

SURFACE ENERGY AND SURFACE PROCESSES IN SOLIDS

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CONTENTS

I. Introduction	129
II. Methods for Determining the Surface Energies of Solids	130
III. The "Natural Roughness" of the Surfaces of Crystals	136
IV. Change of Surface Profile in Single Crystals and Polycrystalline Materials	139
V. The Development of Intergrain Thermal-etching Grooves	147
VI. Liquid Films on Surfaces of Crystalline Materials.	151
VII. Conclusion	153
Literature Cited	153

I. INTRODUCTION

THE conditions of crystals of a polycrystalline specimen with part of their surfaces in contact with their own vapor saturating the space around the specimen are under conditions very different from those of crystals inside the specimen. One of the reasons for the difference is that the average overall orientations of the specific surface energy at the boundaries of the randomly oriented crystals (grains) is much smaller than the specific surface energy of a crystal at its interface with its own vapor.

Another reason for the special conditions of a crystal with a face bounded by vacuum is that processes occurring at the surface, unlike those occurring in the body, can be caused by surface migration of atoms and interactions between these atoms and the gaseous phases of the same and other substances.

In the case of a polycrystalline object free from various kinds of macroscopic defects and microscopic distortions, the existence of an excess free energy, which is the sum of the energy of the surface of the polycrystalline object itself and the energy of the interfaces between the elements of the structure (grains, mosaic blocks, etc.), is the only circumstance that stimulates processes by which the polycrystalline object approaches true equilibrium, i.e., processes tending to convert it into a single crystal with an equilibrium boundary. In this case the excess energy of the internal boundaries will stimulate the process of selective recrystallization, and the excess energy of the free surfaces, which also affects the kinetics of recrystallization, will cause certain specific "surface effects," which are the subject of the present article.

In the case of one-component systems the arguments given here hold of course without regard to the temperature of the crystal. We shall, however, also be interested in processes which occur at high temperatures, somewhat below the melting temperature, at which all processes are activated by the large dif-

fusion mobility of the ions, and in many cases by a large vapor pressure.

In the general case the direction of the processes which occur spontaneously at the surface of a crystalline body at high temperatures is determined by the tendency of the free energy to approach a minimum, i.e., by the direction of decrease of the quantity $E = \iint \sigma_S(\mathbf{n}) dS$ (under the condition $\iint Z(x, y) dx dy = \text{const}$, where $z = Z(x, y)$ is the equation of the surface of the crystal), where $\sigma_S(\mathbf{n})$ is the surface energy, which depends on the direction (\mathbf{n} is the normal to the surface of the crystal). As has already been stated, the final result of this tendency is the formation of a single crystal of equilibrium shape.

On the way to the final (true) equilibrium, at which the absolute minimum of the quantity E is attained, there can occur intermediate states such that transition to them is accompanied by a partial advantage in energy. Under various conditions these processes can have very different appearances and can be accompanied by phenomena which may seem mutually exclusive if not deeply analyzed.

In view of the fact that in crystalline bodies the quantity σ_S is anisotropic, we can, by a formal approach to the expression $E = \iint \sigma_S(\mathbf{n}) dS$ which gives the total surface energy of the crystalline body, point out two essentially different tendencies which lead to the occurrence of intermediate states.

First, it can be energetically advantageous for the surface to increase (or develop) with the appearance of faces with small surface free energy. This possibility is a consequence of the fact that if σ_S is anisotropic the minimum surface area and the minimum surface free energy are not attained together.

In the course of the decrease of the surface free energy a "natural roughness" can appear on the polished surface of an arbitrary section of a polycrystalline body or single crystal. We must include in this same group of phenomena the appearance of so-called "thermal-etching grooves" and "thermal-etching

pits" on the surface of a polycrystalline specimen, at places where intergrain boundaries and discrete lines of dislocations intersect the surface of the specimen.

Second, it can turn out that a decrease of the surface will be the process that mainly provides a decrease of the surface free energy. The tendency toward a decrease of the free surface will be most clearly manifest when the surface of the body has been considerably developed artificially in the initial state. This tendency shows itself in processes of smoothing out ("healing over") of accidental or intentionally produced defects of the surface, or smoothing out of scratches. This group of phenomena includes in particular the well known process of "spheroidization" of dispersed metal particles with a large number of needle-like projections of dendrite shapes.^[123]

In actual cases the tendencies toward decrease of the surface and toward its development are realized simultaneously, so that on the profile of a macroscopic scratch which is being smoothed out (decrease of the surface!) there can appear microscopic steps of "natural roughness" (increase of the surface!).

Besides these two possibilities for decrease of the surface free energy, there is a further quite different possibility, which is realized in the immediate neighborhood of the melting temperature. This is the possibility of the appearance of a liquid film on the free surface of a crystalline body. In such cases, while the area of the free surface remains unchanged, there is a decrease of the surface energy, owing to the discontinuous change of σ_S on melting.

The states of the surfaces of solid bodies, in particular of crystalline bodies, and the phenomena that occur at the free surfaces are extremely important for many processes, particularly processes that occur at high temperatures, at which the diffusion mobility of the atoms and the vapor pressure are large. In this connection we may mention phenomena and processes such as the surface migration of atoms, the interaction of the free surface with the gaseous phase (of the same or other substances), changes in the physical and chemical properties of the surface, in particular of its catalytic properties,^[124] and so on. Surface phenomena play a large part in the sintering of powders (metallic and nonmetallic) and in creep and rupture of solids.

The phenomena that occur at the free surfaces of crystalline bodies at high temperatures are of special interest in connection with the problem of the growth of crystals. In the picturesque language of A. V. Shubnikov, "the entire volume of a crystal was once its surface," and this is a rather complete statement of the importance of surface phenomena in the production of a crystal free from structural defects.

The processes that occur at the surfaces of solid bodies at high temperatures are extremely sensitive to the composition of the ambient gaseous medium

and (other conditions being equal) to the pressure of the substance's own vapor in the space around the crystal. In this article we consider only processes on the surfaces of one-component solids in equilibrium with their own vapors. The many physico-chemical processes caused by the interaction of a crystal with different gases (oxidation, etc.) are not considered here.

II. METHODS FOR DETERMINING THE SURFACE ENERGIES OF SOLIDS

In discussing the phenomena occurring at the surface of a solid we must distinguish the work required for the production of a surface of unit area from the work required for the increase of an existing surface by the same amount (by 1 cm²). This means that we must make a distinction between the surface energy and the surface tension.

Physically the difference arises because in the stretching of a surface the mean distance between atoms in the surface layer will be changed and there will be a corresponding change in the conditions of interaction between them. The connection between the magnitude of the surface energy (σ_S) and that of the surface tension (γ_S) is given by the well known relation

$$\sigma_S = \gamma_S + S \frac{\partial \gamma_S}{\partial S} \quad (1)$$

In the case of a liquid one usually makes no distinction between the quantities σ_S and γ_S , because the equilibrium density of the liquid film in the surface layer is established practically instantaneously after a deformation of the film, i.e., the process of deformation occurs in such a way that $\partial \gamma_S / \partial S = 0$. It must be noted, however, that even in the case of a liquid there are in principle conceivable experimental conditions for which the process of establishing the equilibrium density of the atoms at the surface—the kinetics of which process depend on the mobility of the atoms—may not occur quickly enough after the increase of the surface, and in this case the quantity $\partial \gamma_S / \partial S$ will be different from zero. For example, a particular case in which this can occur is in the determination of the surface tension of a viscous liquid from the propagation of high-frequency surface waves. Thus, generally speaking, the difference between σ_S and γ_S can be appreciable in the case of liquids and can be negligibly small for crystalline substances, if the measurements on them are made at high temperatures and extend over long periods of time.

Let us turn to the description of the experimental methods for determining the surface energy coefficients of solids, and the results obtained by these methods.

1. The method of "zero creep." The idea of the method of "zero creep" is as follows. At a high temperature the effect of the surface-tension forces should

be to change an arbitrary shape of the solid body in the direction of a decrease in the total surface energy. In particular, a freely suspended thin wire or foil should contract in length. On the other hand, under the action of an externally applied force (F) the foil (or filament) can lengthen, owing to viscous flow. Obviously, for some value $F = F^*$ of the applied force the forces of surface tension will just be balanced and the rate of creep will be zero. The experimentally determined F^* can be a source of information about the magnitude of the surface tension.

We note that long filaments (or foils) will be subject to creep even when not loaded, since the capillary forces of axial compression can be smaller than the forces caused by the weight of the filament. We must regard as "long" in this sense a filament in which the pressure caused by the force of gravity ($h\rho g$) exceeds the pressure of compression by capillary forces directed along the axis ($\sim \sigma/R$), i.e., a filament for which the inequality $\sigma_S/R \leq h\rho g$ or $hR \geq \sigma/\rho g$ is satisfied. For a copper filament this is $hR \geq 1.8 \times 10^{-1} \text{ cm}^2$. In these relationships h is the length of the filament, R its radius, and ρ the density.

Let us consider the problem of zero creep, taking the case of a thin foil ($\omega \gg d$) (Fig. 1). The rate of elongation of the foil is given by the relation

$$\dot{\epsilon} = \frac{1}{\eta} (P - P_S), \tag{2}$$

where $P = F/S$, $S = \omega d$ (ω is the width and d the thickness of the foil), and $P_S = P_X = \frac{1}{2} (P_Y + P_Z)$,

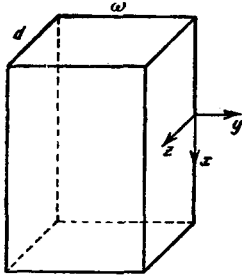


FIG. 1.

where $P_X = P_Y = -2\sigma/d$, $P_Z = 0$. Thus for $\dot{\epsilon} = 0$ we have $P_S = P^* = F/\omega d$, and

$$\sigma_S = \frac{F^*}{\omega}. \tag{3}$$

The relation (2) assumes that the elongation of the specimen in the process of viscous flow occurs uniformly over the entire length. In the case of a crystalline body subjected to viscous flow with the kinetics given by Eq. (2), the coefficient of viscosity at a given temperature is not a single-valued characteristic of the substance, but depends on the geometry of the specimen, and in particular for a polycrystalline specimen on the linear dimensions of the grains. According to Herring^[1] this connection is given by a relation of the type

$$\eta \simeq A \frac{T\bar{L}^3}{D}, \tag{4}$$

where \bar{L} is the average linear grain size, T is the absolute temperature, D is the diffusion coefficient, which increases exponentially with the temperature, and $A = k/\Omega$ (k is Boltzmann's constant and $\Omega = \delta^3$, δ being the interatomic distance). The relation (4) comes from the following ideas about the mechanism of viscous flow of crystalline bodies. In a body subjected to macroscopically homogeneous but nonisotropic stresses there are different normal stresses (P_{ns}) on the different parts of the surfaces of the structural elements (blocks, grains), and hence near these surfaces there are produced different degrees of supersaturation with vacancies, in amounts proportional to P_{ns} :

$$\Delta\xi \simeq \xi_0 \frac{\Omega}{kT} P_{ns}. \tag{5}$$

The effect of the gradients that arise is to produce diffusion fluxes of vacancies (or, what is the same thing, fluxes of atoms in the opposite directions) inside each of the structural elements. These fluxes lead to changes of shape of the structural elements. These mutually consistent changes of shape* lead to the macroscopic change of shape of the specimen, i.e., to its diffusion-viscous flow.† An essential feature of the diffusion-viscous flow of real crystalline bodies is that, as in the case of amorphous bodies, it occurs at arbitrarily small stresses, that is, has no threshold. For precisely this reason it can be used to find σ_S by the method of zero creep, which was first suggested for use with amorphous substances. The relation (4) has been confirmed in many experimental papers.^[2-5]

The idea of the method of "zero creep" has been used for a long time. Tammann and his co-workers^[7,8] determined surface tensions of amorphous substances by this method. In recent years this method has been widely used to determine surface tensions of metals. Experiments have been made with foils^[3,110] and with thin wires.^[9]

Typical experimental data obtained in work on the determination of surface tension by the method of "zero creep" are shown in Fig. 2, from which it is obvious that mutual compensation of external forces and forces of surface tension occurs and can be used to determine the quantity σ_S (Table I).

2. The method of rupture (cleavage) of crystals. It is well known that there have been many attempts

*A consistent mathematical theory of the diffusion-viscous flow of real crystalline bodies has been developed in a book by I. M. Lifshitz.^[126]

†In the case of filaments and foils in which there is only one grain in the cross section ("bamboo" structure) the process of creep is accompanied by relative displacements of the grains, i. e., the development of the free surface of the specimen at the expense of a decrease of the areas of intergrain boundaries.^[2,4,6] This phenomenon can be taken into account in the calculation of σ_S .

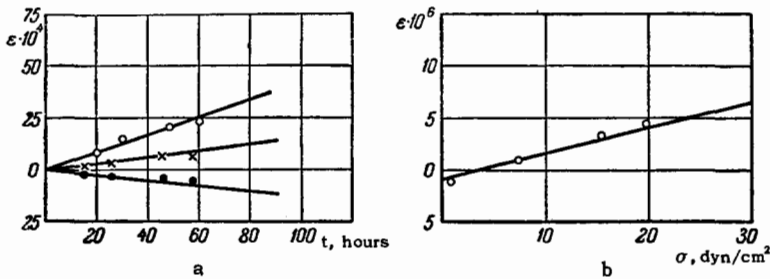


FIG. 2. Experimental data obtained in work on the determination of surface tension by the method of "zero creep" [1]. a) Dependence of fractional elongation on the time at various loads; ○ - 1.940×10^6 dyn/cm²; × - 0.910×10^6 dyn/cm²; ● - 0.044×10^6 dyn/cm². b) Dependence of rate of creep on stress.

Table I. Data on σ_S obtained by the method of "zero creep"

Metal	T, °C	σ_S , erg/cm ²	Reference	Remarks
Copper	950	1420 ± 20	9	Limiting values obtained for specimens of various thicknesses
	1000	1410 ± 40	9	
	1050	1390 ± 10	9	
	960	1680	3	
	975	1680	3	
	1002	1880-1800	3	
	1024	1660-1740	3	
1051	1690-1780	3		
Nickel	1250	1850	110	
	1452	1725	110	
Gold	920	1680	88	
	970	1280	88	
	1020	1400	88	
Silver	700-850	1780 ± 10	107	
	650-850	1140 ± 35	108	

to determine the surface energies of crystalline substances, based on the general idea that the work expended in the rupture of a crystal is equal to the surface energy of the new surfaces that are produced, if the rupture is brittle. These methods have mainly been described in a monograph by Kuznetsov. [16] It is easy to see that the values of the surface energy obtained in such experiments are, strictly speaking, always unreliable, since a part of the work which is hard to estimate is expended in the form of heat in the partial deformation of the crystals and in the energy of plastic deformation remaining in the crystals. The most promising version of a method for determining σ_S based on the cleavage of a crystal was proposed in 1930 by I. V. Obreimov. [17] The idea given in [17] is as follows. A plate is split off from the crystal along a cleavage plane, and the moment of force acting against the surface-tension force causes bending of the plate. The plate can be used as a dynamometer to measure the effort of cleavage. In fact, the work done by the moment M acting at the edge of a plate of thickness t (Fig. 3) while the region of rupture is being lengthened by the amount δx is given by [18]

$$M = \frac{\partial \delta \varphi}{\partial x} = M \delta x \frac{\partial^2 \varphi}{\partial x^2}.$$

Under equilibrium conditions this work must be equal to the change of the surface energy of the system, i.e., to $2\sigma \delta x$. Using the expression for the moment bending a plate (cf. [18]),

$$M = \frac{Et^3}{12(1-\kappa^2)} \frac{\partial^2 \varphi}{\partial x^2},$$

we can obtain the expression for σ_S :

$$\sigma_S = \frac{Et^2}{24(1-\kappa^2)} \frac{\partial^2 \varphi}{\partial x^2}, \tag{6}$$

which was used in [17]. In Eq. (6) E is Young's modulus, κ is Poisson's ratio, and φ is the angle between the tangent to the bent contour of the plate being split off and the direction of motion of the developing edge of the crack.

