

## PHYSICO-CHEMICAL PHENOMENA IN THE DEFORMATION OF METALS

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A new scientific field has arisen during the last ten years, primarily in the papers by the group of Soviet scientists headed by Academician P. A. Rebinder. This is physico-chemical mechanics, which borders on physical chemistry, molecular physics, and mechanics of materials. The basic aim of this new borderline field of knowledge<sup>9</sup> consists of (1) the clarification of the laws and the mechanism of formation of solids of a given structure and with prescribed mechanical properties, and (2) the study of the mechanism of the processes of deformation, working, and fracture of solids, taking into account the effect of physico-chemical factors such as the composition and the structure of the solid, the temperature, and the surrounding medium.

By now considerable experimental material has been accumulated in this field, which is of great significance for the theory of the formation and fracture of solids, and also for the determination of optimum conditions of working them. At the same time in recent years considerable advances have been made in the field of theoretical treatment of the newly discovered laws with the aid of the formalism of dislocation theory.

This article presents the basic results of investigations carried out recently in the field of physico-chemical mechanics of metals, with particular attention to the theoretical treatment of these results from the point of view of dislocation theory.

It has already been established for a long time, through the work of P. A. Rebinder and his associates, that the ability of solids to resist deformation and fracture is reduced as a result of adsorption from the surrounding medium. This phenomenon is associated with a decrease in the surface energy of the deformed solid. The effects of the reduction of strength due to adsorption and of the decrease in resistance to deformation are of a kinetic nature. As a result of a decrease in the surface tension of the solid over its surfaces, they are brought about by the greater ease of formation and development of various types of structural defects and of incipient shear, which in the course of deformation de-

velop over the boundary with the surrounding medium.<sup>1-6\*</sup>

The strength must, evidently, be decreased by adsorption indefinitely with decreasing interphase surface energy at the boundary between the solid and the surrounding medium, since the magnitude of the interphase surface energy determines the probability and the work of formation of surface defects (incipient shear or fracture) appearing in the process of deformation.

The largest adsorption effects due to the surrounding medium, as has been shown,<sup>4,5</sup> are observed during prolonged exposure to appropriate stresses, under conditions of creep or fatigue testing.

Organic surface-active substances (the usual active components of lubricants) can be used only at relatively low temperatures. Surface-active metals and alloys with comparatively low melting points are considerably more active with respect to metals and give rise to a large reduction in their surface tension, i.e., they are more strongly adsorbed.

The case of sufficiently low values of interphase surface tension  $\sigma_{12}$  at the boundary between two phases corresponds, according to Volmer's

\*The papers by Benedicks and Sato<sup>7</sup> appeared long after P. A. Rebinder's first publications on this subject.<sup>1</sup> They pointed out (without mentioning the original source) essentially the same effect of reduction in the strength of solids under the action of wetting liquid media. However, this was accompanied by an erroneous conclusion with respect to the alleged possibility of determining the surface tension of a solid  $\sigma_1$  by making use of Antonov's empirical rule (and moreover applying it erroneously to mutually nonsaturated phases) and extrapolating linearly (!) the initial decrease in strength  $P_m$  with increasing surface tension of the wetting liquid  $\sigma_2$  down to the value  $P_m = 0$ , which should correspond to  $\sigma_1 = \sigma_2$ . This unjustified extrapolation leads to values of  $\sigma_1$ , for example in the case of steel, lower by an order of magnitude than reliable values computed by various indirect methods. In going over to large reductions of strength in liquids, with respect to which the given solid is more lyophilic, we would obtain concave curves which approach the horizontal axis ( $P_m = 0$ ) at considerably higher values of  $\sigma_2$ . It is clear that when a contact angle is definitely not formed the work of spreading is positive and large, and Antonov's rule is obviously inapplicable.

conception,<sup>8</sup> to spontaneous dispersion down to particles of colloid size under the action of thermal motion. In this case a thermodynamically stable colloid solution (suspension or emulsion) is formed which is a completely dispersed two-phase system of two mutually saturated phases that are in equilibrium. The increase in surface energy in the case of such a dispersion is compensated by an increase in the entropy of the system as a result of the uniform distribution of the particles throughout the whole volume of the medium.

An approximate condition for spontaneous dispersion consists of the requirement that  $\sigma_{12} < \sigma_m$ , where  $\sigma_m = \gamma kT / \delta_m^2$  ( $\delta_m$  is the average size of a mosaic block,  $\sim 10^{-6}$  cm), or, according to Rebiner, the dispersion criterion  $Di = \sigma_{12} \delta_m^2 / kT\gamma$  (where  $\gamma \sim 30^{68}$ ) must satisfy the condition  $Di < 1$ . Spontaneous dispersion can occur even at the relatively high values  $\sigma_{12} \cong 0.2$  erg-cm<sup>-2</sup>. As the temperature is increased  $\sigma_{12}$  decreases sharply because of the increase in mutual solubility. The limiting case of the critical point,  $\sigma_{12} = 0$ , corresponds according to Mendeleev to the disappearance of the colloid phase, i.e., to infinite mutual solubility with the formation of a true (single-phase) solution.

For large values of  $\sigma_{12}$  ( $\sigma_{12} > \sigma_m$ ) the dispersion cannot be spontaneous, i.e., it occurs only under the action of external forces, but in this case the strength of a solid in a given liquid phase ( $P_m$ )<sub>A</sub> shows a greater reduction with diminishing  $\sigma_{12}$  in comparison with its strength in vacuo ( $P_m$ )<sub>0</sub>. Under this condition the criterion for dispersion will be of the form:

$$Di = \frac{\sigma_{12} S_m - 3PV_m}{\gamma kT} < 1,$$

while the effect of reduction of strength may attain very considerable magnitude.

Until recently investigations of the effect of low-melting-point metallic fluxes on the mechanical properties of high-melting-point metals and alloys were carried out using polycrystalline samples tested under compression, bending, or tension. The most general result of these investigations is that in the presence of metallic fluxes the plasticity and the strength of samples deformed in such a medium is sharply reduced.<sup>10-16,69</sup> At the same time it was found that the magnitude of the effect of the reduction of plasticity and strength under the action of a flux depends to a large extent on the nature of the metal being deformed and of the low-melting-point flux surrounding it.

In the opinion of many authors, fluxes which form

solid solutions or intermetallic compounds with the basic metal are more effective, while the absence of interaction between a metal and a flux leads to a considerable decrease in the magnitude of the effect. Moreover, the effect of flux action depends on the mechanical characteristics of the initial sample. The effect of the medium is more pronounced if the sample has greater strength and hardness. In the case of steel, brittle fracture can occur both in the elastic and in the plastic range, depending on the elastic limit of the steel.

An essential role is also played by the conditions under which the experiments are carried out: the nature of the stressed state, the rate of deformation or the manner in which the stress is applied, the time of contact of the sample with the flux, and the temperature at which the deformation is produced. Thus, for example, a flux does not produce any effect under the action of compressive stresses, and produces a large effect under the action of tensile stresses. The effectiveness increases as the rate of loading or the rate of deformation of the sample is decreased, or as the time of contact between the sample and the flux before the experiment is increased; the effectiveness of the flux increases appreciably as the temperature of the experiment is increased.

The extensive experimental material accumulated by now on the effect of metallic fluxes on the mechanical properties of high-melting-point metals has not yet received an exhaustive explanation. Many authors attribute these phenomena to the usual intercrystallite corrosion by assuming that as the flux diffuses along the grain boundaries it weakens the binding between the grains by means of some kind of a mechanism.

Of considerable importance for the correct understanding of the phenomenon of the decrease in the strength of metals under the influence of low melting point metallic fluxes are the papers of S. T. Kishkin and Ya. M. Potak, who emphasize the relation between these phenomena and the effect of the decrease in the strength of metals due to adsorption.<sup>16</sup>

We present below the main results of the experimental investigation of the effect of low-melting-point metallic fluxes on the mechanical properties of metals of higher melting points obtained for single crystals of zinc, tin and cadmium by L. A. Kochanova, L. S. Bryukhanova and V. A. Labzin of our laboratory.<sup>17,18,19</sup>

Tin, lead, alloys of tin with lead in varying concentrations, and mercury were used as surface-active fluxes. Single crystals of different orientation were grown by the method of zone crystalliza-

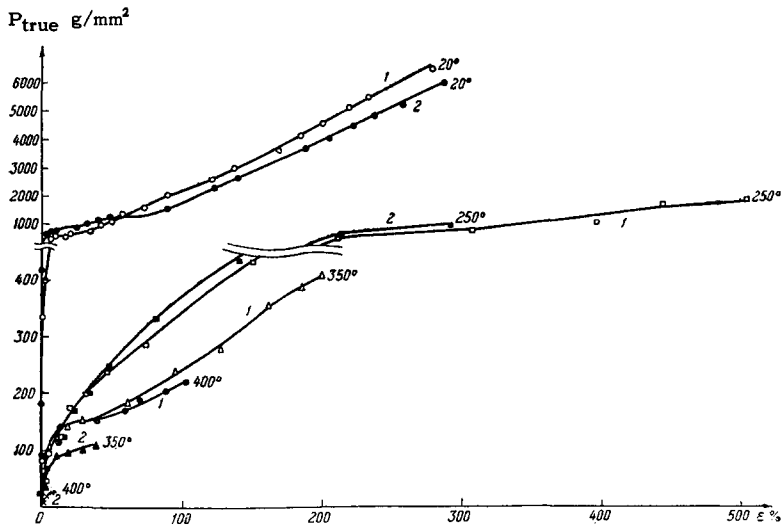


FIG. 1. Dependence of the true stress  $P = P_0 (1 + \epsilon/100)$  on the relative elongation  $\epsilon$  of zinc single crystals ( $\chi_0 = 44^\circ$ ) without external coating (1) and coated with a film of tin (2). The temperature of the crystals is shown on the graph.

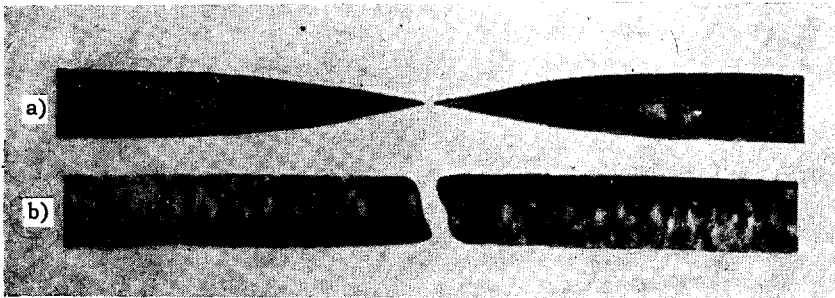


FIG. 2. The usual plastic fracture of zinc single crystals without external coating (a) and brittle fracture (b) of zinc single crystals coated with a film of tin. Both fractures took place at 400°C.

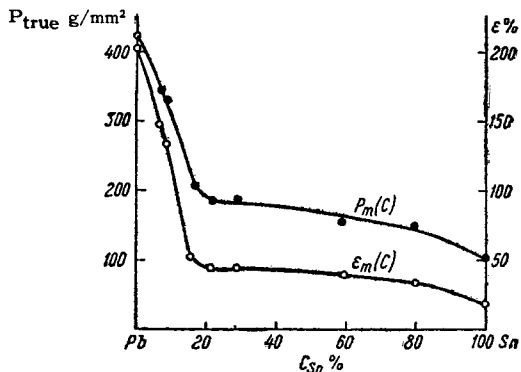


FIG. 3. Dependence of the true strength  $P_m$  and of the greatest elongation  $\epsilon_m$  preceding fracture of zinc single crystals ( $\chi_0 = 42^\circ$ ) on the concentration of tin in an alloy of tin with lead at 350° C.

tion developed in our laboratory.<sup>20</sup>

Figure 1, in which the axes represent the true stress and the relative elongation, presents stress-strain curves for single crystals of zinc at different temperatures. The elongation took place at a constant deformation rate of  $15\% \text{ min}^{-1}$ . The diameter of the single crystals was 0.5 mm. Black points indicate the curves for the elongation of crystals whose deformation was carried out in tin (a thin film of tin of thickness 2 to  $5 \mu$  was deposited electrolytically on the surface of the single crystal of zinc).

Below the melting point of the eutectic ZnSn, the effect of a thin film of tin on the surface of the zinc single crystal results only in a small increase of strength. At higher temperatures (350° and 400°C), in the presence of tin, the strength and plasticity decrease rather sharply (by a factor of 8 to 10). At the same time the nature of the fracture changes from ductile fracture in air to brittle fracture in an active medium (Fig. 2). The pronounced effect of the temperature (in going from 350° to 400°C) is evidently associated with an increase in the solubility of zinc in liquid tin (45% at 350° and 92% at 400°C), which corresponds to a sharp decrease in the interphase surface tension.

A similar investigation was made of the influence of lead-tin fluxes of different tin content on the stress-strain curve of single crystals of zinc. Molten lead taken by itself turned out to be relatively weakly surface-active with respect to zinc. Figure 3 shows that even relatively small additions to the flux of surface-active tin give rise to a fairly sharp decrease in the strength and in the plasticity of single crystals of zinc. At 20% this effect reaches a limit, and further reduction occurs only at a tin content of greater than 80% (when pure tin is approached), which is evidently associated with a sharp increase in the solubility of zinc in such fluxes.

