EVOLUTION OF A DISLOCATION STRUCTURE IN THE SURFACE LAYERS OF SINGLE CRYSTALS DURING HIGH-TEMPERATURE ANNEALING

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The dislocation structure of KCl crystals annealed in a forevacuum has been shown to display a nonmonotonic variation of the density of dislocations in the direction from the surface. Our experiments and estimates showed that the observed redistribution of dislocations near the surface is due to the diffusion of impurities from the atmosphere and the generation of dislocations in the diffusion zone.

High-temperature annealing of crystals is inevitably accompanied by their interaction with the medium, which causes certain changes in the surface properties of the crystals. These changes may be expressed to different degrees and in different ways, depending on the strength of the interaction. In our experiments, in particular, we discovered that under the conditions of high-temperature annealing of crystals in an atmosphere of air the dislocation mobility near the surface changes in the field of applied stresses and a hardening effect is observed. The interaction with the medium, however, can be reduced to the motion, multiplication, and redistribution of dislocations during annealing and in the absence of an external load, i.e., can be reduced to effects which are usually observed in the diffusion contact between different materials [1, 2].

In this work we studied the laws governing the evolution of the dislocation structure during high-temperature annealing, which are due to the interaction of crystals with the ambient medium, and we discussed possible models of the processes.

EXPERIMENTAL PROCEDURE

We chose KCl crystals as the object for our investigations. Since at high temperatures ($T \approx 1023$ K) potassium chloride has a high saturated vapor pressure ($p \approx 10$ Pa), when annealing the samples we used a special vacuum valve, which substantially decreases the vaporizability of the crystals; otherwise, the procedure employed was analogous to that described in [3].

The annealing regime comprised heating, isothermal soaking, and cooling at a rate of about 10^{-2} K/sec, which is dangerous with respect to the generation of new dislocations as a result of relaxation of thermoelastic stresses. In the annealed crystal we studied the dislocation structure with an MIM-8 optical microscope and by the ω-method on a DRON-2.0 x-ray diffractometer [4]. The annealing temperature ranged from 773 to 1043 K and the annealing time, from 1 to 40 h.

RESULTS OF THE EXPERIMENT

The dislocation structure of crystals annealed in a forevacuum ($p \sim 10$ Pa) displayed a markedly nonmonotonic variation of the dislocation density in the direction from the surface. It can be arbitrarily divided into three zones (Fig. 1). In zones 1 and 2 the dislocation density is markedly lower or markedly higher, respectively, in comparison with the original single crystal and with the bulk of the annealed single crystal. In the third zone the dislocation density decreases monotonically. Besides pyramidal pits, zones 2 and 3 also contain flat-bottomed pits of unknown origin, which we shall call the "background" (Fig. 2), by analogy with [5]. Behind zone 3 comes a typical structure of the central part of a single crystal (4).

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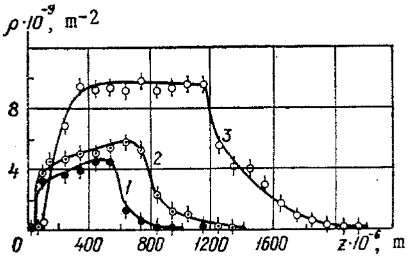

Fig. 1. Dislocation distribution in the diffusion zone near the surface of an annealed KCl crystal: T = 1043 K. Annealing time (h): 1) 4, 2) 12, 3) 40.

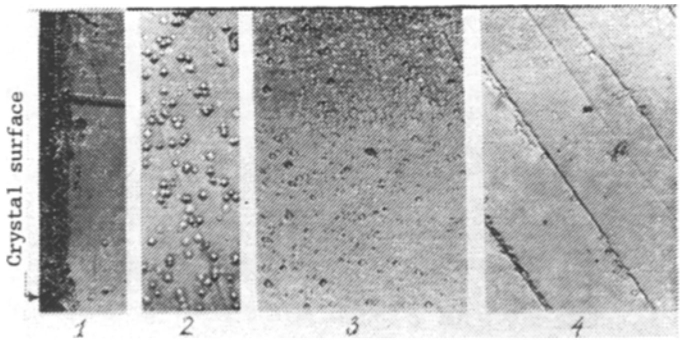

Fig. 2. Surface dislocation-background zone in annealed KCl crystals. T = 1043 K, t = 40 h. × 270.