In [17, 19, 116, 117] studies were made of the splitting of mica, which, as is well known, cleaves perfectly; an interferometric method was used to determine the quantity $\partial^2 \varphi / \partial x^2$. It was shown by preliminary experiments that when a layer is repeatedly split off, after readhesion, the work of separation is the same as for the first splitting.

As has been shown by the experiments of Obreimov and Trekhov, [19] the work of formation of 1 cm² of

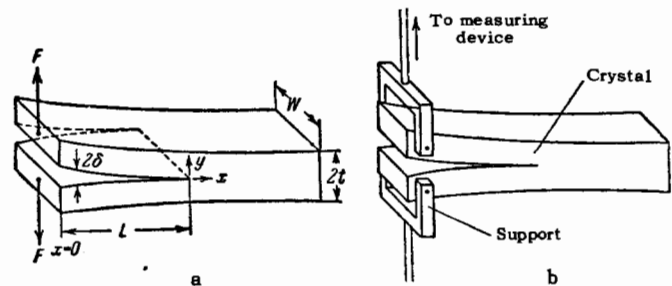


FIG. 3. Diagram of the splitting off of a layer from a crystal. [18]

surface found by means of this method (equal to ~ 375 erg/cm² for splitting of mica in air) is to be regarded not as a measure of the true strength of the crystal of mica, but as a measure of the adhesion of the absorbed layer of air sticking to the mica.

The method of rupture of crystals has recently been successfully applied^[118] for the direct measurement of the surface energies of many crystalline substances. The main measurements in ^[118] were made by forced splitting of the crystal along a definite crystallographic direction, the splitting being accomplished by the development of a previously prepared crack.

The force F required for the development of the crack in the scheme shown in Fig. 3 was measured by means of a sensitive dynamometric device.

In ^[118] it is convincingly shown that under conditions in which the cleavage occurs in the low-temperature region ($T = -195^\circ\text{C}$) the energy dW expended in lengthening the crack by the amount dL consists of two terms—the increase dW_u of the elastic energy of the halves of the crystal as they are split apart, and the free energy dW_s of the surfaces that are formed: $dW = dW_u + dW_s$.^{*} The total elastic energy of the halves of the crystal as they are split apart is $W_u = F^2L^3/6EI$, where E is Young's modulus and $I = \omega t^3/12$, where ω is the width of the specimen. From this we have $dW_u = (F^2L^2/2EI)dL$.

We also have $dW = Fd\delta_0$, where $\delta_0 = (\partial W_u/\partial F)_{x=0} = FL^3/3EI$. Thus $dW = (F^2L^2/EI)dL$. Using the relations that have been written and the fact that $dW_s = \sigma_S \omega dL$, one easily finds that

$$\sigma_S = \frac{6F^2L^2}{E\omega^2t^3}. \quad (7)$$

The relations (6) and (7) are in principle equivalent, since they have been obtained on the same assumptions. A convenience of Eq. (7) is that the measurement of the quantity σ_S is reduced to measurements of F and L , which can be made with great accuracy.[†]

By this method Gilman^[118] measured the surface energies of many crystals with various types of bonding, ionic, metallic, and covalent.

In ^[118] measurements of the surface energy were made on single crystals of the following substances: LiF(100), MgO(100), CaF₂(111), BaF₂(111), CaCO₃(100), Si(111), and Zn(0001). The results found in ^[118] in experiments at $T = -196^\circ\text{C}$, are tabulated here:

Substance	LiF (100)	MgO (100)	CaF ₂ (111)	BaF ₂ (111)	CaCO ₃ (100)	Si (111)	Zn (0001)
σ_S , erg/cm ²	340	1200	450	280	230	1240	105

The values so obtained for σ_S , in particular those for LiF and MgO, are in good agreement with values obtained from the theory of ionic lattices.

3. The method of the "neutral drop." The quantity σ_S can be determined from data on the equilibrium shape of a liquid drop of a different substance (B) placed on the surface of the solid (A) which is being studied.^[120,121] When the drop has its equilibrium shape the point O (Fig. 4, a) must be stationary. From the conditions that the sums of the x and y components of the forces acting on the point O must be equal to zero we get a formula connecting the quantity σ_S with the quantity σ_B and the angles α and β (see Fig. 4, a):

$$\sigma_S = \sigma_B (\cos \alpha + \text{ctg } \beta \sin \alpha). \quad (8)^*$$

The surface tension of the liquid B must be determined independently with great accuracy, and the angles α and β are determined metallographically in the cross-sectional plane of the drop perpendicular to the surface of substance A after the drop has become solid.

The method of the "neutral drop" has been used experimentally by Mazanets and Kamenskaya,^[120] who determined the surface tension of iron in the γ phase. As the substance for the liquid "neutral drop" they chose lead, which has practically zero solubility in iron. The shape of the drop they studied is shown in Fig. 4, b.

Taking $\sigma_B = 40$ erg/cm²,^[122] the authors of ^[120] found for σ_S for iron at $T = 920^\circ\text{C}$ the value 1645 erg/cm².

Let us call attention to some features of this method. This case is not like that in which substance A is also a liquid and the equilibrium shape of the drop of B can be established practically instantaneously; when A is a solid the equilibrium shape will be approached slowly, because the formation of the concavity (pit!) in the substance A under the drop ($\beta \neq 0!$) involves a mechanism much slower than the viscous flow of a liquid. At high temperatures the concavity can be formed by means of a diffusion mechanism. In this case the directed flow of vacancies into the region of the future "pit" will occur under the action of a gradient of the concentration of vacancies $\Delta\xi/L$ (L is a linear dimension of the drop), which is determined by the pressure gradient above the plane surface of A ($P_\infty = 0$) and below the surface of the drop [$P_r \sim (\sigma_B/r) \sim (\sigma_B/L)$]. It follows from these remarks that if the drop is made smaller the time for estab-

^{*}Speaking formally, one should also take into account the kinetic energy associated with the displacements of the halves of the crystal as they are split apart, and the energy associated with possible plastic deformations. We have evidence from estimates made in^[118] and from special experimental tests^[119] that these quantities are negligibly small.

[†]Because, as stated in^[118], the motion of the edge of the crack is rather jerky, the value taken for F was the critical value at which the next sudden motion occurs. The dislocation effects at the edge of a cleavage crack (in the case of ionic crystals) have been studied in detail in^[123].

*ctg = cot

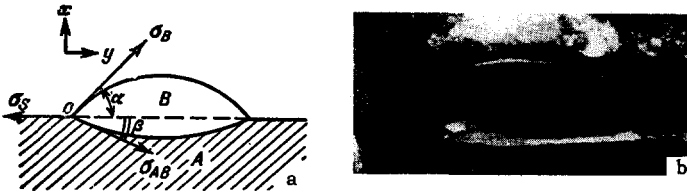


FIG. 4. a) Diagram of a "neutral drop" on the surface of a specimen. b) Actual shape of a "neutral drop" of lead on an iron surface (see^[120]).

lishing its equilibrium shape will decrease for two reasons: because of the decrease of the diffusion path in the transport of matter out of the region of the "pit" ($\tau \sim L^2/D$), and because of the increase of the gradient which causes the transport ($\Delta\xi \sim 1/L^2$).

For very small drops the time for establishing the equilibrium shape can be shortened owing to the fact that, as in the case of the healing over of small scratches (see below), surface diffusion as well as volume diffusion can make an appreciable contribution to the transfer of matter out of the region of the concavity.

4. The method of dissolving powders. In this method the quantity σ_S is found from the data of a calorimetric determination of the difference between the heats of solution of a dispersed powder (q_R) and of a bulk crystal of the same mass (q_0). It is assumed that the crystal lattice in the powder grains is an equilibrium lattice and that the observed difference of the heats of solution is due only to the release of the surface free energy of the grains of powder. The obvious connection between the surface energy of the powder and the additional heat released in the solution of the dispersed powder ($\Delta q = q_R - q_0$) is written in the form

$$\sigma_S = \frac{\Delta q}{S}, \tag{9}$$

where S is the original total surface of the grains of powder that are dissolved. In Eq. (9) it is assumed that the grains are single crystals, free from internal pores and boundary surfaces (such as grain boundaries).

Generally speaking this method can be a very sensitive one in the case of dispersed powders, since with a suitable degree of disperseness of the powder the calorimetric effect can be large enough to be determined with great accuracy, in particular when an ice calorimeter is used.^[20] In fact, even with comparatively large spherical grains with $R \sim 10^{-4}$ cm and $\sigma_S \sim 10^3$ erg/cm² we have

$$\Delta q \simeq \frac{3\sigma}{\rho R} \sim 0.07 \text{ cal/g}$$

(ρ is the density).*

*As is shown in the review article^[111], for extreme degrees of disperseness of the particles the quantity σ_S can differ from the value characteristic of the bulk metal. Taking^[111] $\sigma_{Sr} = \sigma_{S\infty} \times (1 - 2\gamma/r)$, where r is the grain radius and γ is a quantity of the order of 2δ , one easily sees that for σ_S and $\sigma_{S\infty}$ to agree within 1 per cent it is necessary that r have a value a little smaller than 10^{-5} cm.

A source of considerable error in this method is the inaccuracy in the determination of the total surface area of the grains of powder. The usual assumptions that the grains are spherical and that all grains are identical can lead to large errors. For example, in^[21] the value $\sigma_S = 670$ erg/cm² is found for gold, which is clearly too low; this is evidently due to the error in the determination of the total surface area of the grains.

In this method calorimetric measurements must be combined with direct measurements of the total surface area of the powder grains.^[109] We emphasize again that the powder grains used in this method must receive a careful preliminary annealing, because their crystal lattices must be freed from distortions.

Besides the methods we have described there are others which are based on the study of kinetic phenomena in solids.

5. The method of steps of growth and sublimation. As is well known, the growth of a crystal from the vapor phase and the sublimation of the crystal have a laminar-spiral character;^[10] the rate of displacement of an individual step for a given departure of the vapor pressure from its equilibrium value is determined by the curvature of the step and the surface energy at the boundary between the step and the gaseous phase.

To determine the quantity σ_S it is convenient to make use of the fact that on the growth surface one often observes retarded "stationary" steps, whose curvature is such that the equilibrium vapor pressure near the surface of the step is equal to the pressure of the vapor in the space surrounding the crystal. In particular, such stationary steps are formed when a moving step encounters in its path refractory impurities insoluble in the crystal, which are separated by a distance $d < 2r^*$, where r^* is the equilibrium radius of a critical embryonic step (Fig. 5). The condition for equilibrium at the bend of the step can be written in the form

$$\mu_r = \mu_q, \tag{10}$$

where $\mu_r = \sigma_L(\varphi) \Omega/Lr + \mu_0$ is the chemical potential

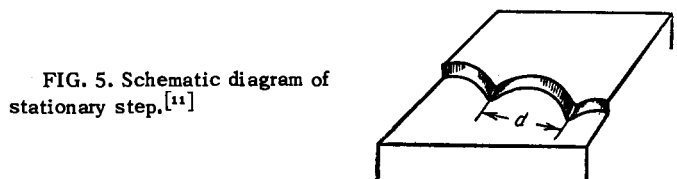


FIG. 5. Schematic diagram of stationary step.^[11]

at the curved surface of the bend of the step and $\mu_q = kT \ln(P_r/P_0) + \mu_0$ is the chemical potential of the atoms in the gaseous phase near this surface; $\sigma_l(\varphi)$ is the energy per unit length of the step, which makes an angle φ with the boundary between the crystal and the gaseous phase, and l is the length of the curved step. For $l \gg \delta$ we can suppose that $\sigma_S(\varphi) \approx \sigma_l/l$, and thus we have

$$\sigma_S \approx \frac{r^* kT}{\Omega} \ln \frac{P_r}{P_0}. \quad (11)$$

In this method one must determine experimentally the value of r^* for a fixed value of the vapor pressure in the space surrounding the growing or evaporating crystal.*

As a variation on this method we can also indicate another possibility, that of determining σ_S from the kinetics of the healing of scratches on the surface of a single crystal in the case in which the transfer of matter occurs through the gaseous phase. Under conditions in which the healing occurs in an atmosphere of the saturated vapor of the crystal itself, the quantity σ_S can be determined from the relation^[12]

$$\sigma_S = \frac{(2\pi m)^{1/2} (kT)^{3/2} L^2}{4\Omega P_0 \tau_{1/2}}, \quad (12)$$

where L is the initial width of the scratch, P_0 is the equilibrium vapor pressure, and $\tau_{1/2}$ is the half-period for healing over of the scratch.

Estimates of the quantity σ_S from data on the smoothing over of scratches have been made in^[50]. †

6. The method of the conical specimen. The quantity directly determined in this method is not σ_S , but σ_{SL} (the interphase surface tension at a solid-liquid boundary) at the melting temperature, and σ_S is determined from the relation^[13]

$$\sigma_S = \sigma_L + \sigma_{SL}. \quad (13)$$

The value of the surface tension of the liquid phase (σ_L) can be determined with adequate accuracy by many methods.^[14]

In this method the possibility of determining the quantity σ_{SL} is based on the fact that the temperature for the equilibrium between the solid and liquid phases, that is, the true melting temperature, depends on the radius of curvature r of the boundary (Fig. 6). In the case of a cylindrical boundary the departure of the actual melting temperature (T_r) from the equilibrium value (T_∞) is given by the law

$$\Delta T = \frac{T_\infty \sigma_{SL}}{q_S r}, \quad (14)$$

The quantity r^ can also be determined on the basis of data on the dependence of the rates of displacement of steps on their curvatures (the function v_r), since $v_r = v_0 (1 - r^*/r)$ (cf.^[10]).

† σ_S can be found not only from data on the half-period for healing over, but also by using the entire curve of the relation $h = \varphi(t)$ (h is the depth of the scratch). The equation of the curve in question is derived in^[59]. This is a more precise version of the method described here.

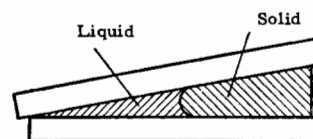


FIG. 6.

where $\Delta T = T_\infty - T_r$, T_∞ is the temperature of the phase equilibrium at a flat boundary, T_r is the temperature of the phase equilibrium at a boundary of radius of curvature r , ρ_S is the density of the solid phase, and q is the heat of fusion.