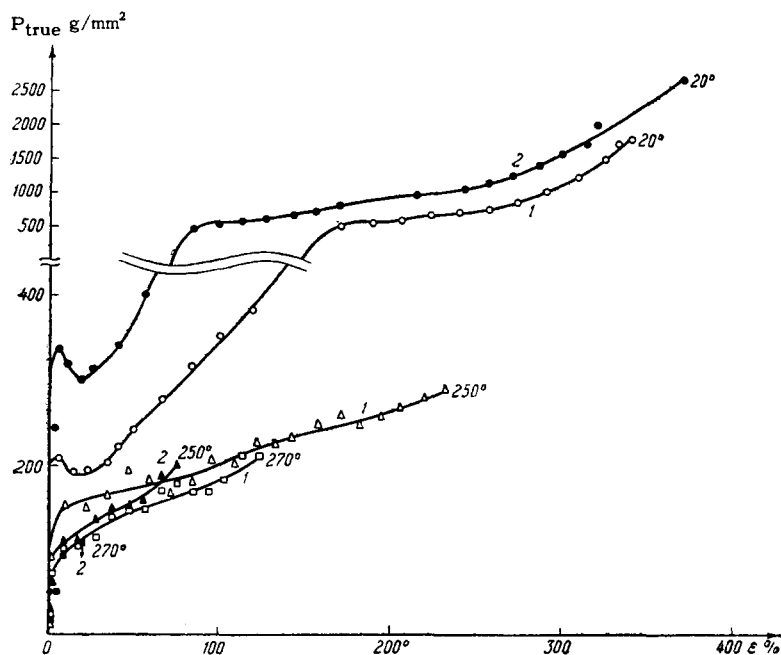


FIG. 4. Dependence of the true stress  $P$  on the relative elongation  $\epsilon$  of cadmium single crystals ( $\chi_0 = 39^\circ$ ) without external coating (1) and coated with a thin film of tin (2). The temperature of the crystals is shown on the graph.

TABLE I. Rate of steady creep of zinc single crystals tested in an inert gas  $(v_m)_0$  and in the presence of a thin film of tin on the surface of the single crystals  $(v_m)_A$ .

$t$ °C	$P$ (g/mm <sup>2</sup> )	$(v_m)_0$ (min <sup>-1</sup> )	$(v_m)_A$ (min <sup>-1</sup> )	$\frac{(v_m)_A}{(v_m)_0}$
200	76	$0.7 \cdot 10^{-4}$	$0.2 \cdot 10^{-4}$	0.3
280	51	$1.7 \cdot 10^{-4}$	$10 \cdot 10^{-4}$	6.0
350	19	$1.0 \cdot 10^{-4}$	$15 \cdot 10^{-4}$	15.0

An interesting result is obtained when a single crystal of zinc covered by a film of liquid tin is maintained for a sufficiently long time without stress at 400°C, and is then placed into liquid lead at the same temperature. If the crystal is then kept in liquid lead for a sufficiently long time the effect disappears completely and the normal strength of single crystals of zinc is reestablished. This experiment indicates that no appreciable role is played by the normal diffusion of tin into zinc. Evidently the penetration of tin and the associated reduction in strength occurs only along the developing surface defects incipient shear and fracture.

We have also obtained considerable reductions in strength and plasticity in single crystals of cadmium in the presence of liquid tin (Fig. 4). The action of liquid tin on single crystals of cadmium is the same as on single crystals of zinc. Our results indicate directly the very important fact that the action of surface-active metallic fluxes is not associated with the presence of boundaries between grains of a high-melting-point metal. This action is observed also in the absence of intercrystalline

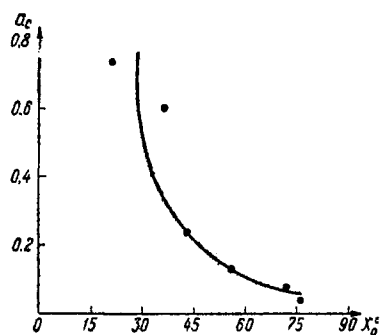
boundaries in the case of metallic single crystals and may attain considerable magnitude under favorable temperature conditions. Of course, this conclusion does not mean that the grain boundaries in a polycrystalline metal play no role at all in the effect of flux action. They may play a very considerable, and in some cases a decisive role; however, we should bear it in mind that a surface-active metallic flux may reduce the strength and the plasticity of an individual grain as much as desired, owing to the sharp reduction in the inter-phase surface tension.

In the presence of such a strong surface-active substance as a metallic flux, even very small normal stresses in high-melting-point metals lead to the formation and development of cracks that result in brittle fracture of the metal. For this it is merely necessary that the kinetics of the development of the crack correspond to the rate of penetration of the surface-active flux along these cracks into the metal undergoing deformation.

In earlier papers on the effect of ordinary organic surface-active substances on the creep of

**TABLE II.** Rate of steady creep at 350°C of zinc single crystals covered by alloys of tin with lead of different concentrations

PbSn alloy	$(v_m)_0 \cdot 10^4 \text{ (min}^{-1}\text{)}$ uncoated	$(v_m)_A \cdot 10^4 \text{ (min}^{-1}\text{)}$ coated	$\frac{(v_m)_A}{(v_m)_0}$
90% Pb—10% Sn	1.3	1.7	1.3
80% Pb—20% Sn	1.0	3.0	3.0
50% Pb—50% Sn	1.1	4.5	4.0
20% Pb—80% Sn	3.3	20.0	6.0


**FIG. 5.** Decrease in the value of the limiting plastic shear ( $a_s$ ) for zinc single crystals as the initial angle of orientation of the base plane ( $\chi_0$ ) is increased at  $-196^\circ$ .

metallic single crystals it was found that the rate of creep is considerably increased by adsorption of surface-active molecules contained in the surrounding medium. In connection with this it is of considerable interest to study the creep of metallic single crystals in such strongly surface-active media as fluxes of low-melting-point metals.<sup>17</sup>

In the presence of a tin coating, starting with 280°C, an appreciable increase in the rate of steady-state creep is observed for single crystals of zinc. Table I gives data on the change in the rate  $v_m$  of steady-state creep of single crystals of zinc at different test temperatures.

Table II gives data for the rate of steady-state creep of single crystals of zinc coated with alloys of tin with lead in different concentrations.

Tin flux, which is a very strongly surface-active for zinc, reduces sharply the level of normal fracture stresses under conditions of elongation at a constant rate of deformation, which leads to a considerable reduction of plasticity (value of deformation before rupture) and strength. However, under conditions of creep, when the constant stress acting on the metal is lower than the stress of brittle fracture, a plasticizing effect due to adsorption appears in the presence of a surface-active flux and manifests itself in a considerable increase in the rate of creep of the metal.

N. V. Pertsov has shown that mercury, like tin, behaves like a very strong surface-active substance

with respect to zinc single crystals and sharply reduces their strength and particularly their plasticity.<sup>21</sup> Even at room temperature single crystal zinc wires become brittle under the action of mercury, i.e., they become characterized by a very small plastic elongation, which ends in brittle fracture along the basal plane (or along the first-order prismatic plane) at not very high tensile stresses.

Since molten metals reduce appreciably the strength and the plasticity of metals of higher melting points by making them brittle, it becomes necessary to make a comparative study of the laws of deformation and fracture of metals in strongly surface-active fluxes, and of similar laws for these metals in a brittle state but in nonactive media.<sup>19</sup>

As is well known, single-crystal zinc wires are very plastic at room temperature, i.e., they are capable of considerable plastic elongations (up to 600%). Brittle fracture along the basal plane does not occur under these conditions (at not very high rates of elongation). The brittle state may be realized in single crystals of zinc by a considerable decrease in temperature. This brittle state has the peculiarity that brittle fracture under the action of normal stresses is always preceded by a fairly considerable shear deformation along the active slip system (basal planes).

A study of the laws of brittle fracture of single crystals of zinc with different initial orientations of the basal plane with respect to the axis of the wire ( $13^\circ \leq \chi_0 \leq 80^\circ$ ) was carried out at the temperature of liquid nitrogen ( $-196^\circ\text{C}$ ) under tension with a constant rate of elongation ( $\cong 12\% \text{ min}^{-1}$ ). The critical shearing stress in the basal plane at the temperature of liquid nitrogen reaches  $\sim 130 \text{ g/mm}^2$  and, as has been shown by extensive experimental material,<sup>22</sup> does not depend on the orientation of this plane relative to the crystal axis (on the value of  $\chi_0$ ).

A study of the laws of brittle fracture (fracture along the basal plane) of single crystals of zinc of various orientations has led first to the discovery that the value of the plastic shear as preceding fracture increases as  $\chi_0$  decreases (Fig. 5).

TABLE III. Values of  $a_s$ ,  $p_s$ ,  $\tau_s$  at the instant of brittle fracture along the basal plane resulting from elongation of zinc single crystals at  $-196^\circ\text{C}$

$\chi_0$	$a_s$	$p_s$ , g/mm <sup>2</sup>	$\tau_s$ , g/mm <sup>2</sup>
21	0.74	93	311
36	0.60	160	314
43	0.24	182	238
56	0.13	249	201
72	0.08	268	128
76	0.04	431	126

At the same time the normal fracture stresses in the basal plane (the slip plane) decrease sharply as the initial angle of orientation  $\chi_0$  of this plane is reduced or, which is the same thing, as the plastic shear preceding fracture is increased. Figure 6 shows the dependence of the normal stresses in the basal plane on the magnitude of the shear occurring in the course of deformation of single crystals of zinc with different initial orientations of the basal plane. Here it is necessary to point out that the area of the basal plane (the slip plane) remains constant to a sufficient degree of accuracy during the process of plastic shear even in the case of quite considerable deformations (up to 600%). The crescent-shaped portions of the slip planes uncovered by the shear amount to some hundredths of a percent of the area of the basal plane and, consequently, this change in area can always be neglected. The dotted curve in Fig. 6 joining the end points (corresponding to brittle fracture along the basal plane) of the individual stress-strain curves of variously oriented zinc single crystals determines, by this very fact, the dependence of the normal fracture stresses along the basal plane on the magnitude of the shear preceding the fracture. This dependence, which has been checked by us on a large number of samples, shows that the normal fracture stresses decrease sharply with increasing shear deformation (along the basal plane) that precedes the brittle fracture (along this plane).

Table III gives values of the normal fracture stresses  $p_s$ , limiting values of the magnitude of the shear  $a_s$  and values of the shear stresses  $\tau_s$  as a function of  $\chi_0$ .

For a proper understanding of this variation it should be pointed out that the crystallographic conditions for the deformation of zinc single crystals, together with the law that the critical shearing stress is independent of the angle of orientation of the basal plane, cause the normal stresses on the

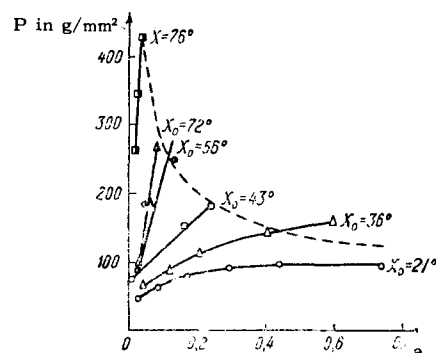


FIG. 6. Dependence of the normal stresses across the basal plane ( $p$ ) on the magnitude of the shear ( $a$ ) during the process of deformation of zinc single crystals with different orientations of the basal plane ( $\chi_0$ ) at  $-196^\circ$ .

basal plane to be relatively small for small values of  $\chi_0$ , while for large values of  $\chi_0$  these stresses increase considerably.

Since the process of plastic shear along the slip plane (the basal planes) is accompanied by a decrease in the angle  $\chi$  (as a result of a deformation  $\chi < \chi_0$ ), then for crystallographic reasons the normal stress along the basal plane must decrease in the course of the slip process. However, an increase in the shearing stress due to hardening leads to an increase in the total tensile stress, which also gives rise to an increase in the normal stress along the shear plane which exceeds the decrease in this stress for crystallographic reasons.

Figure 7 presents the dependence of the limiting plastic shear and of the normal and shearing fracture stresses on the initial angle or orientation of the basal plane. Here we can clearly see the regular decrease in normal fracture stresses corresponding to an increase in the plastic shear preceding fracture. As this deformation increases, the value of the shearing stresses also increases, and this is associated with shear hardening.

From these data it follows first of all that the so-called Zonke's law with respect to the constancy

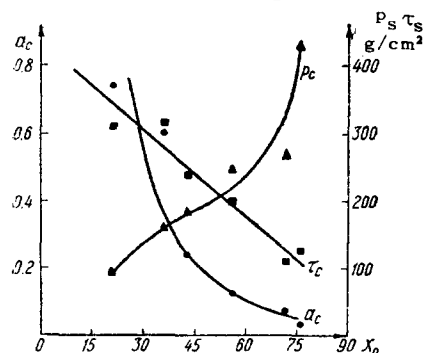


FIG. 7. Dependence of the limiting plastic shear ( $a_s$ ), and the normal ( $p_s$ ) and shearing ( $\tau_s$ ) fracture stresses on the initial angle of orientation of the basal plane ( $\chi_0$ ) of zinc single crystals at  $-196^\circ$ .

