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SURFACE PHENOMENA IN SOLIDS DURING THE COURSE OF THEIR DEFORMATION AND FAILURE

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The fact that deformation and failure are facilitated by the reversible physico-chemical influence of the medium has been established by now for all types of solids: for metals (and also certain covalent crystals) in contact with liquid metals, for ionic crystals and inorganic glasses in the presence of molten salts, water, alcohol, or other polar media, and for molecular crystals of organic compounds in contact with nonpolar and low-polarity organic liquids. In general these phenomena facilitate the breaking and realignment of the interatomic bonds in the presence of certain foreign atoms or molecules (which have sufficient mobility to ensure their penetration into the bond-breaking zone) and can be described as a lowering of the free surface energy of the given solid under the influence of the surrounding medium. The main condition under which the medium exerts a strong influence on the mechanical properties of the body (in cases of reversible adsorption interaction not connected with dissolution, corrosion, or other chemical processes) is that the solid and the medium be of related nature, to make the surface energy low on the boundary between the solid and liquid phases. At the same time, the form and degree of manifestation of these effects depend in a complicated manner on the real structure of the body (defects) and on the deformation conditions (stresses, temperature, strain rate, time of contact, etc.) An optimal combination of these factors makes it possible to use the influence of the medium to facilitate dispersion and treatment, particularly of solid materials that are difficult to work. To the contrary, by eliminating individual factors that lower the strength by adsorption it becomes possible to protect against the influence of the medium.

CONTENTS

1. INTRODUCTION

SURFACE effects in solids become particularly clearly and uniquely manifest in the deformation and failure of the solids in surface-active media, as shown in a number of papers published since 1928 [1-7]. This includes various effects of facilitated plastic flow and reduced strength as a result of reversible physico-chemical action of the medium, which lowers the specific free surface energy of the solid, i.e., the work of formation of new surfaces in statu nascendi in deformation and failure processes. A distinguishing feature of these phenomena is that they are observed only when the action of the medium is combined with a definite stressed state. Of course, real failure processes are always out of balance in one degree or another. Nonetheless, we are speaking of reversible participation of the medium in these processes, bearing in mind primarily the presence of thermodynamically stable interfaces between the given solid phase and the medium, and also the possibility of complete vanishing of the considered effects when the medium is removed, say by evaporation. It is the physico-chemical reversibility and the obligatory participation of mechanical stresses that distinguish such effects from the numerous manifestations of chemical or electrochemical processes, corrosion, or dissolution of the solid in the ambient medium.

This review, in accordance with the authors' scientific interest, is devoted only to the reversible effect of the medium. This reduces to a partial cancellation of the intermolecular forces on the newly produced surfaces, and can be called an adsorption effect, although it is due to the formation not only of an adsorption monolayer, but also of a liquid-phase layer, which can lead to still stronger changes in the mechanical properties corresponding to very low values of the interphase energy.

The combined effect of mechanical and physico-chemical factors on deformation and failure are investigated by the methods of physico-chemical mechanics, which serves as a basis of the physico-chemical theory of strength of solids. In this borderline region, there are two engineering problems:

1) Facilitation and improvement of processes of mechanical finishing by pressure, cutting, fine grinding, increase of productivity and quality of the formed surfaces (and also control of friction and wear by using lubricants).

2) Production of solids and materials with specified finely dispersed structures, with an optimal combination of mechanical and other properties, and with high strength and endurance under real operating conditions.

Indeed, the formation of new surfaces during the course of plastic flow and failure remain the basis of the processes of deformation, working, and dispersion of solids. At the same time, any high-strength and high-endurance material must be highly dispersed—fine-grained or fine-filament, with dense and uniform packing of the particles. Such are the modern alloys, structural materials, and materials based on polymers with fillers, finely crystallized glasses, and composition materials. In all these bodies, the internal interphase surfaces are developed to the limit and the adhesion interactions on these surfaces are of primary importance. Accordingly, the control of the physico-chemical phenomena on the interface between phases in solids and dispersed systems, using correct combinations of physico-chemical and mechanical effects, uncovers effective ways of solving the two indicated problems.