In zone 1 the dislocation density $\rho_d \approx 10^8$ m^{-2} and the zone width is tens of micrometers. The linear dislocation density at the boundaries between blocks is relatively low in this zone. The boundaries change from "large-angle" to "low-angle" and in a number of cases disappear altogether, without reaching the surface of the crystal.

The width of zone 2 is 500-1000 μm and the dislocation density in it is $\rho_d \approx 5\cdot10^9$-$10^{10}$ m^{-2} while the "background" pit density is $\rho_f \approx (4$-$6)\cdot10^9$ m^{-2}.

Zone 3 has a width of 500-1000 μm. The dislocation density in it in the direction from the surface decreases from 10^{10} to 10^8 m^{-2} while the density of "background" pits increases; the pits themselves become considerably smaller (Fig. 2).

CONTROL EXPERIMENTS

Since the structural changes described above occur in the region of the crystal that borders on the surface, they are due either to the penetration of materials from the surrounding atmosphere into the surface layer or to internal processes that are independent of the surrounding medium but are related to the proximity of the free surface. The choice can be made only on the basis of experiments, in which the crystals under study would be either shielded against materials entering from the surrounding atmosphere or put into contact with a completely determined material. Control experiments of two types were performed.

Experiment No. 1. The samples studied were annealed in a molten-tin bath (T_m = 505 K). The annealed crystal was cooled to T ≈ 523 K, then a layer of low-temperature oil was poured on top of the metal, and when the temperature had leveled out, the sample was moved in the oil and after cooling was removed.

In crystals, which had been heat-treated in a bath of molten tin at T ≈ 1023 K for 10 h, a comparatively thin layer of crystal (≈100 μm) with a high dislocation density formed near the surface, after which followed an ordinary dislocation structure that is characteristic of the bulk (Fig. 2).

Experiment No. 2. An internal crack with no connection to the surface was caused in the crystal by means of a pulsed laser. The crack length was of the order of hundreds of microns and its width, of the order of several microns. The crystals with such internal cracks

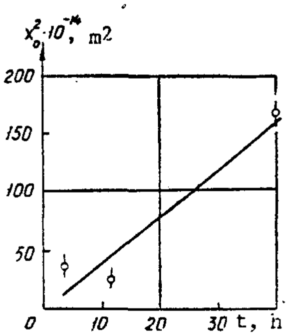

Fig. 3. Total width of dislocation zones as a function of the annealing time: 1) 943 K, 2) 1043 K.

were also annealed at high temperature for a long time. No increase in the dislocation density was observed near the edge of the cracks after the annealing.

Thus, control experiments show that the dislocation redistribution near the surface is associated with impurity diffusion into the crystal from the atmosphere.

DISCUSSION OF RESULTS

We evaluate the diffusion coefficients of divalent cations in control experiment No. 1 and of an impurity of unknown origin in the measuring experiments, making the assumption that the width of the diffusion zone is of the same order of magnitude as the width of the dislocation zone. Since in the first case the dislocation zone width is $Z \approx 10^{-4}$ m and the diffusion time is $t \approx 3.6 \cdot 10^5$ sec, from the relation $Z = \sqrt{D \cdot t}$ it follows that $D_1 \approx 5 \cdot 10^{-13}$ m^2/sec. In the second case $Z \approx 2 \cdot 10^{-3}$ m and $t \approx 2 \cdot 10^6$ sec, whereby $D_2 \approx 10^{-11}$ m^2/sec. Comparing D_1 and D_2 and bearing in mind that the estimate $D \approx 5 \cdot 10^{-13}$ m^2/sec is typical of the diffusion of divalent cations in alkali halide crystals [1], we come to the conclusion that the observed structures evidently are not a consequence of diffusion of a divalent cation impurity.