By supplying heat extremely slowly to a conical specimen enclosed between two plane parallel plates of a substance which is wet by the substance under investigation, one can determine experimentally the width $h = 2r$ of the conical gap where the interphase boundary is located; as the quantity ΔT becomes smaller this boundary is displaced into the wider part of the cone so that the quantity $h\Delta T$ remains constant:

$$h\Delta T = \frac{2T_\infty(\sigma_S - \sigma_L)}{q_S q} = H, \quad (14')$$

from which we have

$$\sigma_S = \frac{q_S q}{4T_\infty} H + \sigma_L. \quad (15)$$

Values of σ_S have been found by means of this method^[13, 87] for several organic substances and for ice. An experimental variation on this method is the case in which the substance being studied is inclosed not between plane parallel plates, but in a conical capillary. Strictly speaking, in this method one is determining not exactly σ_S , but a lower limit on this quantity, since the relation that really holds is not Eq. (13), but $\sigma_S > \sigma_L + \sigma_{SL}$, as is convincingly shown by the phenomenon of "creeping" of a liquid on the surface of the solid phase of the same substance^[15] (see further discussion).

In this method the point of greatest interest to us is not the determination of σ_S , but that of σ_{SL} at the melting point.* As is well known, this quantity σ_{SL} is of great importance in the kinetics of crystallization.

7. The method of the "scratch healing over". It is well known that when a crystal with a scratch on its surface is annealed at high temperature under equilibrium conditions, the scratch becomes smoothed over; for metals, as a rule, the kinetics of this process is determined by the mechanism of surface diffusion. In this case, as a calculation shows,^[58] σ_S is given by the relation

$$\sigma_S = \frac{kT}{16D_S \delta^4} \frac{L^4}{\tau_{1/2}}, \quad (16)$$

where D_S is the coefficient of surface diffusion, $\tau_{1/2}$ is the half-period for the healing over, and L is the original width of the scratch.

*For the reason indicated, the error in the determination of σ_S by this method can be very large, of the order of σ_{SL} (see later discussion).

In the case in which the smoothing over of the scratch is due to the mechanism of viscous flow, the quantity σ_S can be determined by means of the relation [see also Eq. (53)]

$$\sigma_S = \frac{\eta L}{\pi \tau^*}, \quad (16')$$

where η is the coefficient of viscosity, and τ^* is the relaxation time for the process of healing over. For amorphous substances η can be found with sufficient accuracy, and this is the main consideration for the accuracy of the calculation of σ_S from Eq. (16').

8. The method of the coalescence of pores. In a porous solid body at a high temperature a process of coalescence of pores occurs, which has as its driving force the tendency to decrease the free surface of the pores. This process occurs through a diffusion mechanism. A consistent theory of the process of diffusive coalescence has been developed by I. M. Lifshitz and V. N. Slezov.^[23] They have shown that at a late stage in the process, when the asymptotic size distribution of the pores has been established, the time variation of the mean pore size \bar{R} is

$$\bar{R}^3 = \frac{4}{9} D_0 \alpha t, \quad (17)$$

where $\alpha = (2\sigma_S/kT)\Omega$ and D_0 is the volume diffusion coefficient of the atoms. From Eq. (17) we have

$$\sigma_S \approx \frac{9}{8} \frac{kT}{D_0 \Omega} \frac{\bar{R}^3}{t}. \quad (18)$$

According to Eq. (18), in order to determine σ_S we must find by experiment the time dependence of the mean pore size in an ensemble of pores in which the coalescence is occurring. We note that the function $\bar{R} = \varphi(t)$ must be determined from the behavior of pores far from boundaries, external and internal, since the relation (17) has been obtained on the assumption that the ensemble of pores being observed is located in a single crystal of infinite extent (cf.^[23]).

As can be observed from this summary of the experimental methods, at present there is no method which can be used reliably for the experimental determination of the surface tension in the solid phase over a wide range of temperatures. Each of the methods described is restricted in practice either by the temperature or by quantities which can be experimentally determined only with low accuracy.

A shortcoming common to the last two methods is that for the determination of the quantity σ_S it is necessary to know the value of the diffusion coefficient, which, as is well known, is very sensitive to structure and subject to large errors in its experimental determination.

Since the quantity σ_S is anisotropic, it is important to develop methods which will make it possible to determine the dependence of σ_S on the orientation of the surface in question. The first attempt at such a determination was made by Mykura,^[112] who judged the

anisotropy of σ_S from the shape of the thermal etching grooves in the boundary between the parent grain and an annealing twin in metals with the face-centered cubic lattice (see later discussion).

III. THE "NATURAL ROUGHNESS" OF THE SURFACES OF CRYSTALS

1. In view of the general premise that the anisotropy of the coefficient of surface tension does not allow minimum surface and minimum surface energy to be realized simultaneously in a crystalline body, it is natural to expect that under conditions of equilibrium with its own vapor the surface of an arbitrary section of a crystal will not retain the original smoothness forced on it by its preparation, but will become covered with a system of ribbed steps. We are justified in calling such a surface structure the "natural roughness." We note that this "natural roughness," which is a set of macroscopic steps on the surface of an arbitrary section of a crystal which had been ground smooth, is not at all the same as the atomic roughness of the crystal grains with small values of the surface energy, which can be due to thermal fluctuations at high temperatures.^[24]

The problem of the stationary shape of the macroscopic steps formed on an unbounded crystal surface arbitrarily oriented relative to the symmetry elements of the crystal, i.e., described by complicated indices, has been treated in the two-dimensional case in a paper by Lifshitz and Chernov.^[25] The problem solved in^[25] reduces formally to finding a profile of an unbounded portion of an arbitrary section $Y(x)$ of the crystal such that

$$\int [F(P) + \Lambda Y(x)] dx = \min, \quad (19)$$

where $F(P) = \sigma(P)(1 + P^2)^{1/2}$, $\sigma(P)$ is the specific free energy of the surface, $P = Y(x) = \tan \varphi$, and Λ is the Lagrange multiplier introduced when we take into account the fact that the volume of the crystal must be conserved in the development of the steps of roughness. Λ has the dimensions of pressure.

In the general case the function $Y(x)$ must be a continuous function, which may have angular points. In the case of a three-dimensional model the analogous function $Z(x, y)$ must have angular points and lines.

An analysis of the conditions that assure that Eq. (19) is satisfied leads to the conclusion^[25] that when the equilibrium shape of the crystal has edges a crystal face of arbitrary orientation must be a set of macroscopic steps, each of which consists of two intersecting planes. These planes are oriented in the same way as near the edges in a closed crystal which has its equilibrium boundary. An important consequence of the discussion in^[25] is the conclusion that macroscopic steps of "natural roughness" can arise only under conditions for which the equilibrium shape

of the crystal has edges, and these edges are extremely stable with respect to small but finite deviations from equilibrium. In a case in which the equilibrium shape does not have edges no macroscopic roughness will occur, in spite of the fact that the surface energy may be anisotropic.

It is pointed out in [10] and [25] that for $T > 0$ there will be a "smearing" of the edges of convex dihedral angles on the stepped profile of the "natural roughness," but the edges of the concave angles will not be smeared.

The treatment of the stationary problem undertaken in [25] also leads to the conclusion that, since the energy of the edges is negligibly small in comparison with that of the faces, the heights of the macroscopic steps are arbitrary, and a shape once taken is stable in the sense that there will be no spontaneous merging of the steps.

Macroscopic steps on the surface of an arbitrary section of a crystal have been observed in a large number of experimental researches, [26-35] but actually none provides assurance that the observed structure of the surface corresponds to equilibrium, or, in other words, that it is the "natural roughness" in the sense discussed above.

The experimental problem of obtaining equilibrium steps of "natural roughness" is akin to the well known problem of obtaining a crystal of equilibrium shape. Single crystals formed under actual conditions of growth as a rule have a shape close to the equilibrium shape but not completely identical with it, owing to the fact that the experimental conditions are always somewhat different from the ideal conditions under which the equilibrium outer surface could be formed.

According to G. G. Lemmlein [36] the conditions for obtaining experimentally a crystal of equilibrium shape, which also apply to the case of obtaining the "natural roughness," are essentially as follows.

A crystal with equilibrium shape must be obtained not by growth from the gaseous or liquid phase, but through conversion of a nonequilibrium crystal into an equilibrium crystal by a process which must occur spontaneously in a closed space. The process of transformation of the shape of the crystal will continue so long as the solubility (or vapor pressure) is not the same for all of the surfaces bounding the crystal.

Experiments made for the purpose of producing crystals of equilibrium shape must be made with crystals of small dimensions* and at as high temperatures as possible, in order for the process of transformation from nonequilibrium shape to occur in a reasonable time. Another very important condition is careful temperature control.†

*The requirement of small crystal dimensions is not essential for experiments made for the purpose of obtaining the "natural roughness," since in this case the characteristic length for the processes of transfer of material is not determined by the size of

The experiments in which these conditions have been satisfied most fully are those made by Kliya, [37] who observed the changes of a crystal of ammonium chloride contained in a closed droplet of ammonium chloride solution. Experimenting with crystals of linear dimensions $\sim 50 \mu$, Kliya was able to make reliable observations of the equilibrium surface shapes of ammonium chloride crystals. The conditions for the establishing of the equilibrium shape are also well enough satisfied in the case of the growth of "negative crystals," i.e., microscopic cavities filled either with saturated solution [37] or with saturated vapor, [38] as occurs in particular in the formation of diffusion porosity in the mutual diffusion of metals. [39]

2. As already stated, nearly all of the experimental researches in which studies have been made of the structure of surfaces with complicated indices fail to provide assurance that the observed structures were formed under equilibrium conditions, i.e., with $\mu_c = \mu_g$ (μ_c is the chemical potential of an atom in the crystal, and μ_g is that of an atom in the gaseous phase). The cause of the unevennesses can be different in each individual case. With this in mind, let us turn to the consideration of the various papers.

Macroscopic steps on surfaces of arbitrary sections of crystals have been observed experimentally in many researches in which it is clear that equilibrium between the crystal and the gaseous medium was not assured. In particular, we must assign to this group the widely known work of Lukirskii. [27] In this work it was shown that annealing is followed by unevennesses on the surfaces of polished spheres or cylinders turned from single crystals of NaCl. As can be seen from Fig. 7, a, b, c, highlights appear on the surface of a sphere which correspond to the points of emergence of the two- (a), three- (b), and four fold (c) symmetry axes. Analogous observations are also described in [40], which reports on similar experiments on spherical single crystals of copper.

In connection with the experiments described in [27] and [40], which were made at high temperatures, we may also mention the well known experiment of Shaskol'skaya and Shubnikov, [108] who observed the

of the crystal, but by the height of the individual step, which experiment shows to be $\sim 10^{-5}$ cm.

†The allowable fluctuation of the temperature can be estimated by starting from the requirement that the change of the chemical potential ($\Delta\mu T$) associated with an accidental change of the temperature (ΔT) must be much smaller than the difference of chemical potentials ($\Delta\mu$) which determines the flux by which the change of shape of the crystal is accomplished. For the case of a little crystal in a saturated solution we easily find from this condition

$$\text{that } \Delta T \ll \frac{c}{\left(\frac{\partial c}{\partial T}\right)_P} \frac{\Omega \sigma}{kTR}. \quad \text{In the general case the accuracy of the}$$

temperature control must be such that flux involved in the dissolving (or growth) of the crystal is small in comparison with the flux of transfer of material between parts of the surface.

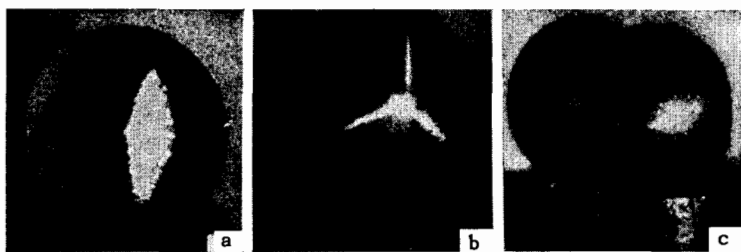


FIG. 7. Exposure of twofold (a), threefold (b), and fourfold (c) symmetry axes after annealing of polished sphere turned out of single crystals.^[27]

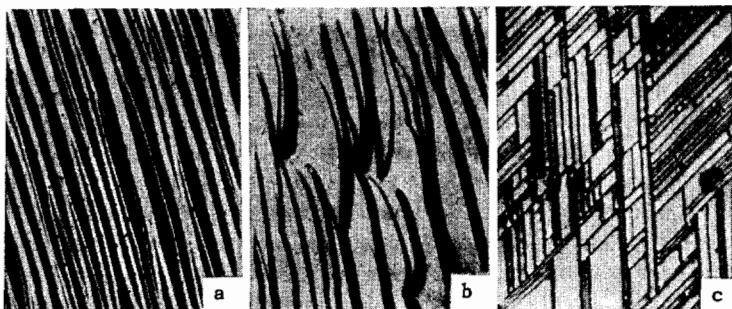


FIG. 8. Appearance of the surface of a single crystal of silver after annealing in air for 150 hours, $T = 900^{\circ}\text{C}$.^[33]
a) Surface of a section ground at angle 20° with (100) face. b) Surface of section at angle 3° with (100). c) Surface of section at angle 7° with (111).

change of shape of a single crystal of alum from spherical to octahedral. In the experiment of Shaskol'skaya and Shubnikov this process occurred during specially produced oscillations of the temperature.

Macroscopic steps and spirals on the surfaces of crystals which had undergone high-temperature annealing under obviously nonequilibrium conditions have been observed in work done by Amelinckx^[41] (with lithium fluoride), Menzel^[42] (with copper), Evans^[43] (with titanium), Dunn and Walter^[44] (with silicon iron), Oding and Lozinskii^[45] (with tungsten), and others.

Apart from this group of researches stand those in which the specimens were annealed in media that could attack them (Shuttleworth,^[32] Moore,^[33] Hondros and Moore^[46]). The most detailed of these studies are those of Moore,^[33] who observed the development of roughness on surfaces of silver when annealed in air. The characteristic structures observed by Moore are shown in Fig. 8.

The main observation made by Moore in this work is that one of the planes bounding a step is simple in the sense that an analogous plane is represented in the equilibrium set of faces of the crystal, and the other is complicated and consists of a large number of small steps. According to Moore^[33] the process of development of steps on a silver surface annealed in air occurs in the way illustrated in Fig. 9.

Moore gives a natural explanation of all the observations made in^[33] in terms of the tendency toward a decrease of the total surface free energy. We note that in one of his subsequent papers^[47] Moore comes to the conclusion that the roughness he observed on the silver surfaces occurs because of evaporation accompanied by a loss of weight of the specimens, and cannot be explained by considerations of decrease of surface energy.