In addition to our laboratories at the Institute of Physical Chemistry of the USSR Academy of Sciences and in the Chemistry Department of the Moscow State University, the effects of surface-active media on the mechanical properties of solids are being diligently studied by a number of other scientific groups and schools: by S. T. Kishkin and Ya. M. Potak and co-workers in Moscow, by G. V. Karpenko and co-workers in L'vov, by W. Rostocker, J. Westbrook, and A. Westwood and co-workers in the USA, and others; the results have been reported in various publications[8-15]. It would be impossible to describe in a single review the entire extensive material accumulated in this field. The purpose of the present article is to describe only the main ideas and trends that have developed in our studies, illustrating them by individual examples from[4-7,16-20] and others.

II. UNIVERSALITY AND CHEMICAL SELECTIVITY OF EFFECTS OF LOWERING THE STRENGTH AND PLASTICITY BY ADSORPTION-ACTIVE MEDIA IN SOLIDS WITH INTERATOMIC INTERACTIONS OF VARIOUS TYPES

In the case of interest to us, that of the participation by foreign atoms (ions, molecules) in the failure process, these atoms of the surrounding liquid medium penetrate into the pre-destruction zone and begin to interact at the instant when the bonds become broken or restructed, thus exerting a definite influence on this interaction and cancelling the new bonds that become exposed. At the present time it is still impossible to solve this problem directly on the basis of the interaction potentials of the components.

The difficulty in calculating the strength P_c of real solids, all the more under the influence of an external medium, are due to a considerable degree to the fact that the structure-sensitive quantity P_c is not a thermodynamic characteristic. To the contrary, the free surface energy σ of the solid phase, appropriately lowered on the boundary with a liquid phase that cancels more or less completely the bonds that become uncovered on the surface, remains a thermodynamic (structure-insensitive) parameter and can be calculated in principle for phases of given chemical compositions by starting from their interatomic-interaction characteristics (for the chosen model of the boundary structure), and can also be measured directly in experiment.[1]

On the other hand, it is possible to establish a connection between the free surface energy and the strength. In the simplest cases of brittle damage, the well-known Griffith relation can be satisfied

$$P_c \sim (E/c)^{1/2}\sigma^{1/2},$$

where E is the elastic modulus and c is the dimension of the defect (crack). In more complicated cases of ductile failure, the real work of formation of new surfaces ("effective surface energy") σ^* includes the work of plastic deformation and the energy w of the distortions in the region of the crack:

$$\sigma^* = \sigma + w.$$

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[1] The theoretical strength P_{id} of an ideal crystal in vacuum (or in its own vapor) is obviously as much a thermodynamic characteristic as is the elastic modulus E; like the ratio σ/b (b is a linear parameter of the order of the atomic dimensions) or Q/V (Q is the sublimation energy and V is the molar volume) they have the same physical meaning of maximum energy density, and are accordingly of the same order of magnitude. On the other hand, under conditions when the uncovered bonds are compensated for by foreign atoms or molecules that enter into the failure zone from the surrounding medium (or are adsorbed from a solution in the given solid), the situation is different: the quantities E and Q/V are in essence volume characteristics and remain practically the same, whereas the strength and the surface energy can change appreciably, thereby reflecting the fact that they pertain not to all the bonds but only to those that become uncovered on the produced surface. At the same time, the use of the parameter σ does not prevent us from taking into account the kinetic non-equilibrium features) of the breaking of the bonds upon simultaneous penetration of foreign atoms, and one can hope that the thermodynamics of the non-equilibrium processes will subsequently become applicable in this case (a similar attempt was made by A. A. Zhukhovitskiĭ and co-workers [21]).