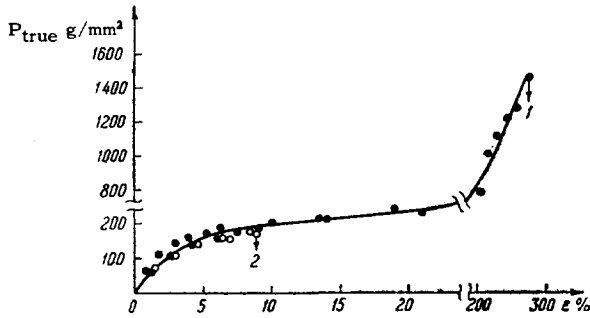


FIG. 8. Dependence of the stress ( $P$ ) on the relative elongation ( $\epsilon$ ) of non-amalgamated (1) and amalgamated (2) zinc single crystals ( $\chi_0 = 48^\circ$ ) at  $20^\circ\text{C}$ .

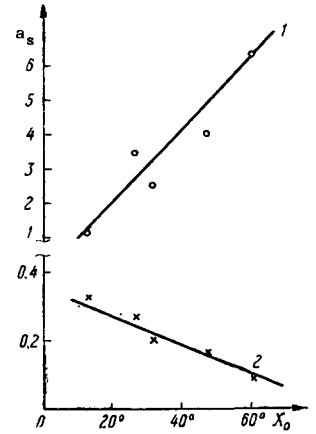
of normal fracture stresses does not hold for brittle single crystals of zinc. This is apparently explained by the fact that at low temperatures brittle fracture of single crystals of zinc is always preceded by an appreciable plastic shear deformation along the slip planes, while in crystals of rock salt, in which this law was discovered, plastic deformation preceding fracture is practically equal to zero. With respect to the work of E. Schmid, who confirmed the validity of Zonke's law for single crystals of zinc at low temperatures, we can say that the result obtained by him can be explained by choosing a comparatively narrow range of orientation of the basal plane in his experimental samples.<sup>22</sup>

At the same time it follows from the data obtained that plastic shear leads to the appearance of defects in the crystal structure which are points of incipient fracture. Even in their early stages of development these structural defects lead to brittle fracture along the slip plane (basal plane) if the level of normal stresses is sufficiently high (for large values of  $\chi_0$ ). However, if the magnitude of normal stresses is small (low values of  $\chi_0$ ), then the development of the defects up to the critical value corresponding to the given level of normal stresses occurs at a larger value of plastic shear.

The observed laws of brittle fracture of single crystals of zinc at low temperatures hold also when the transition into the brittle state is achieved not by lowering the temperature, but by the action of a strong surface-active medium (mercury), in which the deformation of crystals takes place. However, an essential difference between these brittle states is that in the surface-active medium (mercury) the brittle strength of single crystals (the magnitude of the normal fracture stresses) is sharply reduced (by a factor of 3 to 5) while the value of the shear stresses remains practically unaltered.

Mercury was deposited on the surface of the single crystals of zinc in a thin layer ( $\sim 5\mu$  thick)

FIG. 9. Dependence of the limiting plastic shear ( $a_s$ ) of non-amalgamated (1) and amalgamated (2) zinc single crystals on the initial orientation of basal plane ( $\chi_0$ ) at  $20^\circ\text{C}$ .



by immersing the crystals into a saturated solution of mercury nitrate (the higher salt) and holding them in the solution for about 1 minute. Figure 8 shows typical stress-strain curves for amalgamated and non-amalgamated single crystals of zinc ( $\chi_0 = 48^\circ$ ) at room temperature. Here one can clearly see the sharp increase in the brittleness of crystals in the presence of mercury, but at the same time the stress-strain curve for the amalgamated sample coincides with the stress-strain curve for the non-amalgamated crystal.

Figure 9 shows the dependence of the limiting plastic shear  $a_s$  preceding fracture of non-amalgamated and amalgamated crystals on the initial orientation of the basal plane. While in the absence of mercury this limiting shear increases with increasing  $\chi_0$ , (i.e., for a more nearly transverse orientation of the basal plane the crystals turn out to be more plastic), the amalgamated samples behave in a completely opposite manner. Such a radical change in the nature of the functional dependence  $a_s = a_s(\chi_0)$  under the action of mercury is associated with the transition of the zinc single crystals in the presence of mercury from the plastic to the brittle state, and with the resultant new laws governing deformation and fracture.

Indeed, the dependence shown in Fig. 10 of the

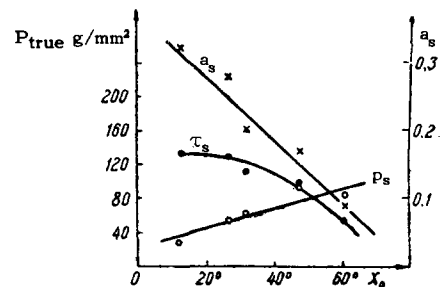


FIG. 10. Dependence of the limiting value of the shear ( $a_s$ ), and the normal ( $p_s$ ) and shearing ( $\tau_s$ ) fracture stresses on the initial orientation of the basal plane ( $\chi_0$ ) of amalgamated zinc crystals at  $20^\circ\text{C}$ .

TABLE IV. Values of  $a_s$ ,  $p_s$ ,  $\tau_s$  at the instant of brittle fracture along the basal plane of amalgamated zinc crystals at 20°C

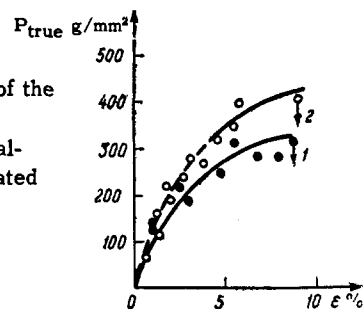
%	$a_s$	$p_s$ , g/mm <sup>2</sup>	$\tau_s$ , g/mm <sup>2</sup>
13	0.33	29	136
27	0.28	58	131
32	0.20	64	114
48	0.17	90	96
61	0.09	85	55

limiting value of the shear, and of the normal and shearing stresses at the moment of fracture, on the orientation of the basal plane is completely analogous to a similar dependence for single crystals of zinc at low temperatures (Fig. 7). Table IV lists values of the limiting shear deformation, and of the shear and normal fracture stresses along the basal plane for brittle amalgamated samples of different orientations at room temperature.

While the normal fracture stresses is lower (by a factor 3 to 5) than in non-amalgamated crystals (at  $-196^\circ\text{C}$ ), the shearing stresses in the basal plane of amalgamated samples remain the same as in the case of non-amalgamated single crystals of zinc at the same room temperature. However, at the temperature of liquid nitrogen the amalgamated samples turned out to be no less plastic than the non-amalgamated ones, while the normal and shearing stresses at the instant of brittle fracture along the basal plane turned out to be even higher in the presence of the mercury film than in its absence (Fig. 11). Since the amalgamated samples were immersed into liquid nitrogen 2 or 3 minutes after the mercury film had been applied and, consequently, there was no time for any appreciable diffusion penetration of mercury into zinc, the effect of the increase of strength of amalgamated samples at low temperatures can be explained by the appearance of a thin polycrystalline coating of mercury on the zinc single crystals, which hinders plastic shear and brittle fracture along the basal plane. Hardening of amalgamated samples in liquid nitrogen can also be observed as a result of the diffusion penetration of mercury into zinc (alloying) if the amalgamated samples are maintained at room temperature for a sufficiently long time prior to the experiment ( $\sim 48$  hours).<sup>23</sup>

Thus, mercury used as a surface-active substance produces in zinc single crystals a brittle state characterized by the same general laws of deformation and fracture as the brittle state due to a lowering of temperature in the absence of surface-active substances. The sharp reduction

FIG. 11. Dependence of the stress ( $P$ ) on the relative elongation ( $\epsilon$ ) of non-amalgamated (1) and amalgamated (2) zinc single crystals ( $\chi_0 = 48^\circ$ ) at  $-196^\circ\text{C}$ .



in the normal fracture stresses in the presence of mercury is due to an appreciable reduction in the interphase surface tension at the boundary between the zinc and the saturated solution of zinc in mercury. The structure defects (micro-cracks) formed during deformation are rapidly filled with mercury by two-dimensional migration, and this greatly facilitates their further development until brittle fracture can occur under the action of even small normal stresses. The high mobility of mercury atoms, which enables them to penetrate sufficiently rapidly into the forming micro-cracks, is a necessary condition for the reduction in strength and plasticity. At low temperatures, when the mercury atoms are not mobile, one observes an increase in the brittle strength of zinc single crystals covered by a mercury film. This is due either to alloying of the zinc with the mercury, or to the resistance of the film itself to shear and fracture.

The experiments described above,<sup>18,19,21</sup> as well as numerous data of other authors, indicate in a convincing manner that brittle fracture of a metallic single crystal is always preceded by plastic deformation of some kind; the stress  $p_s$  normal to the cleavage plane at the moment of fracture is by no means constant, but depends strongly on the magnitude of the preceding plastic shear  $a_s$ , and at the same time on the shearing stress  $\tau_s$  in the slip plane attained at the moment of fracture. In our case of brittle fracture of zinc single crystals when the basal plane is simultaneously the slip plane and the cleavage plane, the interdependence between  $p_s$  and  $\tau_s$  is particularly clearly evident: as the value of  $p_s$  increases crystal fracture occurs at smaller values of  $\tau_s$  (Tables III and IV). In this case one should apparently speak not of the deviations from Zonke's law which have been repeatedly mentioned earlier, but of a complete inapplicability of this law.

It is well known that the actual fracture stress  $p_s$  along the cleavage planes is several orders of magnitude lower than the so called "theoretical" value  $p_{\text{theor}} \cong \sqrt{E\sigma/b}$ , calculated on the basis of some model of interatomic forces for an ideal



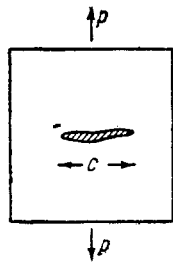


FIG. 12. Illustration for the calculation of  $p_s(c)$ .

crystalline lattice containing no defects,<sup>25, 26</sup> here  $E$  is Young's modulus,  $\sigma$  the specific surface free energy, and  $b$  the lattice constant. Such a discrepancy is usually associated with the presence of various structural defects, primarily micro-cracks, in the actual crystal. The inapplicability of Zonke's law, and the observed dependence of  $p_s$  on  $\tau_s$  and  $a_s$  in the case of brittle fracture of single crystals of zinc, enable us to take the following step in the explanation of the mechanism of brittle fracture.

It is natural to suppose that if the fracture is due to the presence of a micro-crack the magnitude  $c$  of which becomes "dangerous" for a given  $p_s$ , the initiation and the growth of the micro-crack up to the dangerous value are associated with the preceding plastic deformation, in the course of which inhomogeneities of shear lead to sharp local stress concentrations and to the appearance of micro-cavities.<sup>6, 24</sup>

It is therefore necessary first to find the value of the critical normal stress  $p_c$  which is dangerous in the presence of a crack of size  $c$  and then to try to estimate the maximum size  $c$  of the crack that may appear in the crystal at a given shearing stress  $\tau$ .<sup>24</sup>

Following Zener,<sup>27</sup> the simplest and most obvious estimate of the dangerous tensile stress  $p_c$  in the presence of a crack of size  $c$  can be obtained in the following manner (Fig. 12). Prior to the appearance of the crack the density of elastic energy in the solid is  $w = p^2/2E$ . When the crack appears the stress is removed from an area approximately equal to  $c^2$ ; the decrease in elastic energy (per unit length in the direction perpendicular to the plane of the diagram) amounts in this case to  $\cong p^2c^2/2E$ . At the same time the formation of the new surface of approximate size  $2c$  is associated with an expenditure of work equal to  $2c\sigma$ . The total increment in energy is equal to  $\Delta W = 2c\sigma - p^2c^2/2E$ . The curve  $\Delta W(c)$  has a maximum at  $(\partial/\partial c)\Delta W = 0$ . Consequently, a crack of width  $c$  becomes unstable when a "dangerous" stress  $p_c = \sqrt{2\sigma E/c}$  is applied perpendicular to its plane.

A similar formula was first proposed by Griffith.<sup>28</sup> Subsequently several authors have shown

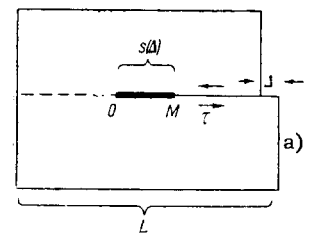
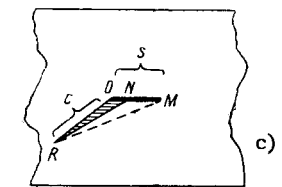
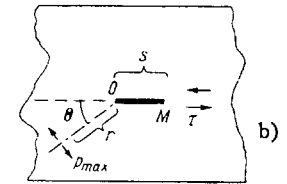


FIG. 13. (a) Appearance of an incomplete local shear in a glide plane. (b) Concentration of normal stresses in the neighborhood of the region of an incomplete local shear. (c) Appearance of a microcrack in the neighborhood of maximum concentration of normal stresses.



that, with the exception of some differences in the numerical coefficient, the result remains the same under very varied formulations of the problem: both for thin and for thick slabs (two-dimensional problem), in the case of a three-dimensional problem (crack in the form of an ellipsoid),<sup>29</sup> and also in going over from the calculation of the energy to a direct determination of stress concentrations at the edge of the crack,<sup>28, 30</sup> in particular in the analysis of interatomic forces and of the location of atoms.<sup>31</sup>

Thus, one can expect that, in the presence of a crack of size  $c$  in the crystal, the dangerous stress normal to the plane of the crack is given by the relation

$$p_s = \alpha \sqrt{\frac{E\sigma}{c}}, \tag{1}$$

where  $\alpha$  is a certain dimensionless coefficient not much different from 1 in order of magnitude. (However, in going over from isotropic media, for which Eq. (1) is derived, to crystals with very pronounced cleavage, the values of  $\alpha$  are apparently appreciably less than unity).