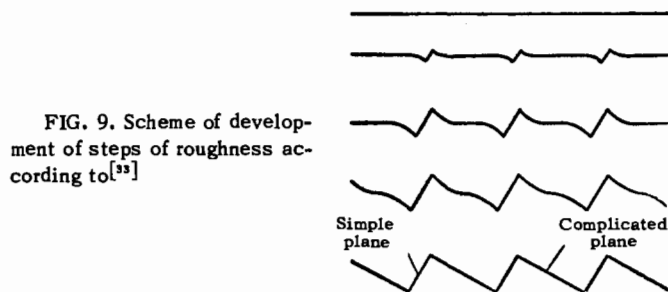


FIG. 9. Scheme of development of steps of roughness according to^[33]

Experiments undertaken for the purpose of observing true "natural roughness" are described in^[28-30],^[35], and^[48].

In^[29] a study was made of the development of "natural roughness" (Fig. 10) on surfaces of polycrystalline specimens of copper. To assure closed volume the specimens were wrapped in copper foil during the annealing.

In that paper it was shown that the development of the steps of roughness occurs over a considerable time. A peculiarity of the observed kinetics of the process^[29] is that at an early stage in the process the steps which have not yet taken shape are already of a discontinuous character (Fig. 11). On the basis of this observation the paper puts forward a hypothesis about the embryonic mechanism of the process. The idea of an embryonic step of roughness seems justified, since in this case, just as in that of a phase transition, one can distinguish the causes that determine the critical size of a "viable embryo." In fact, if we simplify the observed shape of the embryonic step by representing it as tent-shaped, the critical size of the tent-embryo is determined by the competition between the gain of energy owing to the appearance of the lateral surfaces of the tent-embryo and the loss owing to the appearance of the end surfaces.

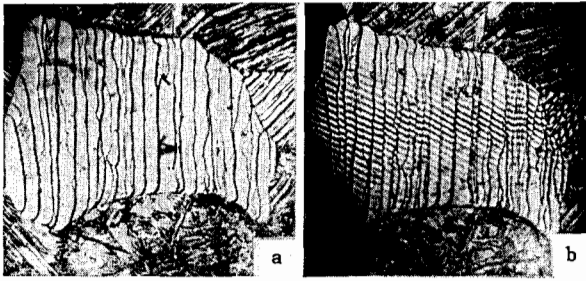


FIG. 10. "Natural roughness" on polycrystalline copper after annealing in an atmosphere of its own vapor at $T = 950^\circ$, $t = 3$ hours. a) Appearance of steps on one of the grains. b) Interference pattern, $\times 270$.^[28]

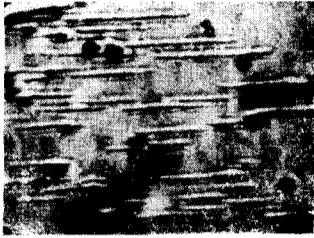


FIG. 11. Embryonic steps of "natural roughness" on copper, $\times 500$.^[29]

A study of the development of roughness of the surfaces of arbitrary sections of single crystals of NaCl under conditions which assure that the weight of the specimen remains constant has been made in ^[48]. The high-temperature annealing of the specimens was carried out in carefully closed ampules turned out of single crystals of NaCl, and in open spaces, i.e., under conditions in which evaporation could occur naturally. It was shown by these experiments that natural cleavage surfaces (100) remain practically smooth after annealing in closed or in open spaces, whereas after annealing in closed spaces without loss of weight planes of types (120), (130), (150), and (180) were covered with systems of parallel steps, which showed different geometries on surfaces of different orientations (Figs. 12, 18). These observations are qualitative evidence in favor of the correctness of the idea that when annealed under equilibrium conditions the surface of an arbitrary section of any crystal whose natural bounding surface has edges will become covered with steps of "natural roughness."

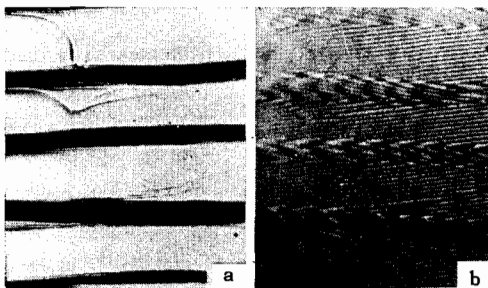


FIG. 12. Appearance of steps on a (150) plane of a single crystal of rock salt (a), and interference pattern^[48] of the same region (b), $\times 500$.

IV. CHANGE OF SURFACE PROFILE IN SINGLE CRYSTALS AND POLYCRYSTALLINE MATERIALS

1. As is well known, at high temperatures the tendency toward decrease of the surface free energy in a polycrystalline specimen manifests itself in a process of selective recrystallization, owing to which the average grain size (\bar{L}) is increased and the surface area of the internal intergrain boundaries (S) is decreased, so that $S \sim 1/\bar{L}$.

Akin to this process is that of the change of the macroscopic profile of the free surfaces of a polycrystalline specimen. As in the case of recrystallization, this process leads to a decrease of the total energy of the boundaries, if the free surface is also included among the boundaries. In the case of a single crystal this tendency will be manifested in a smoothing out of macroscopic defects of the surface. Besides the process of smoothing out macroscopic unevennesses of the surface, in polycrystalline specimens another process can occur—a development of free surface at places where intergrain boundaries intersect the surface of the specimen (development of grooves of thermal etching). The thermodynamic feasibility of the second process is due to the fact that the increase of energy through increase of the external free energy is compensated by the disappearance of part of the surface of an intergrain boundary.

Both of these effects, which are represented schematically in Fig. 13, a, b, are realized by means of the same mechanisms of transfer of material, and the kinetics of both effects are described by analogous equations.



FIG. 13. Schematic nature of the "smoothing out" of a scratch on the surface of a crystalline body (a), and of the development of a thermal etching groove at the place where an intergrain boundary meets the surface (b).

Because of the common features of these two processes—the smoothing out of macroscopic unevenness and the appearance of macroscopic unevennesses where grain boundaries meet the surface—we shall first present the general theory of the change of the macroscopic profile of a surface under the action of surface-tension forces, and afterward apply it to the concrete problems of the smoothing out of macroscopic surface defects and of the development of thermal etching grooves.

2) Following the treatment of Mullins,^[49,61] let us consider the change of the macroscopic profile of the surface, assuming that at the initial time the surface has the form of a sine wave located near the XY plane (Fig. 14):

$$Z = Z(x, 0) = a \sin \frac{2\pi}{L} x = a \sin \omega x. \quad (20)$$

In what follows we shall assume that the macroscopic unevennesses of the profile consist of a small deviation from the XY plane; the corresponding formal requirement is $a\omega \ll 1$ [cf. Eq. (20)].

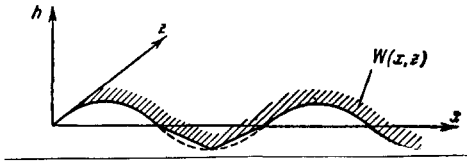


FIG. 14. Schematic diagram of a surface which has a sine-wave departure from ideal smoothness.

A change of the macroscopic profile can occur through four different mechanisms: transfer of material through the gas phase, surface diffusion, volume diffusion, and viscous flow. Independently of which of these mechanisms is the main one under given conditions, the direction of the process is determined by the tendency toward a decrease of the total free energy of the external surfaces, and occurs with conservation of the total volume of the specimen.

Let us consider all of the various mechanisms in succession, on the assumption that the surface energy is isotropic.

1. Transfer of material through the gas phase. For this mechanism we must distinguish two limiting cases, which are realized for different values of the ratio of the mean free path λ^* of a molecule in the gas to the characteristic linear dimension of the unevenness, which in the case of the sine wave is half of the wavelength λ .

1) $\lambda^* \gg \lambda/2 = \pi/\omega$. This case occurs when the specimen is in equilibrium with its own vapor in a space where the pressure of inert foreign gas is negligibly small.

Since the excess vapor pressure over a convex surface is connected with the curvature K by the well known Gibbs-Thomson relation

$$\Delta P = P_0 \frac{\sigma \Omega}{kT} K, \quad (21)$$

and under equilibrium conditions the number of particles incident from the gas phase on unit area of the surface is given by a relation of the form

$$n = \frac{P}{(2\pi mkT)^{1/2}}, \quad (22)$$

the change of shape of the macroscopic profile will be determined by the flux of particles

$$j = \frac{\Delta P}{(2\pi mkT)^{1/2}} = P_0 K \frac{\sigma \Omega}{(2\pi m)^{1/2} (kT)^{3/2}}. \quad (23)$$

The rate r_n at which the profile at a given point is displaced along the normal from the center of curvature is connected with the quantities $\partial Z/\partial t$ and Z' by the obvious relation

$$r_n = (1 + Z'^2)^{-1/2} \left(\frac{\partial Z}{\partial t} \right). \quad (24)$$

Since $r_n = -j\Omega$, and $K = -Z''/(1 + Z'^2)^{1/2}$, we have from Eqs. (23) and (24)

$$\frac{\partial Z}{\partial t} = AZ'', \quad (25)$$

where

$$A = \frac{P_0 \sigma \Omega^2}{(2\pi m)^{1/2} (kT)^{3/2}}.$$

For the case in which the macroscopic profile has a sine-wave shape [cf. Eq. (20)], Eq. (25) can be rewritten in the form

$$\left(\frac{\partial Z}{\partial t} \right) = -A\omega^2 Z. \quad (26)$$

2) $\lambda^* \ll \lambda/2 = \pi/\omega$. This case is realized when the annealing of the specimen occurs in a closed space filled with an inert gas under considerable pressure. The kinetics of the process is then determined by the value of the diffusion coefficient in the gas phase, D_g , and the gradient of the equilibrium concentration of the vapor over the curved surface, ∇n .

Obviously,

$$\frac{\partial Z}{\partial t} = -D_g \Omega \nabla n. \quad (27)$$

Since $\nabla n = \nabla P/kT$, we can write by using Eq. (27) and the value of K from Eq. (21)

$$\frac{\partial Z}{\partial t} = -A' Z''. \quad (28)$$

In the sine-wave case we can write

$$\frac{\partial Z}{\partial t} = -A' \omega^2 Z. \quad (29)$$

In the formulas (28) and (29)

$$A' = \frac{P_0 D_g \sigma \Omega^2}{(kT)^2}.$$

2. Surface diffusion. The directed flux of surface diffusion is produced by the effect of the gradient of the chemical potential, which depends on the curvature at each point of the contour. The change in the chemical potential at a point where the curvature is K is given by the relation

$$\mu(K) = K\sigma\Omega + \mu_0. \quad (30)$$

The rate of migration of atoms along the surface can be written in the form

$$V = \frac{D_s}{kT} \frac{\partial \mu}{\partial s} = -\frac{D_s \sigma \Omega}{kT} \frac{\partial K}{\partial s}, \quad (31)$$

where D_s is the coefficient of surface diffusion and s is length along the profile.

The rate of displacement of the relief contour along the normal is given by the relation

$$r_n \approx -\frac{\partial j_s}{\partial s} \Omega \approx \frac{\partial}{\partial s} \left[\frac{D_s \sigma \Omega \nu}{kT} \frac{\partial K}{\partial s} \right] \Omega = \frac{D_s \sigma \Omega^2 \nu}{kT} \frac{\partial^2 K}{\partial s^2}, \quad (32)$$

where $\nu = 1/\delta^2$ is the surface density of the atoms.

On the assumption that $Z'^2 \ll 1$, we can get from Eq. (32) the equation

$$\frac{\partial Z}{\partial t} = -BZ'''' \quad (33)$$

and in the case of a sine-wave profile

$$\frac{\partial Z}{\partial t} = -B\omega^4 Z, \quad (34)$$

where

$$B = \frac{D_s \sigma \Omega^2 v}{kT}.$$

3. Volume diffusion. In this case, as in that of surface diffusion, the directed flux of material is due to the gradient of the chemical potential and the associated gradient of the concentration of vacant sites in the crystal lattice:

$$j_0 = -D_v \frac{\partial}{\partial s} \Delta \xi, \quad (35)$$

where D_v is the diffusion coefficient of the vacancies and

$$\frac{\partial}{\partial s} \Delta \xi = \frac{\partial}{\partial s} \Delta \mu \frac{\xi_0}{kT} = \frac{\xi_0 \sigma \Omega}{kT} \frac{\partial K}{\partial s}, \quad (36)$$

ξ_0 is the equilibrium volume concentration of vacancies.

In this case the rate of displacement of the relief contour in the direction of the normal to the surface is given by the relation

$$r_n = -j_0 = -\frac{D_0 \sigma \Omega}{kT} \frac{\partial K}{\partial s}, \quad (37)$$

where $D_0 = D_v \xi_0$ is the volume self-diffusion coefficient. Using the expression for K , we find from Eq. (36)

$$\frac{\partial Z}{\partial t} = -CZ'''' \quad (38)$$

and for the sine-wave case

$$\frac{\partial Z}{\partial t} = -C\omega^4 Z, \quad (39)$$

where $D = D_0 \sigma \Omega / kT$.

4. Viscous flow. The differential equation that describes the change of the macroscopic profile of the surface under the action of surface-tension forces can be derived in a straightforward way by the use of the Navier-Stokes equation. This treatment leads to the differential equation

$$\frac{\partial Z}{\partial t} = -FZ' \quad (40)$$

and for the sine-wave case we have

$$\frac{\partial Z}{\partial t} = -F\omega Z, \quad (41)$$

where $F = \sigma/2\eta$, and η is the coefficient of viscosity.

In presenting (41) without proof we remark that it expresses the general law of viscous flow of a Newtonian liquid, with the role of the pressure played by a quantity $\sim \sigma/L$, i.e., the Laplace pressure.

The viscous-flow mechanism can determine the kinetics of the smoothing out of macroscopic unevennesses not only in the case of amorphous bodies, but also in the case of crystalline bodies, for which the coefficient of viscosity depends on the linear dimensions of the blocks and the volume diffusion coefficient and is given by the expression (4). We note that this mechanism can be important only in cases with $n = \bar{L}/l \ll 1$ (where \bar{L} is the average linear dimension of a block and l is the linear dimension of the unevenness). For cases with $n \gg 1$ the mechanism of diffusive-viscous flow does not play any appreciable role; this follows naturally from the nature of the process of deformation in the example we have considered.^[127] As a rule the inequality $n \gg 1$ will hold in the high-temperature region with $l \sim 10^{-3}-10^{-4}$ cm. Possible exceptions are objects whose surfaces have been distorted by grinding and polishing (see further discussion).

The treatment given above is for the case in which the coefficient of surface tension is isotropic.

For many crystals it is not permissible to neglect the anisotropy of the coefficient of surface tension, since it is the anisotropy itself that determines the peculiar kinetics of the smoothing out of a surface defect and determines the intermediate shapes of the profile. In particular, when σ_s is appreciably anisotropic the profile of the defect may not remain smooth, as assumed in the foregoing treatment, and can be characterized by discontinuous changes of the chemical potential along the profile, which will evidently then consist of plane sections for which σ and μ are constant. (In the case of an arbitrarily oriented plane it is reasonable to speak of $\bar{\mu}$.)

When the anisotropy of σ_s cannot be neglected a straightforward general treatment of the problem of the kinetics of the smoothing out of a defect on the surface of a crystal is complicated and assumes a knowledge of the form of the function $\sigma(\varphi)$. For the special case of single crystals of the type of NaCl the problem has been treated in^[50].