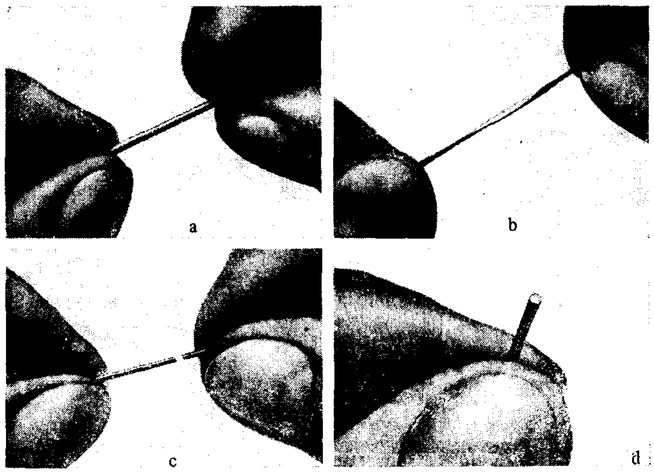

FIG. 1. Elongation of pure zinc single crystals (a, b) and of crystals coated with a thin film of mercury (c, d) [26].

The value of w can exceed the true value of σ by several orders of magnitude. For a correct understanding of this relation, however, it is necessary to bear in mind that the work w itself (corresponding to that degree of distortion that must be introduced in the region of the failure surface to reach the limiting state) is closely related to the value of σ and accordingly decreases sharply when w is greatly reduced; this indeed is the phenomenon of embrittlement by a strong surface-active medium.

1. **Metals.** For hard metals, the liquid media that are close in chemical nature and decrease strongly the surface energy on the interphase boundary are other molten metals with lower melting points[7,16-18]. Many metals and alloys experience a large decrease in strength, increased brittleness, manyfold decrease of endurance, cracking, etc., when they come in contact with liquid metals, as observed in the course of soldering and welding, in the case of superheating and melting of antifriction alloys and anticorrosion coatings under the influence of contact with liquid-metal heat-transfer agents, etc.[8,9,11-15,18-20,22,23]. The strength is decreased by a factor 2–3 and more, and in some cases by a factor of several times 10.[2] A characteristic example is provided by the data on zinc single crystals in the presence of thin (on the order of several microns) liquid films of tin, mercury, and gallium[7,16-18,24-26] (Figs. 1 and 2; see also Fig. 19 below).

A several-fold decrease in strength should correspond to a lowering of the free surface energy by roughly speaking one order of magnitude: whereas in the initial state σ is $\sim 10^3$ erg/cm^2 for metals, when the strength is sharply decreased by contact with molten metal it can be assumed that σ decreases to values on the order of 10^2 erg/cm^2.

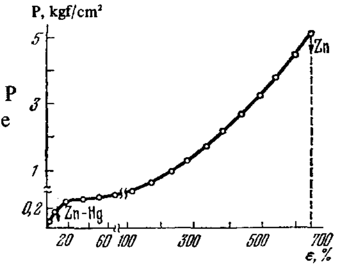

FIG. 2. Dependence of stress P on the strain ϵ for pure zinc single crystals and those with mercury coating [17,25].

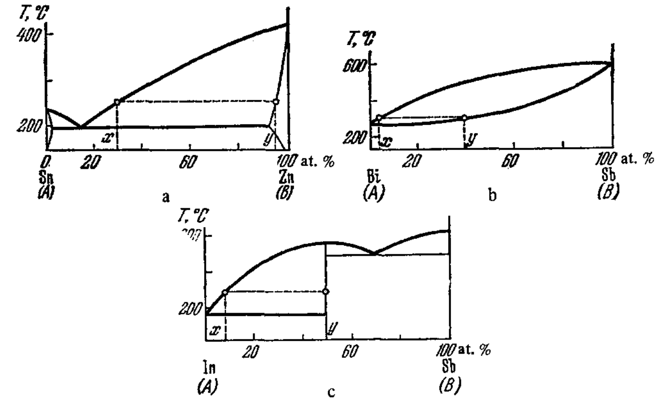

FIG. 3. Binary systems in which embrittlement of the solid phase (y) under the influence of the liquid phase (x) is observed: a) simple eutectic (Zn-Sn), b) with unlimited solubility (Sb-Bi), c) with an intermetallide (Sb-In) [18,32].