Let us assume that under the action of a shearing stress  $\tau$  the crystal has undergone a shear in the slip plane by an amount  $\Delta$  which, however, did not spread over the whole cross section of the crystal, owing to the presence of some sufficiently strong obstacle  $O$  in the slip plane (Fig. 13). In this case the main region of localization of the shear turns out to be the interval  $MO = s$  along the slip plane (the value of  $s$  obviously depends on the initial shear  $\Delta$ ). The stress field around such a defect can be compared to the elastic field

of a cut of length  $s$  parallel to the applied shearing stress  $\tau$ . As is shown in the theory of elasticity (cf., for example, Neiber<sup>32</sup>) the maximum tensile stresses occur in this case along a line that makes an angle  $\Theta$  with the plane of the cut, where they attain a value  $p_{\max} \cong \sqrt{s/r}$  ( $r$  is the distance between the given point and the vertex of the cut).

We assume that a wedge-shaped crack NOR of magnitude  $NR \cong OR = c$  originates in the region of maximum stress concentration (the base of the wedge is approximately equal to the initial shear  $\Delta$ ). Then the high stress concentration will be relieved not only along the surface of the crack NOR itself, but also over a considerably larger area,  $\cong \Delta MOR$ .

In the absence of the crack the density of elastic energy in the region of the interval MO is  $w = p^2/2E \cong \tau^2 s^2/2Er = w(r)$ . The decrease in energy as the crack opens up (per unit length in the direction perpendicular to the plane of the diagram) is approximately given by

$$\iint_{\Delta MOR} w(r) dS \cong \int_{r_0}^c \frac{\tau^2 s^2}{2Er} \left(1 - \frac{r}{c}\right) dr$$

$$= \frac{\tau^2 s^2}{2E} \left( \ln \frac{c}{r_0} - \frac{c-r_0}{c} \right) \cong \frac{\tau^2 s^2}{2E} \ln \frac{c}{r_0}$$

where  $c \gg r$ . (The lower limit of integration  $r_0 \cong b$  is determined by the inapplicability of the equations of the theory of elasticity in the immediate neighborhood of the point O.)

At the same time the formation of the crack requires an expenditure of work  $\cong 2c\sigma$ . The total increase in energy is equal to  $\Delta W = 2c\sigma - (\tau^2 s^2/2E) \ln(c/r_0)$ . The function  $\Delta W(c)$  has a minimum at  $(\partial/\partial c) \Delta W(c) = 2\sigma - (\tau^2 s^2/2E)(1/c) = 0$ . Consequently, as incomplete shears are accumulated in the slip plane in the interval  $s = s(\Delta)$ , a wedge-shaped equilibrium crack of width  $c \cong \tau^2 s^2/4E\sigma$  may appear in the crystal.\*

From the point of view of an analysis of brittle fracture, we are interested in the limiting case of the largest possible  $c$ . We have such a case if in front of the "completely insurmountable" obstacle O the interval  $s$  of high concentration of incomplete shears reaches the same order of magnitude as the dimensions of the whole slip plane  $L$  (in the case of not very thick single crystals,  $\leq 1$  mm,  $L$  is approximately equal to the diameter; in the case of polycrystalline samples,  $L$  equals the grain size).

\*For such an equilibrium crack actually to appear a gain of energy is necessary:  $\Delta W < 0$  with  $c = \tau^2 s^2/4E\sigma$ , or  $\tau^2 s^2/4E\sigma > 2.7r_0$ , i.e., of the order of several  $b$ .

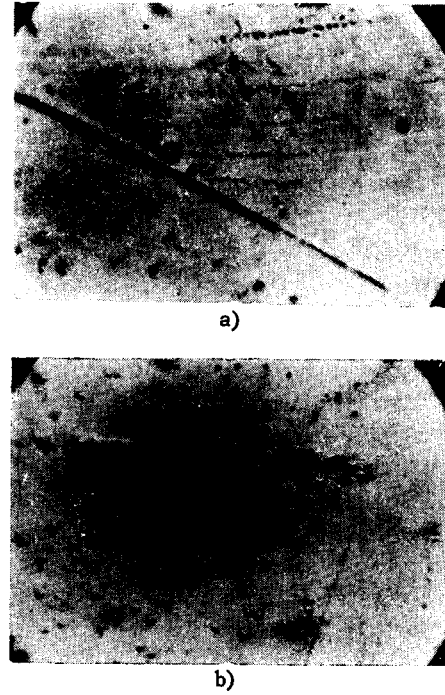


FIG. 14. Microphotographs of etch pit patterns on the surface of zinc crystals (a) and of cadmium single crystals (b); pile-up of dislocations in front of a grain boundary may be seen;<sup>6</sup> 800 $\times$ .

Thus it would appear that when a shearing stress  $\tau$  is applied in the slip plane, a crack can appear in the crystal of dimensions up to

$$c = \beta \frac{\tau^2 L^2}{E\sigma}, \quad (2)$$

where the dimensionless coefficient  $\beta$  does not differ appreciably from unity in order of magnitude.\* A similar relationship can be obtained in a more rigorous manner from the dislocation theory.

The process, discussed above, of the concentration of incomplete shears amounts, evidently, to none other than the formation of pile-up of dislocations stopped by an obstacle in the slip plane. According to Mott's theory such pile-ups act as the principal concentrators of the internal stresses that arise in the crystal in the course of plastic deformation.<sup>33-35</sup> Pile-ups of dislocations have been found experimentally, for example, in investigations of the etching of dislocations on the crystal surface (Fig. 14; cf. also Meleka<sup>36</sup>).

The problem of the location of  $n$  parallel edge

\*From this point of view the increased strength of single crystals as a result of alloying may be due to the decrease in the effective value of  $s$ , and correspondingly of the coefficient  $\beta$  in (2): alloyed single crystals deform in a more homogeneous manner, and under the same stresses the incomplete local shears turn out to be smaller than in pure single crystals.

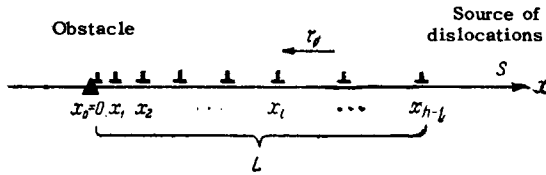


FIG. 15. Pile-up of dislocations in front of an obstacle in the slip plane.

dislocations within a pile-up has been solved for an isotropic medium by the methods of the theory of elasticity.<sup>37</sup> The solution is based on the well-known expression

$$F = b \cdot \tau \quad (3)$$

for the force acting in the slip plane per unit length of the dislocation line<sup>38</sup> ( $\tau$  is the shearing stress in the direction of the Burgers vector of the dislocation  $b$ ), and on the expression for the field of the elastic stresses of an edge dislocation

$$p_{rr} = p_{\theta\theta} = -\frac{Gb}{2\pi(1-\mu)} \cdot \frac{\sin \vartheta}{r}; \quad \tau_{r\theta} = \frac{Gb}{2\pi(1-\mu)} \cdot \frac{\cos \vartheta}{r} \quad (4)$$

(in cylindrical coordinates the angle  $\vartheta$  is measured from the slip plane;  $\mu$  is Poisson's ratio; the functional form of this dependence is well confirmed experimentally<sup>39,40</sup>). The general outline of the argument is approximately as follows.

It is assumed that each point of the glide plane OS (Fig. 15; O is the place at which the leading dislocation has stopped in front of the obstacle, and S is the source of these  $n$  dislocations) is subject to a tangential stress  $\tau(x)$  made up of an external stress in the given plane  $\tau_0$ , of the field of the leading dislocation (whose position  $x_0 = 0$  is fixed), and of the fields of the remaining dislocations (whose coordinates  $x_1$  to  $x_{n-1}$  are to be determined). In accordance with (3) and (4) this stress is equal to

$$\tau(x) = \tau_0 - \frac{Gb}{2\pi(1-\mu)} \cdot \frac{1}{x} - \sum_{i=1}^{n-1} \frac{Gb}{2\pi(1-\mu)} \cdot \frac{1}{x-x_i}$$

The conditions of equilibrium for the dislocations are given by the  $n-1$  equations

$$\tau(x_j) = 0; \quad j = 1, 2, \dots, n-1,$$

whose solution is reduced to the solution of the algebraic equation

$$\frac{d}{dz} \left[ e^z \frac{d^n}{dz^n} (e^{-z} z^n) \right] = 0,$$

where  $z = x \cdot 2\tau_0 \cdot 2\pi(1-\mu)/Gb$ , i.e., the desired coordinates of the dislocations are determined by the  $n-1$  roots of the first derivative of the  $n$ -th order Laguerre polynomial; for large  $n$  and small  $z$  the last equation can be reduced to the Bessel

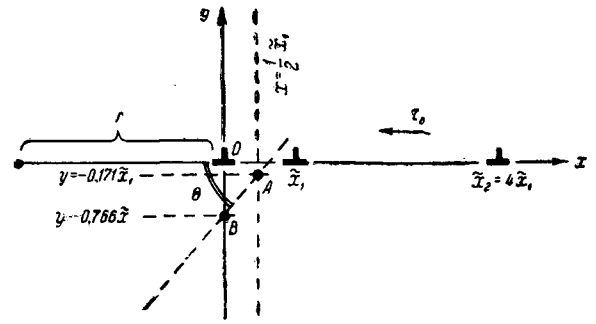


FIG. 16. Concentration of stresses in the neighborhood of the head of a pile-up of dislocations.

equation. The distance  $x_1$  between the two leading dislocations is

$$x_1 = \frac{(3.83)^2 \cdot Gb}{4n \cdot 2\tau_0 \cdot 2\pi(1-\mu)} = 0.42 \frac{Gb}{n\tau_0} \quad (5)$$

If the average values of  $i$  are greater than 1, but considerably less than  $n$ , the following approximation holds:

$$x_i \approx \frac{\pi Gb}{16n\tau_0(1-\mu)} i^2, \quad (6)$$

while the total distance occupied by the concentration of dislocations is given by

$$x_{n-1} = L \approx \frac{nGb}{\pi\tau_0(1-\mu)} \quad (7)$$

The approximate estimate (7) is valid only for large  $n$ ,  $\sim 10^3$ , but is too inaccurate for small  $n$ ,  $\leq 10$ .

A different way of treating the problem of a pile-up of dislocations has been indicated by Leibfried. The pile-up is approximated by a continuum of dislocations with a distributed of Burgers vector; this leads to a solution of integral equations.

A rigorous complete description of the elastic stress field of a pile-up of dislocations requires the summation of series with terms of type (4). Approximate results relating to several special cases were obtained by Koehler,<sup>38,41</sup> who approximated all the values of  $x_i$ , including  $x_1$ , by expression (6). The value of  $x_1$ , obtained from (6) and denoted in Fig. 16 by  $\tilde{x}_1$ , is equal to

$$\tilde{x}_1 = \frac{\pi Gb}{16n\tau_0(1-\mu)} \approx 0.28 \frac{Gb}{n\tau_0} = \frac{2}{3} x_1.$$

According to Koehler's calculations, the maximum tensile stress  $p_{xx}$  along the Oy axis occurs at point A when  $y = -0.766 \tilde{x}_1$  and is equal to  $\sim n\tau_0$ . Along the straight line  $x = \tilde{x}_1/2$  this stress reaches a maximum at point B when  $y = -0.171 \tilde{x}_1$  and has a value of  $\sim 7n\tau_0$ . The author emphasizes that the large stress concentrations obtained are very important in plastic and fatigue fracture of

materials. However, Koehler considers that his results are too high by approximately 50%, owing to the known inaccuracy of the approximation for  $x_1$ . We note that the angle  $\Theta$  between the direction of maximum  $p_{xx}$  and the negative Ox axis amounts to somewhat more than  $\pi/4$ .