The calculation given in^[50] is based on the following observations made in experiments on the smoothing out of scratches with an obtuse angle at the bottom, which were made on a natural cleavage surface of NaCl:

- 1) During the smoothing out of a scratch a flat bottom begins to be formed, which is a (100) plane.
- 2) The decrease of the depth of the scratch, i.e., the rise of the flat bottom, is accompanied by an increase of the distance between the "banks." The speed of the smoothing-out process is determined by the difference of the characteristics of the "bottom" and "bank" planes, as is shown by experiments on the smoothing out of scratches made in different directions on a (100) surface of NaCl.^[50]

The formulas obtained in^[50] differ from those given above only in having a different value of the

quantity σ_g . On the simplifying assumption that during the smoothing-out process the orientation of the "banks" remains unchanged (Fig. 15), $\sigma(\varphi) = (2\sigma_1/\sin\varphi) - 2\sigma_2 \cot\varphi$, where σ_1 and σ_2 are the respective specific surface energies of the "bank" and the "bottom" of the scratch.

When we note the fact that in all mechanisms considered the differential equations describing the kinetics of the smoothing out of a sine-wave profile are of the form

$$\frac{\partial Z}{\partial t} = -\gamma Z, \tag{42}$$

we see that by comparing the values of the quantity γ , which has the meaning of the inverse of a relaxation time τ^* , we can judge the relative importances of the various mechanisms.

Formulas for the characteristic relaxation times are given in Table II.

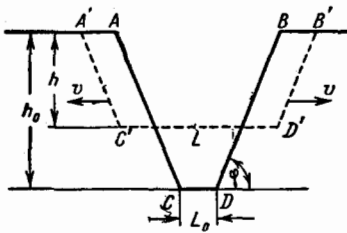


FIG. 15. Schematic diagram of change of profile of a scratch on the surface of a crystal with considerable anisotropy of the surface energy.

Table II. Characteristic relaxation times for the process of smoothing out a surface defect

Mechanism	$\tau^* = 1/\gamma$
Viscous flow	$\tau_b^* = \frac{1}{F\omega} = \frac{\eta L}{\sigma\pi}$
Volume diffusion	$\tau_0^* = \frac{1}{C\omega^3} = \frac{1}{8\pi^3} \frac{kT}{\sigma\Omega} \frac{L^3}{D_0}$
Surface Diffusion	$\tau_s^* = \frac{1}{B\omega^4} = \frac{1}{16\pi^4} \frac{kT}{\sigma\Omega^2 v} \frac{L^4}{D_S}$
Sublimation-condensation	
a) $\lambda^* \gg \frac{\lambda}{2}$	$\tau_g^* = \frac{1}{A\omega^2} = \frac{1}{4\pi^2} \frac{(2\pi m)^{1/2} (kT)^{1/2}}{\sigma\Omega^2} \frac{L^3}{P_0}$
b) $\lambda^* \ll \frac{\lambda}{2}$	$\tau_g^* = \frac{1}{A'\omega^3} = \frac{1}{8\pi^3} \frac{(kT)^2}{\sigma\Omega^2} \frac{L^3}{P_0 D_S}$

Let us first compare the relaxation times in the cases in which the process depends on surface and volume self-diffusion.

The dimensionless ratio of these relaxation times is

$$\frac{\tau_0^*}{\tau_s^*} = 2\pi \frac{\delta D_S}{LD_0}$$

In order for the part played by volume diffusion to be negligible, we must have the condition $\tau_0^*/\tau_s^* \gg 1$, from which it follows that $L \ll 2\pi\delta D_S/D_0$. A numerical estimate ($\delta \sim 10^{-7}$ cm, $D_S/D_0 \sim 10^5$) shows that for $L \ll 5 \times 10^{-2}$ cm we can neglect the effects of the volume-diffusion mechanism.

The relative importance of the mechanisms of surface diffusion and of non-diffusive transfer through the gas phase (when $\lambda^* \gg \lambda/2$) can be estimated from the dimensionless ratio

$$\frac{\tau_s^*}{\tau_g^*} = 10^{-2} \frac{P_0 \delta^2}{D_S (mkT)^{1/2}} \frac{L^3}{L_0^3}$$

from which it follows that the importance of transfer through the gas phase increases with increase of the characteristic linear dimension of the wave. Numerical estimates show that for the majority of metals (Au, Pt, Ni, Cu) for $L \sim 10^{-2} - 10^{-4}$ cm the effect of the "gas" mechanism is practically negligible; it can, however, be of decisive importance for metals with large vapor pressures (Zn, Cd) and for ionic crystals (NaCl, LiF, and so on).

The increase of the importance of surface diffusion in comparison with that of volume diffusion and of the mechanism of transfer of material through the gas phase with decrease of the characteristic length for the defect is a consequence of the fact that the diffusion path (for surface diffusion) is decreased, whereas for the other two mechanisms the flux of material per unit surface remains the same. This means that for some values (which are estimated above) of the linear dimension of the defect the contributions of volume diffusion and of transfer through the gas phase are negligibly small.

The relative importance of the "gas" mechanism can be altered artificially by creating around the specimen an atmosphere of an inert gas at a definite pressure. By setting $\tau_s^* = \tau_g^*$ we can easily obtain an expression for the pressure P^* of the inert atmosphere at which the contributions of the "gas" and "surface" mechanisms will be equal:

$$P^* \approx \left(\frac{kT}{m}\right)^{1/2} \frac{L_0}{D_S} P_0. \tag{43}$$

The dependence of the relative contributions of the various mechanisms of smoothing out of a sinusoidal wave on the characteristic linear dimension (wavelength) and on the temperature is clearly illustrated in Fig. 16.^[51] For the case of nickel Fig. 16 shows the temperature dependence of the logarithm of the reciprocal of the relaxation time for smoothing out of a wave for the mechanisms of surface diffusion, volume diffusion, and transfer of material through the gas phase, when $\lambda^* \gg \lambda/2$, for three different wavelengths of the unevenness.

It is clear from the diagram that in all cases considered and right up to the melting temperature the dominant mechanism is that of surface diffusion. Only in the case of a large wavelength ($\lambda \geq 150 \mu$) can the mechanism of transfer through the gas phase be the dominant one. As has already been stated, this result is a consequence of the fact that as the wavelength of the unevenness is increased the path for transfer of material by the surface-diffusion mechanism increases, but the flux of material from the gas phase

FIG. 18. Kinetics of the development of "natural roughness" on (150) plane of rock salt, $T = 780^\circ\text{C}$. a) $t = 1$ h; b) $t = 5$ h; c) $t = 6$ h; d) $t = 12$ h ($\times 300$).^[48]

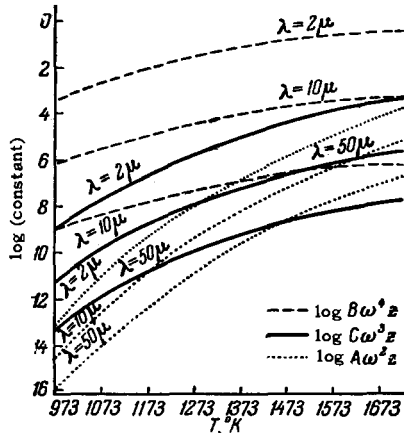
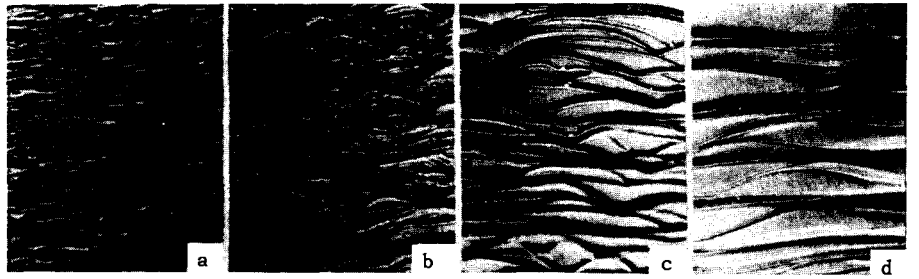


FIG. 16. Variation with temperature of the relative contributions of three mechanisms for the transfer of material in the smoothing of a surface.^[51]

remains the same (if the specimen is not surrounded by an inert atmosphere under pressure).

The general relations obtained above can be used to describe the process of the smoothing out of macroscopic defects of the surfaces of crystals.

Qualitative experimental observations of the tendency toward the smoothing out of defects of surfaces were made long ago. In particular, this tendency has been described by Chalmers and Shuttleworth,^[52] who observed the smoothing out of defects on the surface of polycrystalline silver, by Lukirskii,^[27] who observed the smoothing out of scratches on the surfaces of single crystals of rock salt during the process of high-temperature annealing, and so on.

A convincing illustration of the phenomenon is given by the photographs of Fig. 19, which show that during prolonged high-temperature annealing in the atmosphere of the substance's own vapor both macroscopic projections (a) and depressions (b) on a natural cleavage surface of NaCl are smoothed out.

With a view to the possibilities of comparing calculations with experimental results, let us consider the

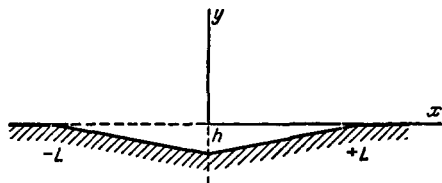


FIG. 17. Shape of cross section of scratch on surface.

solution of Eqs. (28) and (33) as applied to the case of a scratch made with a diamond indenter on a smooth surface (Fig. 17). Because data on the kinetics of the smoothing out of a scratch that has a definite geometry can be a source of information about the surface-diffusion coefficient, we find it suitable to expound the theory of smoothing out as applied to a scratch with a definite geometry. Since the scratches studied experimentally have had small linear dimensions, the case of volume diffusion is not treated here.

In the case in which the healing over occurs through the mechanism of surface diffusion, Eq. (33) must be solved with the following initial and boundary conditions:

$$\left. \begin{aligned} Y(x, 0) &= Y_0(x), \\ Y'(0, t) &= 0, \\ Y''(0, t) &= 0^* \end{aligned} \right\} \quad (44)$$

If we consider a scratch of the initial shape shown in Fig. 17, the general solution of Eq. (33) with the conditions (44) can be written in the form

$$Y(x, t) = -\frac{4h_0}{\pi l_0} \int_0^\infty \left(\frac{\sin \frac{kl_0}{2}}{K} \right)^2 e^{-BK^4 t} \cos Kx \, dx. \quad (44a)$$

According to Eq. (44a) the dimensionless depth along the axis of the scratch can be written in the form

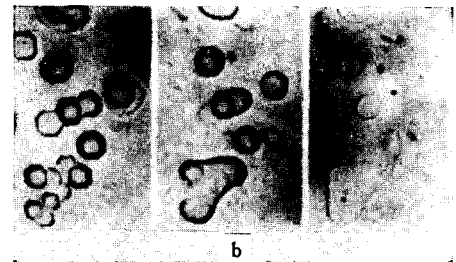
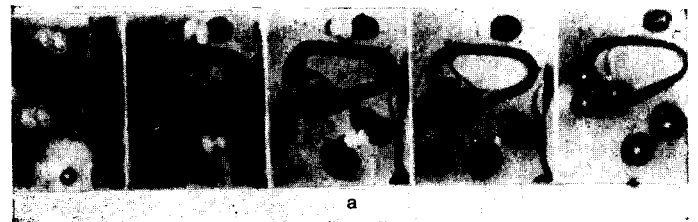


FIG. 19. Successive stages in the smoothing out of projections (a) and depressions (b) on the surface of a single crystal of NaCl.^[53]

*This condition means that during the entire process of smoothing out there is no flux of atoms at the vertex of the scratch.

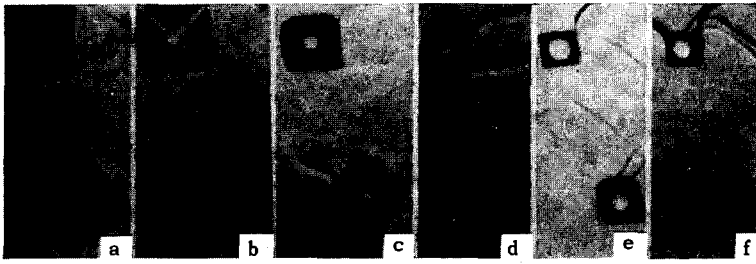


FIG. 20 "Reorientation" and smoothing over of traces of "pricks" with identical initial dimensions $T = 680^{\circ}\text{C}$, $P = 1 \text{ atm}$. a) Initial state; b) $t = 3 \text{ min}$; c) $t = 10 \text{ min}$; d) $t = 50 \text{ min}$; e) $t = 120 \text{ min}$; f) $t = 160 \text{ min}$.^[59]

$$\frac{h}{h_0} = \varphi(\zeta) = \frac{2}{\pi} \int_0^{\infty} \left(\frac{\sin s}{s} \right)^2 e^{-\zeta s^4} ds, \quad (45)$$

where $\zeta = 16Bt/l^4$, and this quantity has the meaning of a dimensionless time.

Figure 21, a, b shows the profile shape of a scratch as it changes with time in the case in which the healing over occurs by the surface migration and "recondensation" mechanisms.

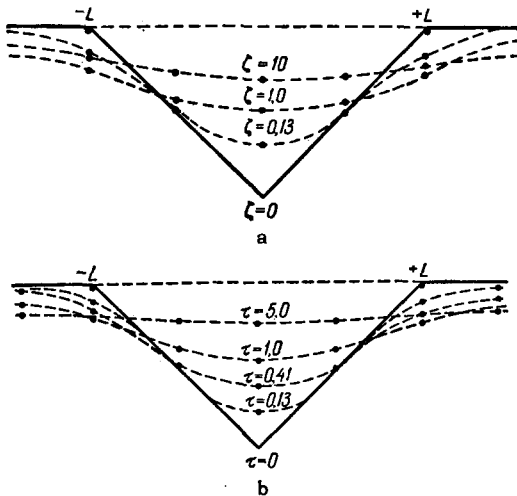


FIG. 21. Successive profiles of a scratch during "healing over" (a) by the surface-diffusion mechanism, and (b) by the "recondensation" mechanism.^[59]

For values $\zeta \gg 1$ the time dependence of the dimensionless depth can be represented with adequate accuracy by means of the asymptotic relation

$$\varphi(\zeta) \approx \frac{\Gamma\left(\frac{1}{4}\right)}{2\pi} \zeta^{-1/4} \approx 0.58 \zeta^{-1/4}. \quad (46)$$

Thus the depth of the scratch changes with the time according to the law $h \sim t^{-1/4}$.

Noting that for $\zeta = 1$ we have $h/h_0 = 1/2$, we can find the time during which the depth of the scratch decreases by half (the half-healing time):

$$t_{1/2} = \frac{l^4}{16B}, \quad (47)$$

and a corresponding expression for the surface-diffusion coefficient*

*Of course Eq. (48), which is the same as (16), is more reliable for the determination of D_S than for that of σ_S , since σ_S is much less sensitive to structure and more weakly dependent on temperature than D_S .

$$D_S = \frac{kT}{16\sigma v^2 n} \frac{l^4}{t_{1/2}}. \quad (48)$$

Thus data on the kinetics of the smoothing out of scratches can be used to find the coefficient of surface self-diffusion without the use of radioactive isotopes. A more reliable way of finding D_S than the use of Eq. (48) is to match an experimental curve of h/h_0 plotted against t and a theoretical curve of h/h_0 against ζ . The matching can be done by finding a scale factor for changing t into ζ .