Theoretical calculations of the surface energy on the interface between a solid and a molten metal[27], including quantum-mechanical approximations, show that actually, the free surface energy on the interface can actually be lowered by one order of magnitude for the pairs of interest to us, such as Cd-Ga, Zn-Hg, Zn-S, or Cu-Bi. Such calculations, however, are mostly approximate. It is therefore useful to employ also the local-coordination ("quasi-chemical") approximation developed by Pines and Geguzin[28,29]. For metals, of course, such an approximation cannot give more than an order-of-magnitude estimate, but its undisputed advantage is its universality, since it is applicable to a great variety of systems[30,31].

The local -coordination approximation makes it possible to establish a simple connection between the character of the phase diagram of the system A-B, or the arrangement of the liquidus [x(T)] and solidus [y(T)] curves, and the parameters describing the interatomic interactions of the components, such as the interaction energies of like and unlike atoms (U_{AA}, U_{BB}, U_{AB}), or the melting temperature and entropy of the components (T_A, T_B, q_A, q_B). We shall henceforth assume usually that the component B has a higher melting temperature than A; here x and y are the molar fractions of the higher-melting-point component B in the liquid and solid coexisting phases, respectively (Fig. 3). A particularly important role is played in such a description by the "mixing energy"

$$U_0 = z[U_{AB} - {}^1/_2(U_{AA} + U_{BB})]$$

which is essentially the only parameter characterizing the difference between the interactions of the like and unlike atoms (i.e., the deviation of the system from ideal); here z is the coordination number since the values of U_{AA}, U_{BB}, and U_{AB} pertain to a single

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[2] Very large effects appear when the metal is highly plastic in the initial state and becomes very brittle on coming in contact with the melt; on the other hand, if the initial state is one in which the plasticity and strength are low, for example under conditions of low-temperature brittleness, then the strength is decreased by the melt by not more than several times in comparison with the given state.

bond, and U_0 pertains to the atom. Using primes and double primes to denote the liquid and solid phases, respectively, we can write the equations of the liquidus and solidus curves in the form

$$\begin{gathered} U''_0(1-x)^2 - U''_0(1-y)^2 = -kT\ln(x/y) + q(T-T_B); \\ U'_0x^2 - U''_0y^2 = -kT\ln[(1-x)/(1-y)] + q(T-T_A) \end{gathered} \tag{1}$$

(in the simplest case it is assumed that both solid phases have identical structures and accordingly $q_A \approx q_B = q$).

At the same time, this scheme enables us to estimate approximately also the free surface energies of the individual components as well as the interphase energy σ of the interface (under definite assumptions concerning the structure of this boundary):

$$\begin{aligned} \sigma = {} & -{}^1/_2 n'z'_b[U'_{AA}(1-x_1) + U'_{BB}x_1 + (2/z')U'_0x_1(1-x_1) \\ & -{}^1/_2 n''z''_b[U''_{AA}(1-y_1) + U''_{BB}y_1 + (2/z'')U''_0y_1(1-y_1)] \\ & + n^*z^*_b\{U^*_{AA}[1-{}^1/_2(x_1+y_1)] + U^*_{BB}\cdot{}^1/_2(x_1+y_1) + (1/z^*)U^*_0[x_1(1-y_1) \\ & + y_1(1-x_1)]\} + n'\sum_{i=1}^{\infty}\{kT[x_i\ln(x_i/x) + (1-x_i)\ln\{(1-x_i)/(1-x)\}] \\ & - U'_0(x_i-x)^2 + (z'_b/z')U'_0(x_{i+1}-x_i)^2\} \\ & + n''\sum_{i=1}^{\infty}\{kT[y_i\ln(y_i/y) + (1-y_i)\ln\{(1-y_i)/(1-y)\}] \\ & - U''_0(y_i-y)^2 + (z''_b/z'')U''_0(y_{i+1}-y)^2\}; \end{aligned} \tag{2}$$

here n is the number of atoms per unit surface in the layer parallel to the interface; z_b is the number of neighbors of the given atom in the neighboring layer; x_i and y_i are the concentrations of the component B in the liquid and solid phase in the i-th layer, respectively, measured from the interface (this takes into account the adsorptions of the components and the "smearing" of the interphase boundary), while x and y are the average values of the volume concentration far from the boundary. The quantities pertaining *directly to the interface* (and having certain averaged values) are marked with asterisks.