It can be easily shown that similarly high concentrations in the neighborhood of a pile-up of dislocations are also attained by the shearing stresses, whose maximum values evidently lie along the extension of the Ox axis towards  $\theta = \pi$ . With the same simplifying assumption with respect to  $x_1$ , the tangential stress at a distance  $r$  in front of the head of the pile-up is

$$\tau(r) = \tau_0 + \frac{Gb}{2\pi(1-\mu)} \sum_{i=0}^{n-1} \frac{1}{r + i^2 \tilde{x}_1}.$$

When  $r \ll \tilde{x}_1$  the sum of all the terms of the series, with the exception of  $i = 0$ , is given by

$$\sum_{i=1}^{n-1} \frac{1}{r + i^2 \tilde{x}_1} \approx \frac{1}{\tilde{x}_1} \sum_{i=1}^{n-1} \frac{1}{i^2} < \frac{1}{\tilde{x}_1} \cdot \frac{\pi^2}{6} \ll \frac{1}{r},$$

i.e., in the immediate vicinity of the head of the pile-up the field coincides with the field of the leading dislocation. When  $r \gg L$ ,

$$\sum_{i=0}^{n-1} \frac{1}{r + i^2 \tilde{x}_1} \approx \int_0^n \frac{d\xi}{r + \tilde{x}_1 \xi^2} = \frac{1}{\sqrt{r \tilde{x}_1}} \tan^{-1} \sqrt{\frac{n^2 \tilde{x}_1}{r}} \approx \frac{n}{r},$$

since  $n^2 \tilde{x}_1 = (\pi^2/16)L < L \ll r$ . This means that at very large distances the field of the pile-up is similar to the field of a single "large" dislocation whose Burgers vector is equal to  $nb$ .

The high stress concentration is particularly significant in the intermediate region  $\tilde{x}_1 \ll r \ll L$ . In virtue of the left hand side of this inequality, the summation can, as before, be replaced by an integration, while in virtue of the right hand side we have

$$\tan^{-1} \sqrt{\frac{n^2 \tilde{x}_1}{r}} \cong \frac{\pi}{2}, \quad \text{and} \quad \tau(r) = \tau_0 + \frac{Gb}{2\pi(1-\mu)} \cdot \frac{1}{\sqrt{r \tilde{x}_1}} \cdot \frac{\pi}{2}.$$

By substituting into this the value of  $\tilde{x}_1$  from (8), and by utilizing (7), we obtain

$$\tau(r) = \tau_0 \left\{ 1 + \sqrt{\frac{L}{r}} \right\} \quad \text{for} \quad \tilde{x}_1 \ll r \ll L,$$

or, approximately,

$$\tau(r) \cong \tau_0 \sqrt{\frac{L}{r}}. \quad (9)$$

An approximate solution for all the components of the stress field of the pile-up in the region  $x_1 \ll r \ll L$ , which is of greatest interest, has been given by Stroh.<sup>42</sup> The distance between the two leading dislocations obtained by him and given by

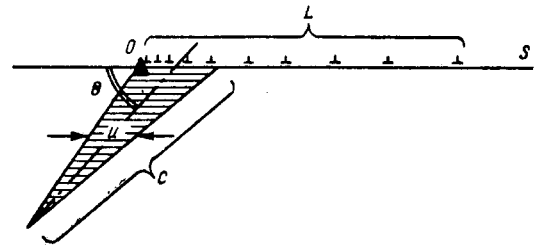


FIG. 17. Appearance of a micro-crack in the neighborhood of the head of a pile-up of dislocations.

$$\frac{Gb}{n\pi\tau_0(1-\mu)} \approx 0.46 \frac{Gb}{n\tau_0}$$

differs only little from the value of  $x_1$  obtained from (5), while the length of the pile-up coincides exactly with the value of  $L$  from (7). For the stress components Stroh obtains

$$\left. \begin{aligned} \frac{1}{2}(p_{xx} + p_{yy}) &= \tau_0 \sqrt{\frac{L}{r}} \cdot 2 \sin \frac{\vartheta}{2}, \\ \frac{1}{2}(p_{xx} - p_{yy}) &= \tau_0 \sqrt{\frac{L}{r}} \cdot \left( 2 \sin \frac{\vartheta}{2} + \sin \vartheta \cos \frac{3}{2} \vartheta \right), \\ \tau_{xy} &= -\tau_0 \sqrt{\frac{L}{r}} \cdot \frac{1}{2} \left( 2 \cos \frac{\vartheta}{2} - \sin \vartheta \sin \frac{3}{2} \vartheta \right). \end{aligned} \right\} \quad (10)$$

The last of these formulas agrees, when  $\vartheta = \pi$ , with the approximate estimate of the largest of the shearing stresses (9). The maximum normal stresses occur, according to (10), along the straight line  $\Theta \cong 70^\circ$  and have the value

$$p_{\max} = \frac{2}{\sqrt{3}} \tau_0 \sqrt{\frac{L}{r}}. \quad (11)$$

Mott has advanced the hypothesis that the high stress concentration near the head of a pile-up of dislocations may give rise to the appearance and development of cracks.<sup>33,43\*</sup> This idea has been developed in a number of papers by Stroh.<sup>44-46</sup>

By assuming that the crack is formed by the merging of all  $n$  dislocations, i.e., that it contains a dislocation with a Burgers vector  $nb$ , Stroh finds all the components of the stress field of a crack making an arbitrary angle  $\Theta$  with the vector  $nb$ , and also the outline of the crack for the case  $\Theta = \pi/2$ : its "thickness" is given by

$$u = \frac{1}{2} nb \left\{ 1 + \frac{2}{\pi} \arcsin \frac{c-2r}{c} \right\},$$

i.e., the crack has the form of a "wedge" with a base  $nb$ , which lies in the glide plane, a result

\*Other dislocation models have also been proposed for the origin of cracks. Thus, Fujita<sup>47</sup> bases his discussion on the consideration of two opposing accumulations of dislocations of opposite signs in neighboring slip planes, while Fisher<sup>48,49</sup> bases his discussion on an analysis of the pile-up of vacancies arising as a result of intersection of dislocations containing screw components.<sup>50</sup>

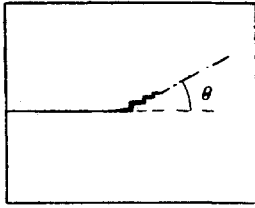


FIG. 18. A schematic representation of the alternation of cleavages along different planes.

which is in excellent agreement with the concept of an edge dislocation interpreted as an extra half-plane inserted at right angles to the glide plane.

By utilizing the method of making an imaginary cut in the solid and pushing apart the edges of the cut, and by utilizing the found components of the field of the crack, Stroh determines its energy (per unit length at right angles to the plane  $xOy$ ):

$$W = \frac{n^2 G b^2}{4\pi(1-\mu)} \ln \frac{4R}{c} + 2c\sigma,$$

where  $R$  is the distance from the crack to the surface of the solid. The author emphasizes that  $W$  does not depend on  $\Theta$ . This expression has a minimum given by

$$W_{cr} = \frac{n^2 G b^2}{4\pi(1-\mu)} \ln \frac{32\pi e(1-\mu) R \sigma}{n^2 G b^2},$$

which corresponds to an equilibrium width of the crack

$$c = \frac{n^2 G b^2}{8\pi(1-\mu)\sigma}. \quad (12)$$

Stroh<sup>46</sup> makes use of this result for a quantitative explanation of the experimental data<sup>51</sup> on the increase in the electrical resistance and on the decrease in the density of nickel after extensive cold working.

Utilizing (7) to estimate the maximum number of dislocations in front of the obstacle we obtain

$$c \approx \frac{\pi(1-\mu)}{8} \cdot \frac{L^2 \tau_0^2}{G\sigma},$$

which completely agrees with expression (2).

Now on substituting expression (2) obtained for the maximum possible size of the crack into Griffith's relation (1) we obtain in place of Zonke's law  $p_s = \text{const}$  the new relation

$$p_s \tau_s = \text{const} = K^2, \quad (14)$$

where

$$K = \gamma' \sqrt{\frac{E\sigma}{L}} = \gamma \sqrt{\frac{G\sigma}{L}}; \quad (15)$$

here  $G$  is the shear modulus, while the dimensionless coefficients  $\gamma'$  and  $\gamma$  are close to unity in order of magnitude. Relation (14) may be characterized as "the condition for the constancy of the product of normal and shearing stresses" in the



a)



b)

FIG. 19. (a) Microphotograph of wavy cracks in a zinc crystal; 200  $\times$ . (b) Microphotograph of steps<sup>6</sup> arising on the surface of a zinc single crystal undergoing brittle fracture; 50  $\times$ .

case of brittle fracture.<sup>24</sup>

It should be emphasized immediately that the stresses  $p_s$  and  $\tau_s$  in relation (14) are applied, generally speaking, to different planes (cf. Fig. 13b). However, in the case of zinc single crystals conditions are considerably simplified, since the only slip plane and the only pronounced cleavage plane (under given conditions) both coincide with the same basal plane.

It is advantageous for the crack to develop in that direction  $\Theta$  where the local concentration of tensile stresses is the highest (according to Stroh<sup>42</sup>  $\Theta \cong 70^\circ$  in a one-dimensional isotropic medium). Since in a hexagonal zinc crystal there is no cleavage plane in the appropriate direction, the initial micro-crack must be like a staircase in shape: cleavages along the basal plane alternate most probably with cleavages along a prismatic plane (Fig. 18). (Such staircase cracks can be seen, for example, in Fig. 19a; Fig. 19b may serve as an example of repeatedly observed<sup>6</sup> small steps on the mirror-like surface of a brittle shear.) But it is much easier for a cleavage to occur along a basal plane rather than along a prismatic plane, and from this point of view it is more advantageous for the "basal" steps to be appreciably longer than the "prismatic" steps. Thus, one can expect that in the case of zinc the angle  $\Theta$  will not be large even during the initial stage of development of the crack, while  $\Theta$  becomes equal to zero after Griffith's criterion (1) has been attained. Consequently, in the analysis of data on brittle fracture of zinc single crystals along the basal plane the stress  $p_s$

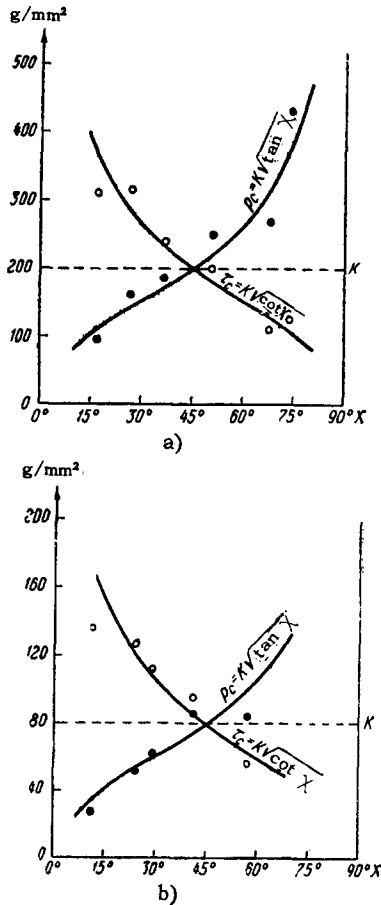


FIG. 20. Normal ( $p_s$ ) and shearing ( $\tau_s$ ) stresses accompanying brittle fracture of zinc single crystals: (a) non-amalgamated single crystals at  $-196^\circ\text{C}$ ; (b) amalgamated single crystals at room temperature. The curves have been constructed on the basis of theory.

under the condition (14) should be referred to the same plane as  $\tau_s$ .

If fracture occurs at an angle  $\chi$  between the slip plane and the direction of tension then  $\tau_s = P_s \sin \chi \cos \chi$  and  $p_s = P_s \sin^2 \chi$ , where  $P_s$  is the true tensile stress at the instant of fracture. Consequently, for purely geometrical reasons, we have

$$\frac{p_s}{\tau_s} = \tan \chi. \quad (16)$$

On solving (16) simultaneously with (14) we obtain

$$\left. \begin{aligned} p_s &= K \sqrt{\tan \chi}, \\ \tau_s &= K \sqrt{\cot \chi}. \end{aligned} \right\} \quad (17)$$

Figure 20a shows that the experimental values of  $p_s(\chi)$  and  $\tau_s(\chi)$  in the case of brittle fracture of zinc single crystals along the basal plane at the temperature of liquid nitrogen agree well with curves corresponding to equations (17), with  $K = 200 \text{ g/mm}^2$ . On assuming for zinc samples  $G = 3 \times 10^{11} \text{ dynes/cm}^2$ ,  $\sigma = 10^3 \text{ ergs/cm}^2$ , and the diameter  $L = 0.1 \text{ cm}$ , we obtain  $\gamma = K/\sqrt{G\sigma/L} = 0.37$ .

Figure 20b presents analogous data for brittle fracture of amalgamated zinc single crystals at room temperature. The experimental points, as before, agree within experimental error with the curves (17), but the constant  $K$  turns out to be approximately  $80 \text{ g/mm}^2$ , which apparently can be associated only with a sharp decrease in the surface free energy of zinc in the presence of mercury. This relative change in  $\sigma$  amounts to  $(K_{\text{Zn}}/K_{\text{Zn-Hg}})^2 \cong 6$  fold (more accurately, somewhat less, if we take into account the dependence of the modulus  $G$  on the temperature), i.e., in the presence of mercury the surface tension in the incipient micro-cracks amounts to approximately  $150$  to  $200 \text{ ergs/cm}^2$ .

A convincing experimental confirmation of the linear dependence of the brittle-fracture stress on  $\sqrt{\sigma}$  is given by experiments<sup>52</sup> on the study of the hydrogen brittleness of steel.

