ranged in thickness from 1000 Å to 3800 Å and were, therefore, ideally suited for electron microscope studies of crystal defects. The electron micrographs of lattice defects obtained from these films were of a quality comparable to that of bulk specimens.

These tin films are presently being used for electron microscope studies of dislocations, small angle grain boundaries, and deformation twins. It has been found that above room temperature the motion of single dislocations under the influence of electron beam bombardment is rapid and wandering. The major slip systems operating are (121) [$\bar{1}$01] and (101) [$\bar{1}$01]. Dislocations of the latter slip system move at considerably faster speeds than those of the former. The wandering characteristics of both dislocations suggests that they have screw character. Cross-slip from (121) [$\bar{1}$01] to (101) [$\bar{1}$01] and *vice versa* has also been observed.

A typical example of slip and cross-slip taking place in these films is shown in the accompanying

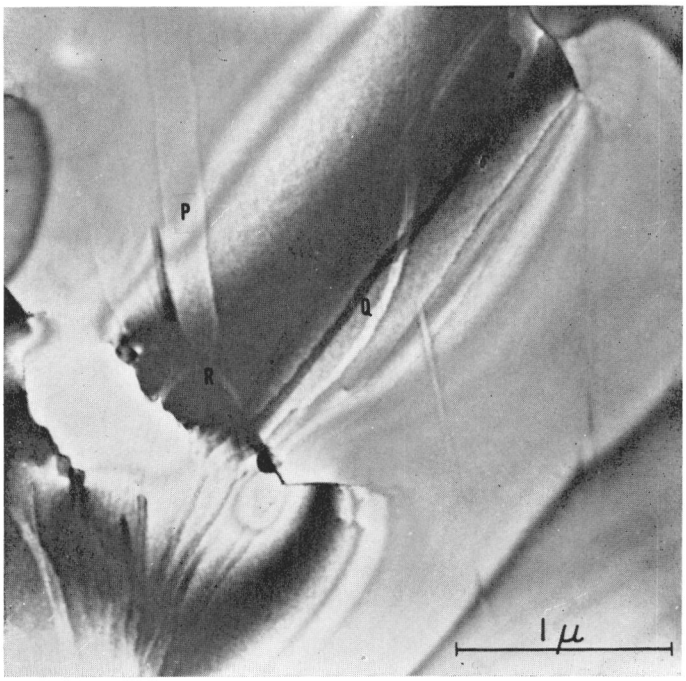


Fig. 1

* Presented by H. G. F. Wilsdorf.