We can assume in the simplest case (bearing in mind the highest possible estimate of σ) that the concentration changes jumpwise on the interface, i.e., that $x_i = x$ and $y_i = y$. We assume also that $U^*_{AA} = U'_{AA}$, $U^*_{BB} = U'_{BB}$, $U^*_0 = U''_0$, and let finally $n'z'_b = n''z''_b = n^*z^*_b$, i.e., there are no "broken" interatomic bonds on the interface. Then expression (2) can be reduced to the following form, which makes it possible to estimate approximately the surface energy on the boundary between a solid metal and a molten one[30]:

$$\sigma \leqslant \sigma_A(Q_{mA}/Q_{vA})(1-y) + \sigma_B(Q_{mB}/Q_{vB})y + (n''z''_b/z'')U''_0(y-x)^2, \tag{3}$$

where Q_{mA} and Q_{mB} are the changes of the energy upon melting, Q_{vA} and Q_{vB} are the changes due to evaporation, and σ_A and σ_B are the surface energies of the pure components (in the liquid state).

The quadratic terms, which contain the mixing energy as a factor, are due to deviation of the given system from ideal. It is easy to separate the following three characteristic cases[30,31,33].

1) The mixing energies of the components (in both phases, as well as the "averaged" value U^*_0 on the boundary) are positive and large:

$$U'_0,\ U''_0,\ U^*_0 \gg kT$$

(for the considered temperature interval). An analysis of the presented relation shows that the value of σ is large in this case and tends in the limit to the sum of the free surface energies of the coexisting phases. This obvious result means that if the components do not interact noticeably (and accordingly their mutual solubility in the coexisting phases is very low), then no significant lowering of the free surface energy of the solid phase can occur in the system when contact is made with the liquid phase, there can be no "compensation" of the bonds that are uncovered, i.e., there should likewise be no reduction of the strength. The phase diagram usually shows lamination into two nonmixing liquid phases in this case.

2) The mixing energies are appreciable in absolute magnitude, but are negative (strong negative deviation from an ideal system). This is the case of intense chemical interaction and formation of intermetallides (or other compounds if we do not confine ourselves to binary metallic systems). The negative values obtained in this case from (2) and (3) for the interphase energy indicate that the two-phase system with an interface is not in equilibrium; the chemical interaction can become manifest in dissolution, corrosion, etc.

In accord with the range of phenomena considered in the present article, we do not deal with such "irreversible" interactions with the medium. A few remarks are in order, however. This group of phenomena is characterized by the following features. For the medium to damage the solid does not call in this case, generally speaking, for participation of mechanical stresses. To change noticeably the cross section of a solid (article) it is necessary in this case that the medium (its active component) have usually an appreciable mass, since the interaction process is essentially of the bulk type, affecting a more or less appreciable part of the volume of the given solid. Accordingly, the process develops usually slowly, as the bulk chemical reaction penetrates into the interior of the solid. Finally, as in all chemical interactions, a characteristic feature here is the increased damaging effect of the medium with increasing temperature. The situation is just reversed, in all these respects, for the phenomena of "reversible" decrease of strength by contact with a medium, which are considered in the present article.

Incidentally, such a contrast is somewhat arbitrary and pertains to idealized "extreme" cases; actually there is no sharp boundary here. The large range of phenomena in which a medium acts on the mechanical properties of solids includes, in particular, an extensive group of processes that are predominantly chemical (or electro-chemical), but require mechanical activation before they can proceed with a noticeable rate; these are the well-known processes of corrosion under stress, corrosive cracking, corrosive fatigue[10,12] (it should be noted, incidentally, that in all these cases the chemical interaction act is usually preceded by an adsorption act[6]). On the other hand, such typically "adsorption" cases (when the *entire interaction with the* medium is localized on the surface and does not affect the volume at all) as the easier deformation or the failure of a metal in the presence of fatty acids (solution of oleic acid in nonpolar oil, etc.) can include the act of chemosorption of active molecules of the medium (saponification); it is precisely this which