Orowan<sup>53</sup> ascribes the decrease in the strength of glass with increasing time of application of the load to a reduction in the surface tension due to the adsorption of gases from the atmosphere. Indirect experimental data enable us to assume that in this case also the strength is reduced in proportion to the square root of  $\sigma$ .<sup>54</sup>

Condition (14) can be written in the following way:  $p_s \tau_s = P_s^2 \sin^3 \chi \cos \chi = K_2$ , where  $P_s$  is the tensile stress at fracture. At  $\chi_{\text{opt}} = 60^\circ$   $P_s$  has a minimum,  $P_{C \text{ min}} = 1.76 K$ . It is natural to suppose that in the case of brittle fracture of a polycrystalline sample the first dangerous crack occurs in the grain for which  $\chi$  is closest to  $\chi_{\text{opt}}$ ; the condition for brittle fracture of a polycrystalline sample is then

$$P_s = 1.76 K = \gamma_p \sqrt{\frac{G\sigma}{L}}, \quad (18)$$

where the dimensionless coefficient  $\gamma_p$  does not differ appreciably from unity in order of magnitude; here  $L$  should be interpreted as the grain size. One should expect  $\gamma_p$  to be larger than the corresponding factor  $\gamma$  in the case of a single crystal, not only because of the "geometrical" factor 1.76, but also as a result of the influence of the neighboring grains (a polycrystalline sample with grain  $L$  is, generally speaking, stronger than a single crystal of diameter  $L$ ). Stroh<sup>45</sup> and Petch<sup>54</sup> arrive at a similar dependence of  $P_s$  on  $L$  from the point of view of dislocation theory.

Petch<sup>54</sup> starts from the following simple considerations. The number of dislocations in the pile-up  $n \sim$  (is proportional to)  $L\tau_0$  [cf. (7)]; the maximum tensile stress in the region of the vertex of the pile-up<sup>38</sup> is  $p_{\text{max}} \sim n\tau_0 \sim L\tau_0^2$  or, more accu-

rately,  $\sim L(\tau_0 - \tau_i)^2$ , where  $\tau_i$  denotes the internal opposing field that prevents the motion of dislocations ("friction" due to the interaction between dislocations and point structural defects). Fracture occurs when  $p_{\max}$  reaches the "theoretical" value  $p_{\text{theor}}$ . From this we obtain  $p_{\text{theor}} \sim L(\tau_s - \tau_i)^2 \sim L(P_s - P_i)^2$ , i.e.,  $P_s = P_i + \text{const}/\sqrt{L}$ . Experiment shows<sup>54</sup> that in the case of zinc the term  $P_i$  is very small, and  $P_s \cong \text{const}/\sqrt{L}$ .

Stroh<sup>45</sup> compares the results obtained by him for the minimum energy of the field of the crack,  $W_{\text{cr}} = \frac{n^2 G b^2}{4\pi(1-\mu)} \ln \frac{32\pi e(1-\mu)R\sigma}{n^2 G b^2}$ , and for the pile-up of dislocations prior to the formation of the crack

$$W_{\text{gr. d.}} = \frac{n^2 G b^2}{4\pi(1-\mu)} \ln \frac{4\pi \sqrt{e}(1-\mu) \tau_0 R}{n G b}$$

The crack originates when  $\Delta W = W_{\text{cr}} - W_{\text{gr. d.}} < 0$ , i.e., when

$$n\tau_0 b \geq 8\sqrt{e}\sigma. \quad (19)$$

Using (7) to eliminate  $n$  and setting  $\tau_s \sim P_s$ , we obtain  $P = \text{const}/\sqrt{L}$ , where  $\text{const} \cong 10^8$  dynes/cm<sup>3/2</sup>.

Experimental data<sup>45</sup> confirm the characteristic dependence  $P_s \sim 1/\sqrt{L}$ , with the constant having a value  $2.3 \times 10^8$  dynes/cm<sup>3/2</sup> in the case of iron and  $1.0 \times 10^8$  dynes/cm<sup>3/2</sup> in the case of zinc. The latter means that  $\gamma_p \approx 6$  in expression (18).

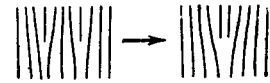
Stroh's criterion (19), which determines for a given  $\tau_0$  the magnitude of the "dangerous" pile-up of dislocations  $n$ , is of particular interest. In connection with this it is necessary to point out certain contradictions in Stroh's scheme. His criterion has been obtained essentially as the condition under which it becomes advantageous for all  $n$  dislocations to merge and to form an equilibrium crack of dimensions  $c \cong n^2 b$ . The calculations are awkward and cannot be regarded as rigorously founded, while the scheme itself excludes consideration of a gradual development of the crack and requires sudden formation of cracks of appreciable size  $c$ . In spite of the fact that condition (19) was obtained for an equilibrium crack, Stroh uses it as the condition for fracture; in doing this he pays attention only to the shearing stress and does not take into account the normal component of the applied stress, i.e., the orientation  $\chi$ . However, comparison with experiment<sup>45</sup> shows that condition (19) holds for polycrystalline samples (when the dependence on  $\chi$  disappears), and, moreover, it is specifically the condition that the crack should no longer be an equilibrium one.

Such a conclusion is reached also in the scheme proposed by us: by eliminating  $L$  from equation (17) with the aid of (7) and by denoting the "dangerous" value of  $n$  by  $N$  we obtain

$$N\tau_s b = k\sigma \cot\chi, \quad (20)$$

where the dimensionless coefficient  $k$  is close to unity in order of magnitude. Now the above criterion already has a definite significance as a condition for the fracture of the crystal, i.e., of the attainment of Griffith's criterion by a crack which was previously an equilibrium crack. At the same time, since we have considered the roles played by the shearing and by the normal stresses separately, we have introduced into equation (19) a dependence on the orientation of the single crystal.

The earlier stages of development of a micro-crack can be represented in the following manner.<sup>6</sup> Already at small shearing stresses  $\lesssim 10^7$  dynes/cm<sup>2</sup> the pile-ups of dislocations in different slip planes of the single crystal (in front of sufficiently strong obstacles) may attain values of  $n \sim 10^2$  to  $10^3$ . On making use of relations (3) to (5) and (8), the distance between the leading dislocations is found to be reduced to a few multiples of  $b$ , becoming smaller than the width of the dislocation,<sup>55</sup> while the forces of repulsion between them exceed the so-called "theoretical" value of shearing stress  $\cong G/2\pi$  to  $G/30$ .<sup>56,61</sup> This means that the linear theory no longer holds in the immediate vicinity of the head of the pile-up. It turns out to be advantageous for the frontal dislocations to merge and to form a hollow dislocation nucleus in accordance with the scheme:



The potential barrier to be overcome is particularly small because the initial hollow nucleus does not yet have a developed surface, i.e.,  $\sigma$  is still very small. As  $\tau_0$  increases, an increasingly large number of dislocations  $n$  may accumulate in front of the obstacle, and an increasingly larger fraction  $n_s$  may enter the developing hollow nucleus. As the nucleus attains a size  $\cong 5b$  to  $10b$ , a crack begins to develop gradually sideways from the nucleus at some average angle  $\Theta$  to the slip plane. The scheme that has led us to relation (2) now becomes valid. Even at low stresses, hollow dislocation nuclei and incipient micro-cracks are capable of producing rapid irregular diffusion — a two dimensional migration of the active adsorbable substance into the crystal; indeed, a single crystal of zinc exhibits great brittleness and weakness im-

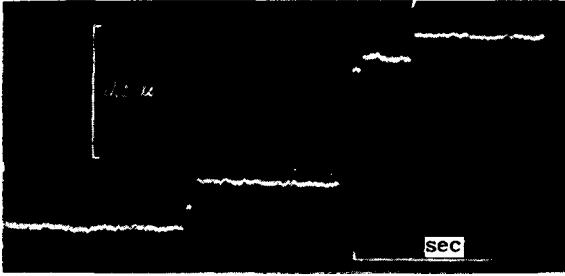


FIG. 21. Oscillogram of staircase deformation of a cadmium single crystal.<sup>6</sup>

mediately after being coated with a mercury film.

Investigations of elementary discontinuous deformations of different metallic single crystals elongated under a constant load near the plastic flow limit<sup>6,57,58</sup> confirm the existence of small equilibrium cracks, which are far from the "dangerous" size, in plastic single crystals undergoing deformation. To carry out these experiments special apparatus was constructed<sup>59,6</sup> to record simultaneously small deformation discontinuities (with an accuracy down to 50 or 100 A) and the accompanying increments in electrical resistance of the samples (with an accuracy down to several thousandths of a microhm); the moving parts of the apparatus have a very low inertia. The main results of such experiments<sup>6,57,58</sup> can be summarized in the following way:

1. The maximum value of an elementary deformation discontinuity, i.e., one which is localized in one slip zone, is 700 to 1000 A in the case of single crystals of zinc, cadmium, and tin 0.5 to 1.0 mm in diameter and for average values of the angle  $\chi$  (we call such steps "single" steps). By regarding such a step as an avalanche release of pile-up of dislocations we find that the maximum number of dislocations in the pile-up amounts under the given conditions to  $n \cong 10^3$ . This agrees completely with the results of the study of slip lines<sup>60</sup> and enables us to obtain a more precise value for the numerical coefficient in (7).

2. The increment in the electrical resistance due to a single deformation step is smaller than the value expected geometrically by approximately  $10^{-8}$  ohm (i.e., by 25%). This decrease can be caused only with the healing of the micro-crack which gradually develops ahead of the pile-up of dislocations as the pile-up increases (the accumulation of an incomplete local shear), and which disappears together with the additional resistance contributed by it when the avalanche reaches the surface.<sup>6</sup> The quoted value of  $10^{-8}$  ohm then corresponds to a crack measuring several microns.<sup>46</sup> An analysis of relation (12) shows that the crack must have contained under these conditions  $n_S \sim$

100 to 200 dislocations; the remaining (greater) part of the pile-up represents a "tail" which did not merge.

3. Since the resistance introduced by the crack  $\sim c^2 \sim n_S^4$ ,<sup>9</sup> while  $n_S$  is determined in turn by the total number  $n$  of dislocations in the pile-up it is natural to expect the difference between the actual and the geometrically-expected increment of resistance to diminish rapidly with increasing avalanche. Indeed, in the case of elementary steps smaller than a unit step, experiment gives good support to this hypothesis.<sup>6,58</sup>

4. With very rare exceptions, oscillograms show no stepwise resistance increments not accompanied by deformation steps or considerably greater (apart from experimental error) than the values predicted geometrically. Consequently, apparently no micro-cracks of appreciable size developed suddenly in these experiments.<sup>6</sup>

5. The fraction of staircase deformation increases sharply when impurities are present in the crystal, sometimes reaching 100% (Fig. 21); consequently the presence of foreign atoms (point defects) in the crystal lattice appreciably aids the formation of dislocation avalanches.

If we now substitute into (20) the experimentally obtained values  $n \sim 10^3$  and  $\tau \sim 2 \times 10^7$  dynes/cm<sup>2</sup> (for average orientations  $\chi \sim 45^\circ$ ), we obtain for zinc  $k \cong 0.6$  if  $\sigma \sim 10^3$  erg/cm<sup>2</sup> and  $b \sim 3 \times 10^{-8}$  cm.

If a pile-up of incomplete shears  $\Delta = nb$  occurs in a plane oriented at an angle  $\chi$  with respect to the applied tensile stress, the single crystal undergoes brittle fracture when  $n$  reaches, at a given  $\tau_0$  (or  $P$ ), the "dangerous" value

$$N = \frac{k\sigma}{b\tau_0} \cot \chi = \frac{k\sigma}{bP} \frac{1}{\sin^2 \chi}; \quad k_{2n} \sim 1. \quad (21)$$

However, whether under given conditions the crystal will in fact be brittle or plastic will depend upon the values that can be attained by the incomplete local shears, i.e., upon the actual maximum number  $n$  of dislocations in the pile-up.

One can expect that, for small shear stresses (up to the plastic flow limit),  $n$  will be determined essentially by the "effective" size of the slip plane  $L$ , in accordance with relation (7):

$$n^{(1)} \cong \kappa \frac{L\tau_0}{Gb}; \quad (22)$$

since experiment gives  $n \sim 10^3$  for  $L \sim 0.1$  cm and  $\tau_0 \sim 100$  to 200 g/mm<sup>2</sup>, the dimensionless factor  $\kappa$  turns out to be somewhat larger than given by (7).

For large shear stresses the size of the pile-ups is determined, apparently, by the nature of the



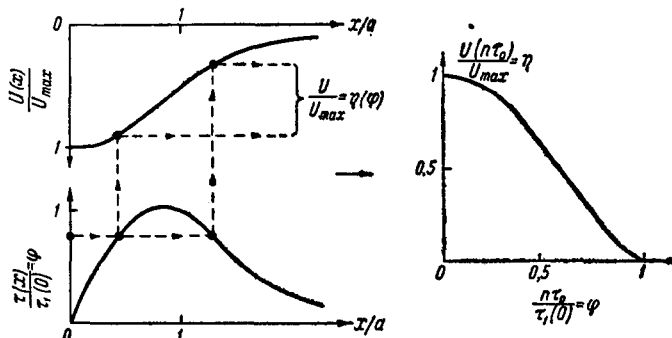


FIG. 22. Method of computing the function  $\eta(\varphi)$  from the known function  $U(x)$ .

obstacles encountered by the dislocations in the slip plane, specifically by the distribution of obstacles and the ease with which they can be overcome. In single crystals of pure metals the resistance to shear is determined in particular by the interaction of parallel dislocations lying in neighboring slip planes, by stationary dislocations, by the interaction of intersecting dislocations, and by the appearance of jogs when they cross, jogs which may give rise during subsequent motion to the appearance of chains of vacancies or of interstitials, etc. In polycrystalline samples the decisive role is played by the grain boundaries. In alloys the dislocations must overcome in the course of their motion inclusions of foreign atoms with some degree of dispersion; an obstacle to motion is also provided by adsorption on the dislocations of solute atoms ("Cottrell atmosphere").<sup>61-63</sup> Of particular interest to us is the interaction of dislocations with the free surface of the crystal.