The formation of the observed dislocation structures, therefore, should be assumed to be caused by diffusion of nonmetal atoms. The most probable diffusing components are the oxygen ions O^{-2} and OH^-. The rate of penetration of these components into the crystal, as seen from the estimates, is substantially higher than that of divalent cations. As follows from [8], it is most likely that the penetration of O^{-2} into the crystal is mediated by the formation of an intermediate oxide phase on the surface (of the Me_2O type).

Before discussing the mechanism of rapid penetration of O^{-2} or OH^- ions into the crystal, we consider the reasons why dislocations appear in the diffusion zone. First, the in-diffused impurity causes mechanical stresses in the diffusion zone. If we use the model of diffusing atoms – rigid spheres causing local dilatation of magnitude $\beta = \Delta V/\bar{V}$, $\Delta V = V_p - V_a$ and $\bar{V} = (V_p - V_a)/2$, where V_p and V_a are the volumes of the impurity and matrix atoms, respectively, then the stresses σ can be evaluated from the relation [6]

$$\sigma = E\beta C/3(1-\nu), \qquad (1)$$

where E is Young's modulus, ν is the Poisson ratio, and C is the impurity concentration.

If we take into account the ionic radii, e.g., the oxygen ion O^{2-} ($1.36 \cdot 10^{-10}$ m) and the chlorine ion Cl^{1-} ($1.81 \cdot 10^{-10}$ m), then for $E \approx 3 \cdot 10^{10}$ Pa, $C \sim 10^{-4}$, $\beta \approx 0.81$, and $\nu \approx 0.25$, we have $\sigma = 10^6$ Pa.

This is, of course, a fairly rough estimate. It does show, however, that the diffusion stresses undoubtedly exceed the yield stress of the crystal ($\approx 10^5$ Pa), especially at high temperatures, and causes plastic flow in the diffusion zone.

Second, the appearance of dislocations is associated with the possible precipitation of particles of different phases from the supersaturated solid solution during cooling of the samples and the loss of a coherent bond between these particles and the matrix. These dislocations can disappear as the result of dissolution by diffusion [7]. A narrow dislocation-free zone near the surface is observed in the completely cooled samples. Under the given conditions, therefore, dislocations of this type managed to disappear almost completely and will thus not be discussed further.

We shall assume that the dislocations observed after cooling appeared as a result of the relaxation of diffusion stresses.

The mechanism of the observed rapid spread of impurities in the crystal is the following, in our view. It cannot be ruled out that the core of a dislocation possesses an enhanced diffusion permeability. As is known, in metals [6] the coefficient of diffusion along a dislocation is 4-5 orders of magnitude higher than in the bulk. Since the bulk diffusion coefficient in the premelting stage is $D_V \approx 10^{-12}$-10^{-13} m^2/sec, it is $D_d \approx 10^{-8}$-10^{-9} m^2/sec along dislocations and a time $t_d \approx Z^2/D_d \approx 10^2$-$10^3$ sec is required for diffusion penetration to a distance of about 10^{-3} m. This is two or three orders of magnitude shorter than the time of working anneals. Furthermore, the impurity diffuses into the crystal from internal sources (dislocations), which are separated by a distance of the order of $\ell_d \approx \rho^{-1/2}$. For $\rho \approx 10^8$-10^9 m^{-2} this separation is $\ell_d \approx 10^{-4}$ m. The diffusion front takes a time $t \approx \ell_d^2/D_V \approx 10^4$-$10^5$ sec to move such a distance. This is the lowest estimate since the impurity concentration levels out during diffusion and, therefore, the diffusion driving force decreases. Clearly, the characteristic of the leveling out of the concentration is longer than the estimate given above. Bearing in mind this circumstance and the fact that the annealing time is of the order of $3\cdot(10^5$-$10^6)$ sec, we can assume that the estimate given here incontrovertibly attests to the reasonableness of such a mechanism of impurity propagation in a crystal.