Table I

$B-A$	U'_0 10^{-13} erg/atom	U''_0 10^{-13} erg/atom	σ, erg/cm²	$B-A$	U'_0 10^{-13} erg/atom	U''_0 10^{-13} erg/atom	σ, erg/cm²
Ag—Bi	1.59	1.87	130	Cu—Ag	2.08	4.56	180
Ag—Cu	1.68	2.90	90	Cu—Bi	2.70	—	220
Ag—Pb	1.46	3.89	190	Cu—Pb	4.08	5.81	350
Al—Sn	1.90	5.73	260	Ge—Sb	0.68	4.67	280
Al—Zn	2.54	3.51	60	Ge—Ag	2.24	—	210
Be—Al	4.78	—	360	Ni—Cr	1.36	1.59	150
Be—Si	4.81	—	130	Pd—Cr	0.84	1.10	110
Co—Bi	0.14	—	110	Sn—Zn	0.89	3.31	40
Cr—Ni	0.67	2.44	130	Zn—Sn	1.22	4.81	150
Cr—Pd	2.94	8.29	220	Zn—Ga	0.60	1.84	110

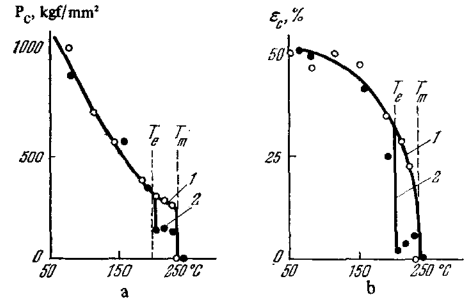

FIG. 4. Temperature dependence of the strength P_c (a) and of the maximum deformation ϵ_c (b) when pure polycrystalline samples of tin (1) and samples coated with a thin film of zinc (2) are stretched [36] (T_m = 232°C is the melting point of tin).

causes, in such an "irreversible" process, the large decrease of the effective surface energy (as the work of formation of the new surface), and accordingly produces considerable chemical effects.

If an intermetallide is formed in the given binary (metallic) A-B system, then the influence of the molten phase A on this intermetallide is very important. Different cases are possible here a priori, ranging from very strong embrittlement to cases when the melt produces no effect. Particularly interesting are the various phenomena observed when a third component C that interacts actively with B is introduced into the liquid phase (component A). This can greatly reduce the strength of the solid metal, increase the rate of corrosion cracking, etc. (for example in contact between steel and liquid alkali metals containing oxygen[23]) or, to the contrary, a weakening of the effect, thus revealing prospects for protection against it. An example of a model system corresponding to the last case is the Cu-Bi pair. As shown in our laboratory by V. S. Yushchenko, when tin, which produces intermediate compounds with copper, is introduced into the liquid phase (even at low concentrations of the tin), bismuth is prevented strongly weakening the copper, whereas introduction of lead, which is "inactive" with respect to copper, is effective only in melts with large lead contents[11].

3) The mixing energies of the components A and B are small in absolute magnitude; in this case the liquid phase (with the larger content of A) and the solid phase have related and similar chemical characteristics and structures. The principal difference between this case and the preceding one is the presence of a thermodynamically-stable two-phase system with an interface having a finite (possibly very low, but positive) free interphase energy.

Of course, the "simplest" example of such an interaction is that between a solid and liquid phase of the same metal. Calculations show that the interphase surface energy can decrease in this case quite strongly, by one order of magnitude or more in comparison with the free surface energy of the given condensed phases[28]. Such cases are of interest in connection with the analysis of nucleus formation, for example in crystallization from a melt; they may be the cause of the observable and hidden cracks in welding of stressed mechanical parts. Contact with water (if the appropriate kinetic conditions are satisfied) can facilitate the breaking of ice.

Yu. V. Naĭdich and co-workers recently used an organic crystal (salol) as a model system and demonstrated by an independent direct experiment that contact with its own melt causes an appreciable lowering of the surface energy of the crystal (as revealed by the wetting angle) and a decrease in hardness (as measured with a pendulum sclerometer).