The first very rough approximation<sup>64</sup> consists of an investigation of obstacles of only one type, those which are most significant under given conditions and which are characterized by a potential barrier  $U(x)$ . The height of the barrier  $U_{max}$  (erg/atom) determines the activation energy for overcoming the obstacle at  $\tau_0 = 0$ , while the quantity  $|\text{grad } U(x)|_{max}/b^2 = \tau_1(0)$  is the local shearing stress required for breakthrough in the absence of thermal activation, i.e., at  $T = 0^\circ\text{K}$ .<sup>61,65</sup> If the pile-up contains  $n$  dislocations, the force per unit length of the leading dislocation is  $nb\tau_0$ ,<sup>38</sup> in this case the activation energy is  $U(n\tau_0) = U_{max} \cdot \eta(\varphi)$ , where  $\varphi = n\tau_0/\tau_1(0)$ ; the function  $\eta(\varphi)$  is determined by the shape of the barrier  $U(x)$  (Fig. 22). (The parameter  $a$  in Fig. 22 characterizes the extension of the obstacle in the direction of motion of the dislocation and is close in order of magnitude to atomic distances). Assume that  $v$  dislocations arrive at the obstacle each second. Then the rate of their pile-up  $\dot{n} = v - \nu\lambda \exp[-U(n\tau_0)/kT]$ , where  $\nu$  is the fre-

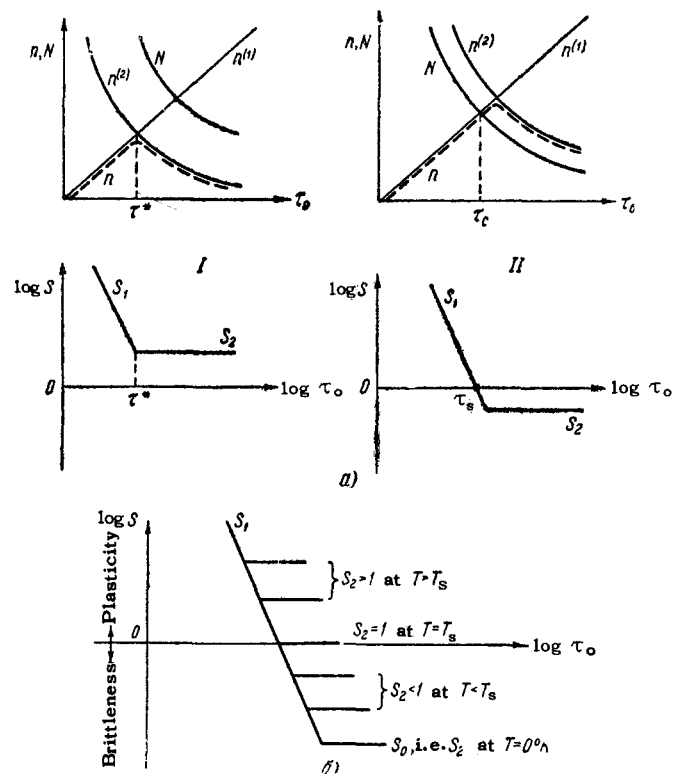


FIG. 23. (a) Dependence of the maximum number  $n$  of dislocations in a pile-up, of the "dangerous" number of dislocations  $N$ , and of the branches of the deformability criterion  $S_1$  and  $S_2$  on the applied shearing stress  $\tau_0$ : I)  $n^{(2)} < N$  and  $S_2 > 1$ ; the crystal is plastic,  $\tau^*$  should be interpreted as the plastic flow limit; II)  $n^{(2)} > N$  and  $S_2 < 1$ ; the crystal is brittle,  $\tau_s$  is the fracture strength. (b) Temperature dependence of the branch  $S_2$  of the deformability criterion.

quency of lattice oscillations and  $\lambda$  is the number of points at which a breakthrough is possible (it is assumed that to release the dislocations it is sufficient to have a breakthrough at one spot<sup>45</sup>). Dynamic equilibrium corresponds to  $\dot{n} = 0$ ; consequently, for fairly large values of  $\tau_0$ , when the obstacles become surmountable, the maximum number of dislocations in a pile-up is determined by the relation  $n^{(2)} = \tau_1/\tau_0$ , where the local stress is  $\tau_1 = \tau_1(0)\varphi(\eta)$  and  $\eta = kT \ln(\nu\lambda/v)/U_{max}$ .

The parameter  $v$  introduced by us is directly related to the rate of shear  $\dot{\epsilon}$  and to the micro-inhomogeneity of the deformation (localization of shears along the slip lines), including the average thickness of slip bands  $h$ . The shear  $\dot{\epsilon}$  referred to  $h$  cm and measured in units of  $b$ , i.e., the quantity  $v_0 \sim \dot{\epsilon}h/b$  gives approximately the average number of dislocations crossing the crystal per second, within the limits of one slip line. The decisive role is played, however, not by this average value but by its maximum value  $v = v_0u$  where the deformation micro-inhomogeneity factor  $u$  has the meaning of the ratio of the total number of

slip lines to the minimum number of active lines. If we note that for average orientations of the crystal  $\chi$  the rate of shear  $\dot{\alpha}$  is close in order of magnitude to the rate of elongation  $\dot{\epsilon}$ , we obtain for the parameter  $v$  the following approximate estimate:

$$v \sim \frac{\dot{\epsilon} h u}{b}. \quad (23)$$

When  $\dot{\epsilon} \sim 10\% \text{ min}^{-1}$  and the deformation has the greatest possible homogeneity on the micro-scale, i.e., when  $h \sim 10^{-4} \text{ cm}$  and  $u = 1$ , the rate of local slipping amounts to  $v_0 \leq 10$  translational units per second. The second extreme value of  $v$  occurs when  $h u \sim 1 \text{ cm}$  and (within the limits of macroscopically smooth flow at a constant rate,  $\sim 10\% \text{ min}^{-1}$ ) attains a value  $v_{\text{max}} \sim 10^5 \text{ sec}^{-1}$ ; also of the same order of magnitude is the rate of slipping for the elementary deformation jumps<sup>6,57</sup> which we have observed and which produce a shear of  $500b$  to  $1000b$  within a time of the order of several milliseconds, at small average rates of elongation  $\dot{\epsilon} \sim 0.01 - 1.0\% \text{ min}^{-1}$ .

For the true maximum value of the number of dislocations in a pile-up it is evidently possible to take  $n = \min \{n^{(1)}, n^{(2)}\}$ . The condition  $n < N$  corresponds to dislocations overcoming the barrier and to plastic flow; for  $n > N$  a nonequilibrium crack is developed, meaning that brittle fracture occurs. Therefore the value  $S = N/n$  has the meaning of a criterion for the deformability of a crystal.<sup>64</sup> By making use of the values of  $N$ ,  $n^{(1)}$ , and  $n^{(2)}$  found above we can write the criterion  $S$  in the following form:

$$S \begin{cases} S_1 = A \frac{\sigma G}{L} \frac{1}{\tau_0^*} \cot \chi & \text{for } \tau_0 < \tau^*, \\ S_2 = B \frac{\sigma}{b \tau_1} \cot \chi & \text{for } \tau_0 > \tau^*, \end{cases} \quad \tau^* = C \sqrt{\frac{G b \tau_1}{L}}, \quad (24)$$

$$\tau_1 = \tau_1(0) \varphi(\eta) = \tau_1(0) \varphi\left(\frac{kT}{U_{\text{max}}} \ln \frac{\nu \lambda b}{\dot{\epsilon} h u}\right), \quad (25)$$

where  $A = k/\kappa$ ,  $B = k$ , and  $C = 1/\sqrt{\kappa}$  are dimensionless coefficients close to unity in order of magnitude; for a qualitative discussion they can be omitted.<sup>64</sup>

If  $S_2 < 1$ , brittle fracture occurs at  $S_1 = 1$ , i.e., at a stress  $\tau_S = \sqrt{A} (\sigma G/L) \cot \chi$ , which rigorously corresponds to Eq. (17); we note that  $k/\kappa^2 = \gamma^2$ . If  $S_2 > 1$ , then  $\tau^*$  has the meaning of the plastic flow limit. The characteristic dependence of the plastic flow limit on the grain size  $L$  (in the case of polycrystalline samples) has been well substantiated by experiment.<sup>45</sup>

According to (24) and (25) the critical tempera-

ture  $T_C$  of the transition from brittleness to plasticity is equal to<sup>6,64</sup>

$$T_S = \frac{U_{\text{max}} \eta(S_0)}{k \ln \frac{\nu \lambda b}{\dot{\epsilon} h u}}, \text{ where } S_0 = \frac{\sigma}{b \tau_1(0)}. \quad (26)$$

In accordance with the definition of  $v$ , the "probability" of one leading dislocation becoming free during the time  $1/v$ , i.e., during the time between the arrivals of successive dislocations from the source, is given for  $\tau_0 = \tau_S$  by

$$M = \frac{\nu \lambda}{v} e^{-\frac{U_{\text{max}} \eta(S_0)}{kT}} = e^{-\frac{U_{\text{max}} \eta(S_0)}{k} \left(\frac{1}{T} - \frac{1}{T_C}\right)}. \quad (27)$$

At  $T = T_S$  this quantity is equal to 1, for  $T < T_S$  it rapidly tends to 0, while for  $T > T_S$  it increases sharply. The quantity  $M$  can be called the "measure of plasticity" of the solid. However, for comparison with experiment it is more convenient to redefine this quantity in such a way that it gives a value of unity for  $T \rightarrow \infty$ ; this result will be obtained if we regard the function

$$W = 1 - e^{-M}. \quad (28)$$

as the "probability of plastic flow."

A completely analogous expression can be obtained, according to Stroh,<sup>45</sup> in the following manner. Let  $\Lambda$  be the length of a fixed segment of a dislocation line. Then, assuming that this segment is held fixed by a condensed atmosphere of interstitial atoms,<sup>65</sup> we obtain for the possible number of points at which a breakthrough may occur  $\lambda = \Lambda/b$ . Further, let  $U$  be the activation energy of the process at a stress  $\tau_0$ . Then the probability of a breakthrough of a dislocation past the obstacle during a time  $dt$  is equal to  $w = \nu \lambda e^{-U/kT} dt$ .

If  $p$  is the probability that the breakthrough has not yet occurred at the time  $t$ , the probability of its occurring during the time interval from  $t$  to  $t + dt$  is equal to the product  $pw$  of the probabilities. According to the definition of  $p$ , it gives the decrement in  $p$  during the given time interval:  $p \nu \lambda e^{-U/kT} dt = -dp$ . Integration of this equation yields

$$p = \exp \left\{ - \int_{-\infty}^t \nu \lambda e^{-U/kT} dt \right\}.$$

By assuming that  $U$  is approximately independent of  $t$  and on taking for our range of integration a certain value  $t_1$  (Stroh<sup>45</sup> interprets it as the "time required for a crack to occur,"  $\sim 10^{-6} \text{ sec}$ ), we have for the probability of plastic flow:  $W = 1 - p = 1 - e^{-\nu \lambda t_1 e^{-U/kT}}$ , which coincides with (28) for  $t_1 = 1/v$ .

In accordance with (28), the quantity  $W$  varies from 0.1 to 0.9 within the limits of the following

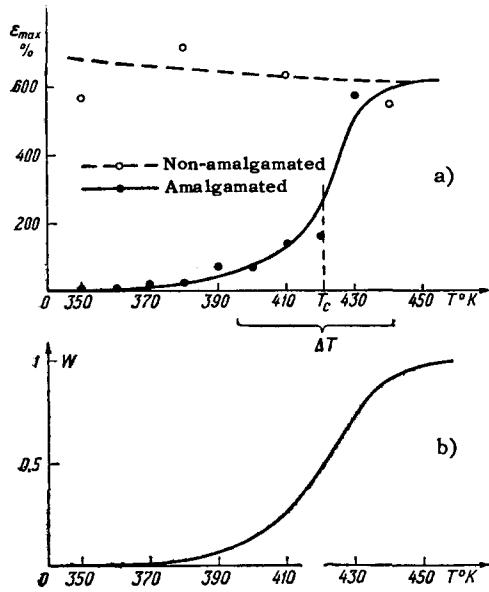


FIG. 24. (a) Dependence of the limiting deformation preceding fracture  $\epsilon_{max}$  on the temperature for pure and amalgamated zinc single crystals at  $\dot{\epsilon} \cong 15\% \text{ min}^{-1}$  and  $\chi \cong 45^\circ$ . (b) Theoretically calculated temperature dependence of the "probability of plastic flow"  $W$  for amalgamated single crystals.<sup>6,21</sup>

temperature interval situated in the neighborhood of  $T_S$

$$\Delta T \approx 3.3 \frac{kT_S^2}{U_{max} \eta(S_0)} \quad (29)$$

In our case of brittle fracture of amalgamated single crystals of zinc (Fig. 24),  $T_S \cong 420^\circ\text{K}$ , while the transition interval  $\Delta T$  amount to 40 – 50°; correspondingly  $U_{max} \eta(S_0) = 1.1 \pm 0.1 \text{ ev}$ . (Since  $\sigma$  is small in this case,  $S_0$  is considerably less than 1, while  $\eta(S_0) \cong 1$ , i.e.,  $U_{max}$  has approximately the same value, 1.1 or 1.2 ev.) The relatively small critical value which appears in the logarithm of (26) can be estimated as follows:

$$\ln \frac{\nu \lambda b}{\epsilon h u} \approx 3.3 \frac{T_S}{\Delta T} \quad (30)$$

in this case  $3.3 T_S / \Delta T = 31 \pm 3$ . The function  $W(T)$  which corresponds to these estimates is plotted below in Fig. 24 and agrees completely with the experimentally determined function form of  $\epsilon_{max}(T)$ .