In the case of healing over of a scratch by the mechanism of transfer through the gas phase (when the inert-gas pressure is small), we can solve Eq. (26) with account of the conditions

$$\left. \begin{aligned} Y(x, 0) &= Y_0(x), \\ Y'(0, t) &= 0. \end{aligned} \right\} \quad (49)$$

In this case the formula for the time dependence of the dimensionless depth of the scratch can be written

$$\frac{h}{h_0} = \Phi(\tau) = \operatorname{erf} \frac{1}{\tau^{1/2}} - \left(\frac{\tau}{\pi} \right)^{1/2} (1 - e^{-1/\tau}). \quad (50)$$

In the expressions (49) and (50) $\tau = 4At/L^2$, and this quantity has the meaning of dimensionless time.

The dependence of $h(t)/h_0$ on the dimensionless time and the nature of the changes of profile in this case are shown in Figs. 21, b and 22.

In this case the half-healing time is given by the formula

$$t_{1/2} = \frac{L^2}{4A} = \frac{L^2 (2\pi m)^{1/2} (kT)^{3/2}}{4P\sigma\Omega^2}. \quad (51)$$

Just as the data on the kinetics of the smoothing over of a scratch in a case when it occurs by the surface-diffusion mechanism can be a source of information about the value of the surface-diffusion coefficient, the data from analogous experiments made under conditions in which the kinetics of the process are determined by the transfer of material through the gas

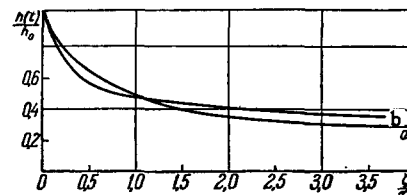


FIG. 22. Curves of the dependence of $h(t)/h_0$ on the dimensionless time for the cases of the surface-diffusion mechanism (a) and the "recondensation" mechanism (b).^[59]

phase can be a source of information (when the equilibrium vapor pressure is known) about the value of the surface tension in the solid phase, σ_S . In this case the surface tension is given by the relation (12).

In the smoothing out of a scratch on an amorphous body owing to viscous flow the dimensionless depth h/h_0 will vary with time according to the law

$$\frac{h}{h_0} = e^{-\tau}, \quad (52)$$

where $\tau = t/\tau_b^*$ is the dimensionless time.

There have been several experimental studies of the smoothing out of surface defects with definite geometries.^[53-58]

In^[54-56] interferometric methods were used to observe the process of smoothing out of scratches on polycrystalline copper. By varying the degree of distortion of the surface layer the authors of^[55,56] established the following fact. In cases in which the layer near the surface was strongly deformed by grinding and polishing, the profiles of scratches remain smooth during the smoothing-out process at high temperatures, and change with time in the way predicted by the calculation made on the assumption that the smoothing out occurs by surface migration. This is the basis for the use of the results of these experiments to find values of the surface-diffusion coefficient D_S .

The values of D_S found from the data on the smoothing out of scratches on the surface of copper are presented in Table III.

Strictly speaking, it is somewhat surprising that in these experiments^[55,56] the profile of the scratch remains smooth during the process of smoothing out. This would be natural for scratches made on a surface of glass (see below).

Table III. Data on the surface-diffusion coefficient of copper (in cm^2/sec)

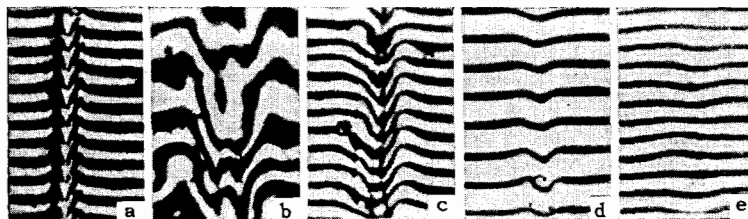
T, °C	From data on the healing over of scratches ^[56]		From data on thermal etching grooves	
	original depth of scratches		from [55]	from [52]
	4 μ	10 μ		
750	$1.7 \cdot 10^{-6}$	—	—	—
850	$1.1 \cdot 10^{-5}$	$0.72 \cdot 10^{-5}$	—	—
930	—	—	$2.7 \cdot 10^{-5}$	$3 \cdot 10^{-5}$
950	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	—	—
1035	—	—	—	$1.3 \cdot 10^{-4}$
1065	—	—	$1.2 \cdot 10^{-4}$	—

A possible explanation of the observations is that the surface layer of the specimen subjected to grinding and polishing has an extremely disperse structure. There is agreement with this assumption in the results of experiments (Fig. 23) in which the scratches were made on specimens whose surfaces had been subjected to treatments of various degrees of severity. It can be seen from the interferometer photographs that previous polishing has a decisive effect on the nature of the healing process, and that scratches on the surfaces of polished specimens are smoothed out more rapidly.

The cause of the temperature stability of this structure, i.e., its stability against the process of selective recrystallization, may lie in the partial loss of connection of its separate elements. A possible factor causing this stable disconnectedness is the condensation on the boundary of the structural elements of the excess vacancies which arise in the annealing of the distorted layer. It is well known that annealing of plastically deformed metals, of electrolytically deposited metals,^[56] and also of single crystals which have been subjected to deformation,^[60] is accompanied by the appearance of excess vacancies and their subsequent condensation on various kinds of structural inhomogeneities. Excess vacancies can also appear as a consequence of thermal decomposition of thin layers of oxides deposited on the boundaries of the structural elements of the surface layer. We note that as a rule the polishing process is accompanied by a partial oxidation of the surface.

We shall call attention to some features of the process of smoothing out of scratches made on undistorted surfaces of grains in various orientations relative to the plane of the section. Experiments made on polycrystalline specimens of copper^[55] and nickel^[51] show that the speed of the smoothing out of scratches is different in different grains. According to the data of^[51] if we assume that the cause of the observed difference in the speeds of smoothing out of the scratches is the dependence of the surface-diffusion coefficient on the orientation of the grain, then there is a great difference in the values of D_S for different grains, amounting to as much as two orders of magnitude. It must be noted that there is no sufficient ground for relating a given value of the diffusion coefficient, found from the smoothing out of a scratch, to a plane coinciding with the surface of the specimen, since the part that controls the rate of flow of mate-

FIG. 23. Healing over of scratches on surfaces of copper specimens with different states of the surface layer $T = 950^\circ\text{C}$, $t = 60$ min. a) Original state; the scratches were made on previously annealed sections; b) without additional treatment; c) after additional polishing; d) after sanding with No. 3, 4, and 5 papers; e) after working with a cutting tool, grinding, and polishing.^[54]



rial into the scratch may be the distorted part of the profile, where there is a spectrum of orientations.

In various parts of a scratch made on the surface of a polycrystalline specimen of copper or nickel [55,51] one observes straight-line sections, which represent planes with minimal indices. This phenomenon is particularly clearly marked on specimens of rock salt, where a flat "bottom" is formed at the vertex of the scratch (cf. [53]).

The relative importance of the mechanisms of surface diffusion and of transfer of material through the gas phase in the healing over of surface defects has been studied experimentally for rock salt. The idea of the experiments was to weaken the effect of the gaseous mechanism artificially by varying the pressure of an inert gas surrounding the sample being annealed. When the pressure of the inert gas is varied the diffusion coefficient D_g in the gas phase, which appears in Eq. (29), varies according to the law $D_g \sim 1/P$. Since the pressure of the inert gas can easily be varied through several orders of magnitude, large changes in the importance of the "gaseous" mechanism can be produced.

The experiments indicate [53,50] (see Fig. 24) that the speed of the smoothing-out process decreases sharply with increase of the pressure of the inert gas, and this shows that the mechanism of transfer through the gas phase predominates in the smoothing out of scratches on the surface of NaCl.

The fact that the process obeys the relation that describes the kinetics of smoothing out of scratches by the mechanism of transfer through the gas phase is illustrated by the graphs of Figs. 25 and 26, in which the coordinates are chosen so that the kinetic relations are represented by straight lines.

Additional information about the relative importances of the mechanisms of surface diffusion and of transfer of material through the gas phase, for a case in which there is a clearly marked anisotropy of the surface tension, is contained in experiments [58] on the smoothing out of the traces of "pricks" on surfaces of single crystals of rock salt. In these experiments it was shown that during high-temperature annealing in the atmosphere of the substance's own vapor a definitely shaped trace from a "prick" is smoothed out in the course of time, and becomes "reoriented" if its original orientation was "unfavorable" from the point of view of minimum surface energy (Fig. 20). "Reorientation" occurred for those "prick" traces

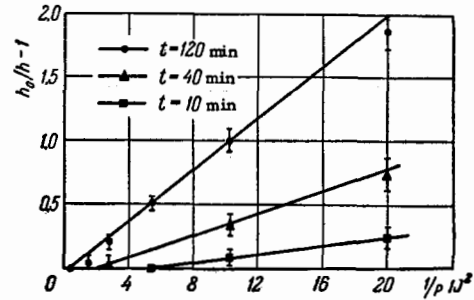


FIG. 25. The dependence of $h_0/h-1$ on $1/P$, [50] $T = 725^\circ\text{C}$

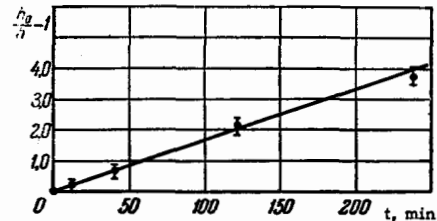


FIG. 26. The time dependence of $h_0/h-1$, [50] $T = 725^\circ\text{C}$, $P = 50$ atm.

whose edges made an angle with the fundamental crystallographic directions [01] and [10].

We note that the reorientation of a "prick" is a phenomenon analogous to the formation of a flat "bottom" in the healing over of a crack, since the "prick" can be represented as a square well in which each corner is a scratch perpendicular to the (100) plane (Fig. 27). In the experiments in question it was shown that the formation of a flat bottom (and the analogous phenomenon of reorientation) is due to surface diffusion of atoms. Convincing evidence for this is the fact that the speed of the process of "reorientation of pricks" is independent of the pressure of the inert atmosphere. In fact, it is extremely improbable that atoms coming to the region of the defect

FIG. 27. Schematic representation of the process of "reorientation" of an infinitely deep well of square cross section.

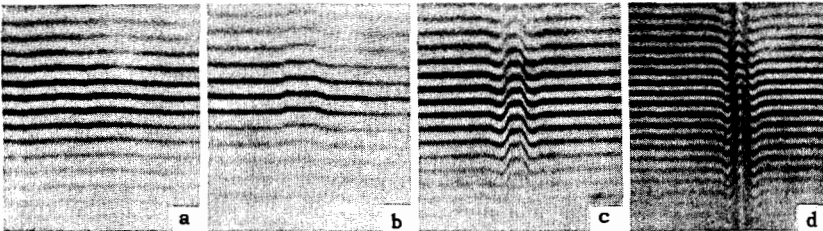
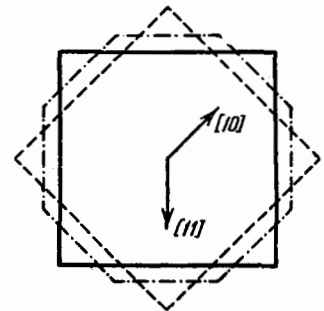


FIG. 24. Dependence of the speed of the process of smoothing out of a scratch on the surface of NaCl on the pressure of an inert gas. $T = 780^\circ\text{C}$, $t = 15$ min. a) $P = 1$ atm; b) $P = 5$ atm; c) $P = 15$ atm; d) $P = 50$ atm. [50]

from the gas phase would at once arrange themselves in a plane without subsequent surface migration. The rate of smoothing out of a "prick" (and also of a scratch) was found to depend on the pressure of the inert atmosphere, i.e., to be determined by the transfer of matter through the gas phase.

The mechanism of viscous (Newtonian) flow is the main factor in the kinetics of the smoothing out of surface defects in amorphous bodies. This has been shown experimentally in [57], in observations on the healing over of scratches on the surface of glass. We note here that experiments with very simple techniques on the smoothing out of scratches on surfaces of amorphous bodies can be a source of information about the values of the viscosity coefficients.

V. THE DEVELOPMENT OF INTERGRAIN THERMAL-ETCHING GROOVES

1. Let us turn to the problem of the development of thermal etching grooves along lines in which intergrain surfaces intersect the outer surface of the specimen.

The kinetics of the development of the grooves is described by the same differential equations as the smoothing out of scratches. In the solution of these equations together with the boundary conditions one must take into account the intergrain surface tension.

Independently of the mechanism of development of a groove, in the case of a groove that is symmetrical relative to the intergrain boundary the angle at its vertex is given by the obvious relation

$$\sigma_i = 2\sigma_s \sin \beta, \tag{53'}$$

where σ_i is the surface energy of the intergrain boundary.

In the general case in which anisotropy of σ_s must be taken into account Eq. (53) must be written in the form (cf. [101])

$$\sigma_i = \sigma'_s \sin \beta' + \sigma''_s \sin \beta'' - \left(\frac{\partial \sigma'_s}{\partial \beta'} \cos \beta' + \frac{\partial \sigma''_s}{\partial \beta''} \cos \beta'' \right). \tag{53a}$$

In Eqs. (53') and (53a) σ_i is the surface energy of the intergrain boundary, σ'_s and σ''_s are the surface energies of the adjoining grains (at the vertex of the groove), and β' and β'' are the respective angles between the tangents to the profile of the groove at its vertex and the surface of the specimen. It is easy to see that if we neglect the anisotropy of σ_s

$$\left(\sigma_s = \sigma'_s = \sigma''_s, \frac{\partial \sigma'_s}{\partial \beta'} = \frac{\partial \sigma''_s}{\partial \beta''} = 0 \right),$$

and then in the case of a symmetrical groove ($\beta' = \beta'' = \beta$) Eqs. (53a) and (53') become identical. The calculation given below is for the case of isotropic σ_s and a symmetrical groove.

Let us treat the problem of the development of a thermal etching groove for the cases in which it is determined by the mechanisms of surface migration

and transfer of material through the gas phase.^[61] In the former case the stationary profile of the groove can be determined if we solve Eq. (33) with the following conditions:*

$$Z(x, 0) = 0, \quad Z'(0-0, t) = \text{tg } \beta = C.$$

The second of these conditions means that the angle at the vertex of the groove is determined by the value of the intergrain surface tension.

The corresponding solution is of the following form:

$$Z(x, t) = -2c(At)^{1/2} \text{erfc} \frac{x}{2(At)^{1/2}}, \tag{54}$$

where erfc is the tabulated integral.