We do not discuss the formation of a "dislocation-free zone" near the surface. A dislocation near the surface is acted upon by a mirror image force F_i and a force F_j from the other dislocations of the pile-up. Since $F_i \approx F_j$ for the dislocation structure formed near the surface [9], when making further estimates we can consider the action of only the mirror image force. Uhder the effect of this force the dislocations will diffuse toward the surface with velocity v_i, which is determined by the relation $v_i = D\Omega\sigma/\kappa T b$ [9], where D is the self-diffusion coefficient and Ω is the atomic volume. Using this relation, we link the width x_0 of the surface "dislocation-free layer" observed in the experiment with the time t,

$$x_0^2 \approx D\Omega G t/\pi(1-\nu)\kappa T. \tag{2}$$

Next, from the graph of $x_0^2 = f(t)$ (Fig. 3) it follows that the self-diffusion coefficient of KCl single crystals at T = 1043 K was $\approx 10^{-13}$ m^2/sec, which is an entirely reasonable value and, therefore, a "dislocation-free zone" can indeed form near the surface under the effect of the mirror image force.

CONCLUSION

1. A nonmonotonic distribution of dislocations has been detected near the surface of annealed single crystals, i.e, a "dislocation-free zone" and a wide zone with a markedly increased dislocation density have been observed near the surface.

2. The large width of the dislocation region is associated with the rapid penetration of anion crystals along dislocation tubes with a further distribution of the impurity in the crystal between dislocations.

3. The appearance of a "dislocation-free zone" is due to the emergence of dislocations on the surface under the action of mirror image forces.

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SLIP ALONG A BOUNDARY FORMING AN INCOMMENSURABLE STRUCTURE

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The boundary dividing a plane with rational indices, for example, (100) and (110) in a cubic lattice, is considered. The planes are oriented so that the direction [001] is common. Then the interatomic distances are incommensurable in the perpendicular direction. The conditions of thermal activation slip along such a boundary are studied. For sufficiently small stresses the dependence of the derivative of the slip velocity on the stress has a discontinuous nature.

Comparatively great attention has been paid to the thermodynamic properties of physical systems forming incommensurable structures [1], while the kinetic phenomena of the rearrangement of an incommensurable structure under the influence of external forces have been discussed much less in the literature. In particular, the slip of the crystals on whose interface an incommensurable atomic structure forms is one of these forces.

In this report we confine ourselves to the case of one-dimensional incommensurability, when the interatomic distances are incommensurable in the boundary plane in the τ direction, but are commensurable in the perpendicular direction in the boundary plane. Such a boundary can be both interphase and intergranular. A boundary at which the faces (100) and (110) adjoin crystals with cubic structures can serve as an example.

We denote the crystallite periods in the direction of τ by a_1 and a_2. In the above the crystallographic directions [010] and [$\bar{1}$10] of adjacent crystallites are located along τ, while the direction [001] is common to them. Then $a_1 = a$, $a_2 = a\sqrt{2}$, where a is the lattice constant.

We first consider the geometric pattern of the superpositions in the boundary plane. The positions of the atomic sites in the aggregate form a vernier in the τ direction. We denote by ξ the displacement (distance) between two atoms of neighboring crystallites in the τ direction. It is characteristic of incommensurable periods that all ξ will be different and equally probable. The value $\xi = 0$ will be satisfied for only one pair of atoms.

We introduce the density function $n(\xi)$ of the distribution over ξ. We plot the atomic sites of one crystallite in the τ direction along the x axis, and the other along the y axis. Then the plane is covered by a rectangular lattice of points, each of which corresponds to a pair of sites. The distance ξ between the pair of sites of the incommensurable structure will be equal to the section of a straight line, parallel to the y axis and enclosed between the point corresponding to this pair of sites and the bisector $y = x$. If we now construct the straight lines $y - x = \xi$ and $y - x = \xi + \Delta\xi$, the number of points per unit length which are between these straight lines is equal to the number of atoms with distances from ξ to $\xi + \Delta\xi$, equal to $n(\xi)\Delta\xi$. Evidently, the point density is expressed in the form

$$n(\xi) = 1/a_1 a_2. \tag{1}$$

The relative displacement $\Delta\xi$ of the crystallites along the boundary will be accompanied by coincidences of the positions of the atomic sites of neighboring crystallites at certain

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