Figure 25 gives a qualitative idea of the distribution of the branches of the criterion  $S$  for pure and amalgamated single crystals of zinc corresponding to  $\dot{\epsilon} \sim 10\% \text{ min}^{-1}$ ,  $L \sim 0.1 \text{ cm}$ , and  $\chi \sim 45^\circ$ . Crystals of pure zinc exhibit brittleness at low temperatures; at ordinary temperatures they are highly plastic, and their plastic flow limit is not very high. In the case of crystals coated

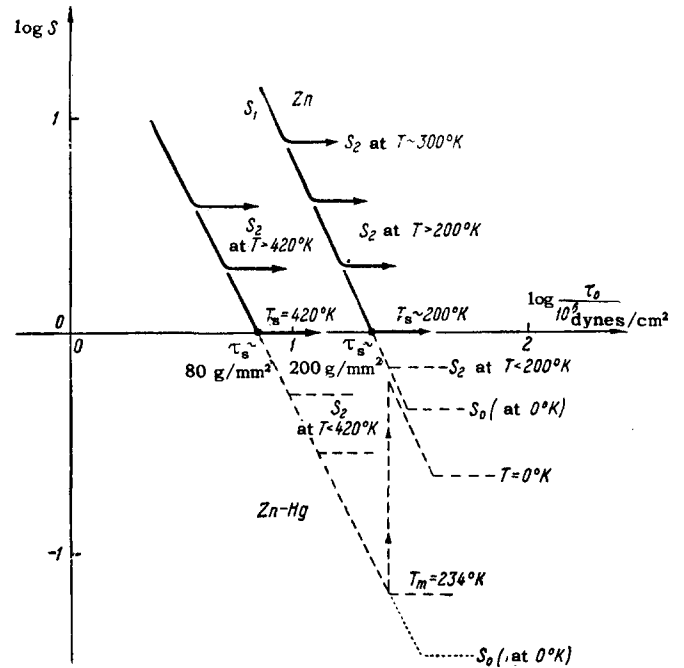


FIG. 25. The deformability criterion  $S$  for pure and amalgamated zinc single crystals at  $\dot{\epsilon} \sim 10\% \text{ min}^{-1}$ ,  $L \sim 0.1 \text{ cm}$  and  $\chi \sim 45^\circ$ .

with mercury  $\sigma$  decreases sharply not only on the surface of the crystal, but also on the internal micro-surfaces, owing to the rapid two-dimensional migration of mercury atoms along hollow dislocation nuclei and along the resultant micro-cracks. The straight lines  $S_1$  and  $S_2$  are displaced downwards; a further lowering of  $S_2$  may be due to a higher value of  $U_{max}$  for amalgamated crystals. The new position of the branches of  $S$  indicates catastrophic brittleness with a considerable decrease of strength up to  $T_S = 420^\circ\text{K}$ ; a high degree of plasticity is re-established for  $T > T_S$ . Below  $T_M = 234^\circ\text{K}$ , mercury stops migrating and consequently  $\sigma$  stops and ordinary strength is re-established. As a result of a discontinuous jump  $S_1$  becomes coincident with the line  $S_1$  for pure crystals; only a difference in the temperature dependence of  $S_2$  may remain, corresponding to a high degree of hardening of crystals with interstitial foreign atoms.<sup>23</sup>

If the melting point of the original metal is  $T_M$ , while that of some low melting point component (or coating) capable of producing a considerable decrease of  $\sigma$  is  $T_M$ , the following three cases are possible:<sup>64</sup>

(a)  $T_M < T_S < T_M$  – brittleness accompanied by decreased strength in a restricted temperature range  $T_M - T_C$  (for example, Zn-Hg<sup>21</sup>);

(b)  $T_M < T_M \lesssim T_S$  – brittleness accompanied by diminished strength from  $T_M$  up to  $T_M$  (for example, Zn-Sn<sup>18</sup>);

(c)  $T_S < T_m$  — absence of an effect (condition for the suitability of a given additive).

A completely different picture presents itself for weak (organic) adsorption-active media, which do not make the crystal brittle, but which are capable under certain conditions of making it plastic.<sup>3-5,64</sup> A small change in  $\sigma$  cannot by itself displace noticeably the branches of  $S$ . However, if under given conditions of deformation the interaction between the dislocations and the free surface of the crystal plays an essential role, even a small decrease in  $\sigma$  can raise the branch  $S_2$  appreciably and thereby displace to the left the plastic flow limit point  $\tau^*$ .

The corresponding energy barrier,  $U_{\max} = b^2\sigma = 0.5$  ev, is due to the formation of a step at the place where the dislocation reaches the surface and is quite steep, for example,  $U(x) \sim -U_{\max} \times [1 + (x/a)^3]^{-1}$  ( $a$  is of the order of atomic distances), i.e., in the immediate neighborhood of the surface the force determined by it predominates over the slowly varying repulsive "image force."<sup>61</sup> (It is not excluded that a still more important role is played by surface defects which block individual points on the trace of the slip plane on the surface; in this case the barrier may be higher and may have another form, but as before it retains its short-range character and depends essentially on  $\sigma$ .)

Then, in accordance with (24) and (25), we have the following expression for the decrease in the plastic flow limit as a function of  $\sigma$ :<sup>64</sup>

$$\frac{\Delta\tau_c^*}{\tau_c^*} = \frac{1}{2} \left( 1 + \frac{\eta}{\varphi} \left| \frac{\partial\varphi}{\partial\tau_1} \right| \right) \frac{\Delta\sigma}{\sigma}. \quad (31)$$

Equation (31) means that when  $\eta \sim 0.9$  a decrease in  $\sigma$  of only a few tens of ergs/cm<sup>2</sup> should reduce the plastic flow limit by a factor of two. The optimum in the plasticizing action of the adsorption-active medium at a given rate of deformation corresponds, from this point of view, to the value  $\eta \sim 1$ , i.e., the upper temperature limit of the effect of the above potential barrier is given by:

$$T_{\text{opt}} \sim \frac{U_{\max}}{k \ln \frac{\sqrt{\lambda} b}{\delta h u}}. \quad (32)$$

The dependence of the optimum in the effect of the adsorption-active medium on the temperature and on the rate of deformation were studied by Likhtman et al.<sup>66</sup> They found  $T_{\text{opt}} \sim 290^\circ\text{K}$  for  $\dot{\epsilon} \sim 10\% \text{ min}^{-1}$ , and  $T_{\text{opt}} \sim 370^\circ\text{K}$  for  $\dot{\epsilon} \sim 500\% \text{ min}^{-1}$ . In accordance with (32), we obtain from this  $U_{\max} \sim 0.5$  ev, which is in full agreement with our assumption concerning the nature of the obstacle that gives rise to the plasticizing effect. The logarithmic

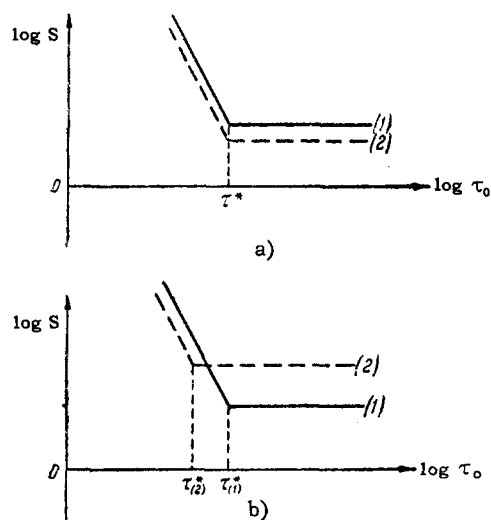


FIG. 26. (a) Change in  $S$  due to a small change in  $\sigma$ , if  $U$  does not depend on  $\sigma$ . (b) A possible change in  $S$  corresponding to a small change in  $\sigma$ , if  $U \propto \sigma$ .

mic term equals approximately 20 (in this model the dislocation is fixed only at the end that emerges on the surface, i.e.,  $\lambda \sim 1$  is much smaller than in the case discussed above).

Nevertheless, when  $\eta \sim 1$  expression (31) cannot, generally speaking, give a quantitative estimate of the effect, since in this case only the surface energy barrier is taken into account. The simplest method of taking into account the superposition of hardening factors in this model is to replace  $\tau_1$  [cf. (24)] by the sum  $\tau_1 + \tau_i$ , where  $\tau_i$  takes into account the remaining hardening factors and depends in the first approximation only on the magnitude of the deformation  $\epsilon$  (shear  $a$ ), but not on the temperature.

Applications of the model described above are closely associated with a careful analysis of the temperature dependence of the hardening factors and of the spectra of their activation energies. Calculation of local stresses  $\tau_1(T)$  due to overcoming barriers requires, like in references 61 and 65, the introduction of specific models of interaction between dislocations and obstacles. But even a qualitative investigation along these lines leads to a number of interesting conclusions.

Thus, it is natural to expect that when  $\dot{\epsilon}$  is reduced by several orders of magnitude the critical temperature  $T_S$  for the transition from brittleness to plasticity drops, in accordance with (26), sufficiently to eliminate brittleness produced by a low-melting-point coating. Moreover, in accordance with (31), there even exists in this case the possibility of plasticizing, a possibility previously masked by the embrittlement due to a sharp decrease of  $\sigma$  on the incipient micro-cavities and,

to a certain extent, by the effect of alloying. Indeed, the experiments of reference 17 show convincingly that at creep rates  $\dot{\epsilon} \sim 10^{-4} \% \text{ min}^{-1}$ , coating of single crystals of zinc with molten tin increases the rate of steady creep by a factor of approximately two, while at  $\dot{\epsilon} \sim 10\% \text{ min}^{-1}$  the same coating results in brittleness accompanied by sharply reduced strength.

However, it is necessary to point out a basic limitation on the applicability of the above approximate method of deriving the criterion of deformability. This limitation is determined, apparently, not so much by taking into account only one type of potential barrier as by identifying the obstacle in front of which the "dangerous" accumulation is formed, and the obstacles that determine the plastic flow limit. In particular, the plastic flow limit turns out in this case to depend essentially on the process of formation of pile-ups of dislocations. Such an approach is valid if the predominant role in both processes is actually played by obstacles of one type (for example, grain boundaries in polycrystalline samples); in other cases it may turn out to be, generally speaking, insufficient.

Indeed, let us examine the following possible case. Suppose that at least one active slip plane contains a very strong obstacle (practically insurmountable), in front of which an accumulation of dislocations is formed, while obstacles to shear scattered in other glide planes may be overcome even at not very large values of  $\tau_0$ , for example, by single dislocations. In such a case, the branch  $S_2$  loses its significance, while the first branch assumes the form:

$$S_1 = A \frac{\sigma G}{L} \frac{1}{\tau^2(\dot{\epsilon}, T, a, \dots)} \cot \chi, \quad (33)$$

where  $\tau(\dot{\epsilon}, T, a, \dots)$  is the plastic flow stress determined by the total crystal volume and, in particular, by the mechanical hardening due to an increase in the shear  $a$ . Interpreted in this way the quantity

$$\frac{S_1}{S_2} = \frac{\kappa \sqrt{\cot \chi}}{\tau} \quad (34)$$

is, evidently, the ratio of the "dangerous" shearing stress determined by the condition (17) to the value of the actual shearing stress at a given stage of deformation and under given conditions (temperature, rate of elongation). In this latter form the criterion  $S$  corresponds to an investigation of the transition from brittleness to plasticity in accordance with the well known method proposed by A. F. Ioffe.<sup>67</sup>

If the temperature dependences of the plastic flow limit and of the hardening coefficient are

known expression (34) allows us, obviously, to calculate the limiting deformation  $\epsilon_{\max}$  and the fracture stress  $P_S$  for a single crystal with arbitrary initial orientation  $\chi_0$ , since the glide plane and the cleavage plane coincide.

But if the dangerous crack develops at an angle  $\Theta$  to the glide plane, then the factor  $\sqrt{\cot \chi}$  should be replaced by the appropriate more complicated function  $f(\chi, \Theta)$ .

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