The normalized groove profile given by the relation (54) is plotted in the coordinates $Y/c = \varphi(x)$ as the dashed curve in Fig. 28.^[61]

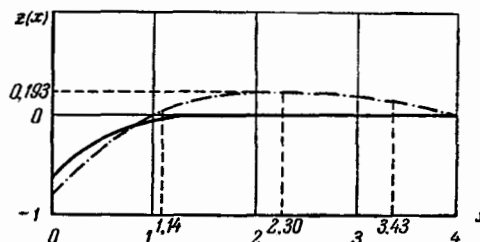


FIG. 28. Normalized profile of a developing thermal etching groove. Solid line – development owing to transfer of material through the gas phase; dashed line – development owing to transfer by surface diffusion.^[61]

For convenience in comparing the calculation with experiment we write the relation which gives the maximum depth of the groove:

$$h = Z(0, t) = -1.13c(At)^{1/2}. \tag{55}$$

In the case in which the groove develops owing to transfer of material through the gas phase the equilibrium profile can be found by solving Eq. (28) with the following conditions:

$$Z(X, 0) = 0, \quad Z'(0-0, t) = \text{tg } \beta = C, \quad Z''(0, t) = 0.$$

In this case the equilibrium profile of the groove is given by the equation

$$Z(x, t) = C(Bt)^{1/4} \sum_{n=0}^{\infty} a_n U^n, \tag{56}$$

where $U = x/(Bt)^{1/4}$ is a dimensionless parameter. The normalized groove profile constructed from this formula is shown by the solid curve in Fig. 28.

The essential difference between the normalized groove profiles in these two cases is that in the case of the groove formed by means of surface diffusion there are convexities on its sides owing to the transfer of material from the central part of the groove, and these convexities are absent for the groove formed by the transfer of material through the gas phase. The depth h of the groove and the distance L between the

* $\text{tg} = \tan$

maxima on the prominences are given by the formulas

$$\left. \begin{aligned} h &= 0.973C(Bt)^{1/4}, \\ L &= 4.6(Bt)^{1/4}. \end{aligned} \right\} \quad (57)$$

We note that the normalized groove profiles have been determined on the assumption that the groove is formed owing to redistribution of material only. It can happen that in an actual polycrystalline body which has internal "sources" of vacancies in the form of defects of various kinds, which heal together at a high temperature (pores, cracks, dislocations), the groove that is formed can have a much larger volume than indicated by the calculation, owing to the fact that excess vacancies will diffuse to the groove out of the volume of the specimen, along the intergrain boundary. The arrival of vacancies in the region of the groove as it forms will assist its development. This effect has been studied in [22].

When the orientations of the grains relative to the surface of the specimen are such that there is decided anisotropy of σ_S , the effect of the third term in Eq. (53a) can be so large that there is thermodynamic justification for the development not of a groove, but of a ridge. The first clear observations of this were made with specimens of nickel by Mykura, [112] who showed that for certain orientations of the plane of the cut section relative to an annealing twin a groove develops along the line of intersection of one of the boundaries of the twin with the plane of the section, and a ridge develops along the other intersection. An analogous observation with gold has been made in [54]. Mykura [112] used interferometric data on the shapes of grooves and ridges at the boundaries of twinning layers to estimate the dependence of σ_S on the orientation.

The profiles of intergrain thermal etching grooves have been studied experimentally in a number of papers, either for the purpose of finding the value of the surface energy at the boundary between grains or for that of finding the surface-diffusion coefficient.

One of the first researches in which the shape of a groove was used to find the intergrain surface tension was that of Greenough and King, [66] who measured the angle at the vertex of the groove in bicrystals of silver as a function of the relative orientations of the grains. The use of bicrystal specimens assured that the grooves were symmetrically shaped. These authors measured the angle at the vertex of the groove by an optical method. Obviously [see Eq. (53)] all that can be determined in these experiments is the ratio σ_1/σ_S .

The relation $\sigma_1 = \varphi(\theta)$, where $\theta = 2(2\pi - \beta)$, has been treated by the authors of some papers as a consequence of the dislocation structure of the boundary. We shall not discuss this group of papers, since this has been done in a monograph by D. Maklin. [71]

Several experimental papers [62-65, 51] have been devoted to the detailed study of the kinetics of the development of the profile of intergrain grooves.

In [62, 65] experiments on specially grown bicrystals of copper showed that the observed kinetics of the development of grooves agrees with the predictions from calculations, and in particular that the increase of the width with time follows the $t^{1/4}$ law (Fig. 29).

Using similar specimens, Gjostein and Rhines [65] studied not only the size of the groove, but also its profile, which was found to be in good agreement with the predictions of Mullins' theory. In [65] the information about the profile of the groove was obtained by the interferometric method (Fig. 30).

Information about the development of thermal etching grooves on the surface of polycrystalline copper were used in [62] to find the surface-diffusion coefficient. The values found agreed closely with those determined from the kinetics of the smoothing out of scratches (Table III).

Similar experiments have been made with specimens of polycrystalline nickel, and the data on the value of D_S are shown in Table IV.

In the case of specially grown bicrystalline specimens a developing thermal etching groove naturally has a symmetrical shape. On the surface of an actual polycrystalline specimen, where there are grains in the neighborhood which are oriented in an arbitrary way, the grooves are often decidedly asymmetrical. This asymmetry can be due to several causes. For example, it can be caused by the anisotropy of the quantities σ_S and D_S , which, as we know, determine the kinetics of the development of the grooves. A

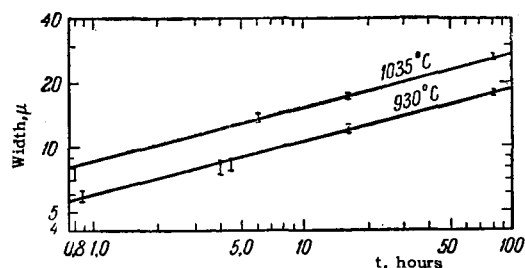


FIG. 29. Time dependence of the width of a thermal etching groove, according to data from experiments with bicrystals of copper. [65]

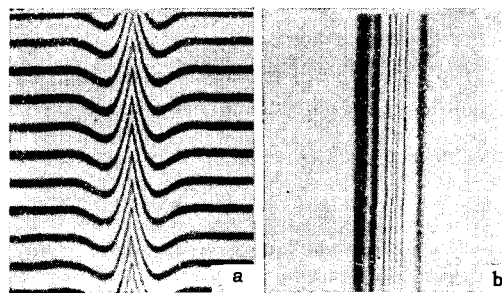


FIG. 30. Interferometric determination of the width of a groove. [65] In (a) the interference fringes are directed across the groove; in (b), along the groove.

Table IV. Data on the surface-diffusion coefficient of nickel^[51] (in cm²/sec)

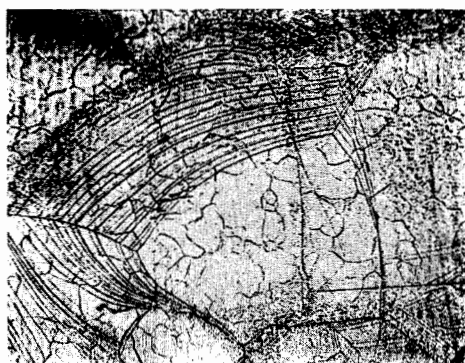
T, °C	From data on healing over of scratches		From data on thermal etching grooves
	Pure nickel	Contaminated nickel	
1200	$1.5 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	—
1100	$0.9 \cdot 10^{-6}$	$0.6 \cdot 10^{-6}$	—
1000	$0.65 \cdot 10^{-6}$	$0.4 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
900	$0.27 \cdot 10^{-6}$	—	—
800	$0.14 \cdot 10^{-6}$	$0.08 \cdot 10^{-6}$	—

more important cause of the asymmetry of the grooves, however, is the fact that the intergrain boundary is usually not perpendicular to the surface on which the groove is developing. This is indicated, in particular, by the fact that when the time of high-temperature annealing accompanied by selective recrystallization is increased the number of asymmetrical grooves and the degree of asymmetry are decreased. This is clearly due to the fact that during the process of recrystallization larger and larger numbers of intergrain boundaries come to be directed normal to the surface. This is one of the types of interconnection between the two processes—the development of grooves and the increase of grain size in the surface layer through recrystallization.

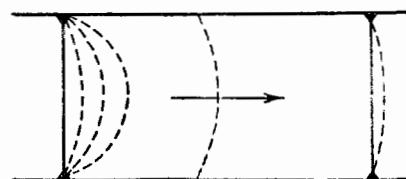
The development of thermal etching grooves can be one of the factors determining the specific kinetics of the recrystallization displacement of intergrain boundaries which intersect the free surface of the specimen. The peculiarity of the phenomenon is the spasmodic (discontinuous) shifting of the boundaries.

The discontinuous displacement of boundaries has been observed experimentally in many researches.^[72-75] A definite indication that a boundary is being shifted spasmodically is the simultaneous presence of a family of grooves spaced at various distances from each other (Fig. 31). Each of these grooves is a place where the moving boundary stopped for a time.

The discontinuous shifting of boundaries in the process of grain growth by recrystallization has been explained by Mullins^[75] in the following way. If a

**FIG. 31.** Spasmodic displacement of boundaries on the surface of copper.^[75]

boundary makes the angle $\gamma < \pi - \alpha$ with the axis of a groove (with vertex angle $\pi - 2\beta$), then the displacement of the boundary is inexpedient from the thermodynamic point of view, since it would mean lengthening the boundary and increasing the intergrain energy. Therefore the recrystallization displacement of a boundary attached at the vertex of a groove must occur with bending of the boundary until the inequality $\gamma \geq \beta$ begins to hold, whereupon a breaking loose of the boundary from the vertex of the groove will give a shortening of the boundary. A similar process will occur at the next temporary stopping place of the boundary, at which it arrives when it has straightened somewhat, so that $\gamma < \beta$. At each of these stopping places a groove will develop, as illustrated in Fig. 32.

**FIG. 32.** Schematic picture of the spasmodic displacement of boundaries in connection with the process of development of grooves.

A direct consequence of this phenomenon of the checking of a moving boundary by a groove is the well known dependence of the grain size in a thin plate on the thickness, for thicknesses such that a grain extends clear through the plate. In particular this has been shown by Beck,^[76] who made experiments with plates of thicknesses up to 3 mm. We note that extremely large grains can be grown in thin films and plates if the network of intergrain boundaries that is developed is not the only factor by which the plate departs from thermodynamic equilibrium. In particular, in plates which have been subjected to plastic deformation and then annealed while subject to the constant action of a small load grains can grow with linear dimensions which exceed the thickness of the plate by orders of magnitude.

Besides the factor we have discussed, the process of checking of the recrystallization of grains that are near the surface can also be caused by the following factor. If a "natural roughness" has been formed at the surface of a grain, then the reorientation of the grain in the process of recrystallization must be accompanied by the loss of the gain of energy which was associated with the presence of the steps of "natural roughness." As was shown in^[74], this can affect not only the dimensions of the "surface" grains, but also the average size of the grains in a layer near the surface.

2. Just as an equilibrium thermal etching groove arises at the place where a grain boundary intersects the free surface, there must also be a departure from ideal smoothness where a dislocation line meets the surface of the specimen. For the case in which there

is disturbance of the equilibrium between crystal and gas phase, the kinetics of the development of a thermal etching pit at the emergence of a dislocation has been discussed in detail in papers by Cabrera,^[77,78] and for conditions in which aggressive etching agents act on the surface of the crystal it has been discussed in papers by Gilman and Johnston.^[79] We shall be interested in a different case—the appearance of a thermal etching pit under equilibrium conditions—which has been treated in a paper by Frank.^[80] According to^[80], when equilibrium conditions hold at the place where a line dislocation intersects the surface what appears is not a pit, but a well, with the dislocation line as its axis. The appearance of a well of radius r is associated with a change of the free energy of the system given by

$$dF = 2\pi\sigma_S dr - \omega 2\pi r dr, \quad (58)$$

where ω is the density of elastic energy around the dislocation.

From the condition $dF/dr = 0$ we have for the equilibrium radius of the well

$$r^* = \frac{\mu b^2}{8\pi^2 \sigma_S}, \quad (59)$$

where μ is the elastic modulus and b is the Burgers vector.

It of course makes sense to speak of a well only when $r^* > \delta$, i.e., $\mu b^2/8\pi\sigma_S > \delta$, or when the Burgers vector satisfies the condition $b^* > 2\pi(2\sigma_S\delta/\mu)^{1/2}$. At the surface the well has a broadened top,^[80] with its profile given by the condition

$$\sigma_S \left(\frac{1}{R_2} - \frac{1}{R_1} \right) = E(r) = \frac{r_0^* \sigma_S}{r^2}, \quad (60)$$

where R_1 and R_2 are the principal radii of curvature.

The normalized profile at the emergence of the well is shown in Fig. 33.

We note that in cases in which the Burgers vector is smaller than the value b^* neither a well nor a pit should appear under equilibrium conditions.

3. In our discussion of the question of the mechanism of the processes that lead to decreases of the total surface energy, we have repeatedly returned to

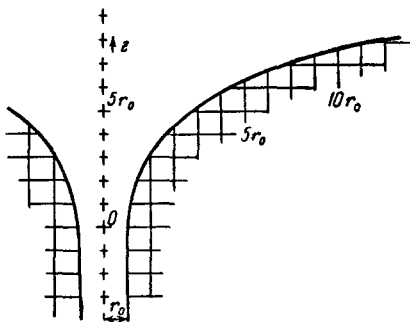


FIG. 33. Normalized profile of the emergence of a well to the surface at the intersection of a line dislocation with a plane section.

the elucidation of the role of surface diffusion. Experiments described earlier provide a basis for obtaining a somewhat more precise idea of the mechanism of the surface migration of atoms, in particular in the case of a distorted surface.

We owe the modern development of our ideas of the mechanism of surface diffusion mainly to the work of Frenkel'.^[24] The situation in the case of surface diffusion is different from that of volume diffusion, where from the point of view of displacement by self-diffusion all of the atoms are equivalent and their displacements are characterized by a definite activation energy for displacement. In the case of surface diffusion one must distinguish as to their mobilities several groups of atoms, whose mobilities are determined by different activation energies.

In the case of a surface of a polycrystal which has been subjected to grinding and polishing, i.e., in which the layer near the surface has been distorted, there is reason to suppose that the experimentally determined surface-diffusion coefficient relates not to the surface proper but to a "thick" surface layer, which is pierced through by boundaries of substructural units, by dislocation lines, and so on.

Thus clearly one must distinguish between true surface diffusion and "near-surface" diffusion, which occurs in such a layer. The thickness and structure of this layer depends on the previous history of the specimen.

The coefficient of true surface diffusion must be a constant of the material, depending only on the temperature, whereas the coefficient of diffusion in the surface layer is structure sensitive, and consequently depends on the character of the treatment of the surface previous to the diffusion anneal.

These considerations agree with the experiments we described earlier on the smoothing out of intentionally produced scratches on a surface, in which in spite of the anisotropy of σ_S the profile remained smooth during the process of healing over, if the scratch had been made on a previously deformed copper surface.

We have evidence of the reasonableness of the ideas about "near-surface" diffusion in the results of^[81], in which there was proposed and experimentally demonstrated a method for the separate determination of the effective coefficient of surface diffusion and the thickness of the layer in which the diffusion occurs.

In experiments on surface self-diffusion in iron (by the use of the isotope Fe^{59}) it was shown^[81] that the layer in which the displacement of an atom is facilitated has a thickness of the order of hundreds of atomic layers. We note that this result provides a basis for supposing that there is an analogy between the structure of the surface layer and that of the boundary between grains with a large angle of disorientation.

VI. LIQUID FILMS ON SURFACES OF CRYSTALLINE MATERIALS

1. One of the consequences of the general tendency toward a decrease of the surface free energy is that near the melting temperature a liquid film may appear on the surface of a solid body. The energetic advantage of the appearance of a liquid film is due to the fact that the following inequality holds between the quantities σ_L , σ_S , and σ_{SL}

$$\sigma_S > \sigma_L + \sigma_{SL}. \tag{61}$$

Calculations of the quantity σ_{SL} made in the configuration approximation^[82,83] give a connection between this quantity and the change of volume on melting ($\Delta\rho/\rho$), and the heats of fusion (Q_f) and of evaporation (Q_e):

$$\sigma_{SL} \simeq \frac{4}{9} \sigma_L \left(\frac{\Delta\rho}{\rho} \right)^2 + \frac{1}{4} \sigma_L \left(\frac{Q_f}{Q_e} \right)^2. \tag{62}$$

From the terms in Eq. (62) we get a value $\sim 10^{-2} \sigma_L$. In the same approximation

$$|\sigma_S - \sigma_L| \simeq \frac{Q_f}{Q_e} \sigma_S. \tag{63}$$

Since $Q_f/Q_e \sim 10^{-1}$, it follows from Eqs. (62) and (63) that the inequality (61) holds. Other evidence in favor of the inequality (61) is found in the experimental data collected in Table V, which show that the quantity $q = \sigma_S - (\sigma_{SL} + \sigma_L)$ is positive and about equal to σ_{SL} .

Table V

Metal	σ_S , erg/cm ² ^[89]	σ_L , erg/cm ² ^[83]	σ_{SL} , erg/cm ² ^[88]	q , erg/cm ²
Copper . .	1650	1240	177	233
Silver . .	1130	930	200	74
Gold . .	1350	1135	215	83

The presence of a liquid film on a solid surface near the melting temperature is the reason for the well known fact that under ordinary conditions a crystalline substance cannot be overheated.

In practice overheating of a crystal can be realized by the observation of certain precautions, as has been done in particular in the experiments of Khaikin and Bene,^[90] who produced a slight overheating in a tin wire by artificially keeping its surface at a lower temperature than its interior.

2. The arguments about the thermodynamic advantageousness of the presence of an equilibrium liquid film on a solid surface in the premelting range of temperatures, which means the arguments for the relation (61), can be illustrated experimentally by a simple experiment, the idea of which is as follows. If a solid surface and a melt are in immediate contact it is obviously natural to expect that the liquid will "creep" over the solid surface, and the result will be to decrease the surface free energy. An experi-

ment on this "creeping" can be made by using a liquid that can be easily undercooled.

In^[15] and^[92] a film of menthol (of thickness 10–30 μ) was melted on a glass plate; as is well known, menthol can be greatly undercooled and is above the limit of metastability at room temperature (18–20°C). A menthol needle of diameter $\sim 100 \mu$ was introduced perpendicular to the plane of the glass support. Thereupon a conelike thickening formed at the foot of the needle. This unequivocally showed that the thickening occurred on account of "creeping" of liquid menthol on the surface of the solid menthol needle (Fig. 34).

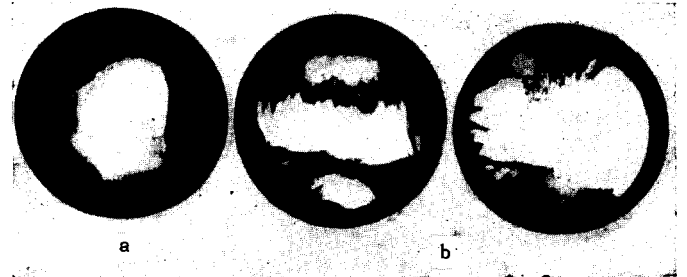


FIG. 34. a) Formation of an enlargement on a needle owing to the effect of "creeping" of the liquid on a solid surface of menthol ($\times 30$).^[15] b) Appearance of the space surrounding this enlargement on the needle ($\times 30$).^[15]

In particular this phenomenon of the "creeping" of a liquid on the surface of the solid phase can be used to explain the widely known phenomenon of the periodic crystallization of melts in thin layers.^[93,108,92] What happens is that a thin film of the melt crystallizes on the amorphous support in the form of families of concentric circles centered on embryonic crystals. These rings are reminiscent of the waves from a stone thrown into water. Within each family the individual rings are separated from each other by annular spaces where the support is practically bare. The phenomenon of periodic crystallization was observed clearly in the experiments described in^[92], from which we have taken Figs. 35 and 36.

The reason for this peculiar kinetics of the crystallization of thin layers may be as follows.

It is well known that the kinetics of the growth of crystals of the solid phase arising in the volume of a liquid is essentially determined by the magnitude

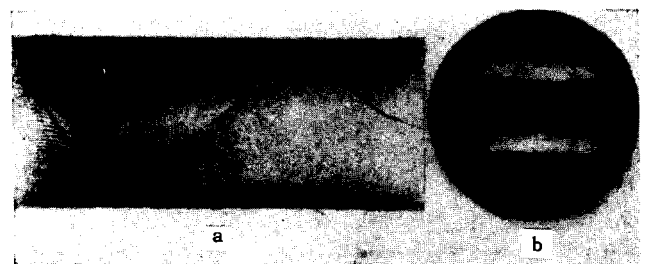


FIG. 35. a) Crystallized film of menthol on glass (natural size). b) View of menthol film enlarged by 30 diameters.^[92]

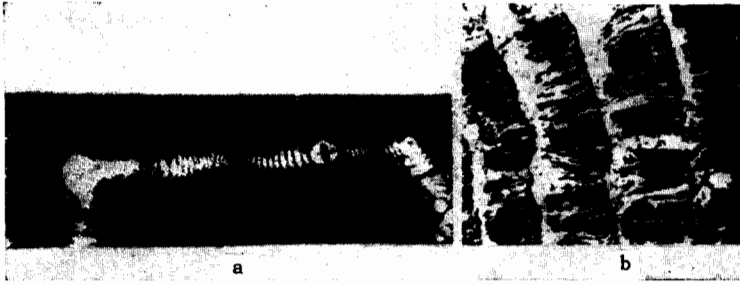


FIG. 36. a) Crystallized film of salol on mat glass (natural size). b) View of film of salol magnified 30 diameters.^[92]

of the interphase surface tension. This same quantity, along with the undercooling of the liquid, also determines the critical size of a viable embryonic crystal. In cases in which a thin film of the liquid is crystallizing, there is a real possibility that besides the "growing crystal-liquid" boundary there can appear another boundary, "growing crystal-vacuum." The surface energy at the "solid phase-vacuum" boundary greatly exceeds the interphase surface energy at the "crystal-liquid" boundary, so that there is reason to suppose that the appearance of a "solid phase-vacuum" boundary will affect the kinetics of crystallization in thin films.

In fact, the appearance of a "solid phase-vacuum" boundary is thermodynamically unfavorable, since it is associated with an increase of the free energy of the system. We note that the appearance of a "solid phase-vacuum" boundary should not occur in true equilibrium kinetics of crystallization.

An important part in the development of the periodic structure is played by the "creeping" of the liquid on the already crystallized solid phase where it is adjacent to vacuum. The surrounding liquid "creeps" onto the surface of the central embryonic crystal, so that the space around it is left bare. The next ring arises in a similar way. Each of the concentric rings is not to be regarded as the development of a single embryo. Within the volume of each ring there are many small crystallites, whose initiation may be provoked, in particular, by "whiskers" from the preceding ring.*

The "creeping" of a liquid on the solid phase of the same substance is like the phenomenon of the flow of a liquid of eutectic composition over the surfaces of touching grains of the pure components of the eutectic alloy, which is observed in experiments on so-called contact melting.^[94] A calculation^[92] shows that the flow of the eutectic liquid is a consequence of the inequality $\sigma_{A-B} > \sigma_{e-A} + \sigma_{e-B}$, where σ_{A-B} is the surface tension at a surface of contact of the pure components of the eutectic mixture, and σ_{e-A} and σ_{e-B} are the respective surface tensions of boundaries between the eutectic liquid and the components. This calculated result agrees with the experimentally observed flow of the liquid phase of a

eutectic alloy over the surfaces of the components.

3. The possibility of the appearance of a liquid film on a crystalline surface can determine the main features of the kinetics of the growth of a crystal from the gas phase. It has been shown in papers by Lemmleĭn and his coworkers^[105] that near the triple point the rate of growth of a crystal from the gas phase does not vary linearly with the temperature of the crystal. A possible cause of this is the formation of a liquid film, which can act as an intermediary between the gas phase and the crystal. This assumption, which agrees with the general "rule of stages," is confirmed by work of Kowarski^[96] and of Dukova,^[97] who observed the appearance of drops of the liquid phase on the surface of a crystal growing in a gaseous medium. In many cases these drops ($d \sim 10 \mu$) disappeared, evidently spreading out over the end faces of the steps growing on the crystal. Evidence in favor of the idea of a liquid film as an intermediary between a gaseous medium and a growing crystal is provided by observations of Kliya,^[98] who directly observed the appearance of a liquid film in a microscopic study of the healing over of cracks on ice crystals.

4. The fact that the appearance of a liquid film on the surface of a crystalline body leads to a decrease of the total surface energy is one of the reasons for the fact that the melting temperature of a substance is lower when it is in the form of a dispersed powder or thin film than it is for a massive specimen. This is a special case of a more general effect, experimentally observed and discussed in a paper by Bublik and Pines,^[99] which consists of a change of the conditions of phase equilibrium in thin layers. When surface energy is taken into account the chemical potentials for crystalline and liquid films of thickness h can be written in the form*

$$\begin{aligned}\tilde{\mu}_S &= \mu_S - \frac{\sigma_S \Omega}{h}, \\ \tilde{\mu}_L &= \mu_L - \frac{\sigma_L \Omega}{h}.\end{aligned}\quad (64)$$

From the condition $\tilde{\mu}_S = \tilde{\mu}_L$ and the fact that for small amounts of undercooling $\mu_S - \mu_L = (q\Omega/T_\infty) \Delta T$, we easily find that

$$\Delta T = \frac{2(\sigma_S - \sigma_L)}{qh} T_\infty.\quad (65)$$

The factor two in Eq. (65) is obtained because we in-

*One can attempt to explain the observed periodicity of the process of crystallization,^[92] by using the idea of the spontaneous appearance of embryonic crystals.^[95]

*A term $\sim \alpha \Omega/h^3$ (cf.^[91]) has been omitted in the expression for $\tilde{\mu}_L$, since for thicknesses $\sim 10^{-6}$ cm it is small in comparison with $\sigma_L \Omega/h$.

clude both surfaces of a free film. In Eq. (65) T_∞ is the melting temperature of a bulk specimen, and $T_\infty - T = \Delta T$ is the lowering of the melting temperature for a film.

In the case of disperse particles of spherical shape (radius r) a formula analogous to Eq. (65) is written in a similar way. We note that degrees of undercooling can be specified for which it can be thermodynamically favorable that there should exist a laminated film, with a crystalline layer between liquid films.^[100]

The lowering of the melting temperature of disperse powders has been observed experimentally in a large number of papers.^[21,101-103]

In particular, Takagi^[103] observed a lowering of the melting temperature of highly dispersed particles of a metal, which were condensed on an amorphous substratum in vacuum. In^[103] the instant of melting was detected by electron diffraction. Takagi found that particles of lead with linear dimensions $\sim 500 \text{ \AA}$ melted at a temperature 7 degrees lower than the melting point of the bulk metal, and for particles of size $\sim 50 \text{ \AA}$ the depression of the melting temperature was 41 degrees. The melting of thin condensed layers of tin and bismuth has been studied by Palatnik and Komnik,^[104] who used condensed layers of various thicknesses. They showed that, in agreement with Eq. (65) and Takagi's results, the melting temperature of a film of condensate having a grainy (globular) structure decreases with increasing (sic) particle size (Fig. 37, taken from^[104]).

Estimates of the quantity $\Delta\sigma = \sigma_S - \sigma_L$ made by means of Eq. (65) lead to the reasonable value $\sim 10^2$ erg/cm².

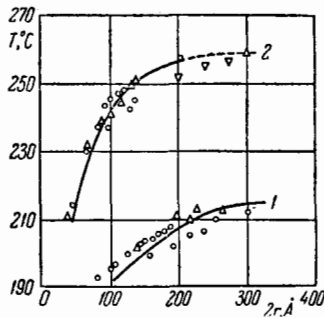


FIG. 37. Dependence of melting temperature of a film of condensate on average particle size. 1 - tin; 2 - bismuth.^[104]

VII. CONCLUSION

As can be seen from the foregoing account, processes occurring at the surfaces of solid bodies are important in many phenomena, some of which have been considered in this article. A consistent solution of practically important problems of the behavior of solids at high temperatures, some of which were mentioned in the introduction, leads necessarily to a discussion of the part played by processes that occur at the surfaces of solids, and thus further study of these processes is a matter of great interest.

In this connection we wish to point out certain problems whose solution is in our opinion important for the development of this branch of solid state physics.

One of the most important problems is that of developing reliable methods for the experimental determination of the surface energies of solids. Strictly speaking, by present methods one can obtain only more or less credible estimates, with an accuracy clearly inadequate for tracing the temperature dependence of σ_S , for example.

The study of processes occurring at the surfaces of solid alloys can be of great interest. In work with liquid metallic alloys much information relating to adsorption effects has now been accumulated. In particular, studies have been made of the temperature and concentration dependences of the process of enrichment of a surface layer in a component which lowers the surface tension. In the case of solid alloys there is practically no such information, whereas processes of adsorption at free solid surfaces of alloys clearly must strongly affect phenomena such as the development of cracks in the high-temperature deformation of alloys involving creep processes, the healing of macroscopic defects in porous materials, the sintering of pressed powder mixtures, and so on. At the surface of a solid alloy and in the layer next to the surface kinetic effects not characteristic of the liquid phase can be realized in practice. For example, it can be expected that in analogy with the phenomenon of diffusive segregation of one of the components of a solution, which occurs in an alloy with a macroscopic inhomogeneity when the diffusive mobilities of the components are characterized by different partial volume-diffusion coefficients,^[113,114,115] there must be an effect of surface-diffusion segregation at a surface flawed with protrusions and depressions, owing to possible differences in the surface-diffusion coefficients of the components.

It is also important to study the effects of gases dissolved in the surface layer on the magnitude of the surface tension. Fragmentary and discordant evidence on this question indicates that the effect is an important one.

We note that besides their scientific interest the problems we have been discussing may have considerable interest for applications, in particular in connection with the possibility in principle of producing high-temperature smoothing out of surface defects without the use of special treatments which distort the layer next to the surface. Preliminary tests indicate that such "thermal polishing" may be really useful.

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