In the case of contact between a solid phase and a "foreign" melt, in systems with two (and more) components, the least deviations from ideal (the smallest absolute values of the mixing energies of the components) correspond to unlimited mutual solubility in both the solid and liquid phases, i.e., in particular, to a diagram of the "cigar" type. An example of such a system with in which the solid and liquid are very closely related is the Sb-Bi pair, which undergoes a noticeable decrease of strength of the solid when in contact with the corresponding liquid phase (with which it is in equilibrium)[32]. Incidentally, the indicated binary systems with full mutual solubility in the solid phase (which come close, in essence, to being single-component systems) are of only limited interest, since the region of temperatures and compositions in which these effects can be observed is narrow and, principally, is not very far from the melting point of the component that is harder to melt. In this case, however, in spite of the strong decrease of σ, the strength may not decrease if a change from brittleness to plasticity takes place already at lower temperatures (see Sec. 2a of Chap. III).

Principal interest attaches to binary A-B systems of simple eutectic type with finite, usually small, solubility of the components in the solid phase. It is precisely for such systems that one observes most frequently a strong embrittlement of the solid metal B in contact with the molten A (or with the liquid phase of the eutectic composition)[35]. The mixing energy U'_0 of the components in the liquid phase for such systems is usually close in order of magnitude to kT_e, where T_e

is the eutectic temperature; the corresponding values of U_0'' for the solid phase are as a rule higher. Approximate estimates with the aid of relations (2) and (3) show, in good agreement with the measurements of the decreased strength, that the free energy on the interphase boundary actually decreases here strongly, by one order of magnitude and more[30]. Table I gives the mixing energies in the liquid and solid phases, U_0' and U_0'' calculated from Eqs. (1), and the values of the interphase surface energy σ calculated from Eqs. (2) and (3), for certain eutectic systems (it is assumed that the concentration of the component B is higher in the solid phase).

Systems with such moderate deviations from ideal behavior and with simple eutectic diagrams exhibit a unique symmetry: the easy-melting liquid phase can be in equilibrium (thereby greatly lowering the free surface energy) both with the solid phase, which has a higher melting point (the component B), and with the second solid phase (the component A). An example is provided by the data on the lowering of the strength and plasticity of tin under the influence of tin-zinc liquid solutions (Fig. 4)[36]. This circumstance must be borne in mind in the analysis of the causes of the lowering of the heat endurance of alloys containing as small impurities components that have even higher melting points. A decrease of the strength of the two solid metals forming the eutectic system is clearly observed when they come in contact at a temperature near T_e (i.e., under conditions of "contact" melting)[34,37].

One can classify as eutectic systems also pairs made up of the component A and the compound A_nB_m; for example, we have observed a considerable decrease in the strength of indium antimonide single crystals (by 40%) on which drops of liquid indium were placed[32].

Direct measurements of σ for the considered metal-melt systems are still very scanty, owing to experimental difficulties. L. S. Bryukhanova and co-workers [38] of our laboratory performed a series of investigations of the lowering of the surface energy of zinc and cadmium in the presence of small additions of gallium, tin, etc., by the Tammann-Udin method (zero creep of thin sheets). The value obtained for the interphase energy σ on the boundary of cadmium with a gallium film (more accurately, of the corresponding solutions) was 150—200 erg/cm², which is several times lower than that of cadmium itself.

A. Westwood and co-workers[14,15] used the Obreimov-Gilman method (determination of the critical force required to split a single crystal along a cleavage plane) to estimate the surface energy of zinc in the presence of mercury. There are also isolated data obtained by other methods (relative and indirect) on the following: the dihedral angle etched out by a drop of melt from a grain boundary emerging to the surface (for example, for the copper-bismuth pair), the dependence of the temperature of transition from brittleness to plasticity on the size of the grain, etc.[11] In these cases the authors indicate an appreciable decrease (by a factor of several times) of σ of the solid metal on the boundary with the melt (as a rule, the data pertain just to eutectic systems).

So far we have discussed the decrease of σ_{sl} of a solid metal at the contact with a liquid phase. If the amount of the easily-melting component does not exceed its solubility in the solid phase, then only an adsorption layer can be produced on the free surface of this solid phase (under thermodynamic equilibrium), and there is no liquid-phase film[3]; these conditions correspond to the possible lowering of σ by adsorption in the narrow sense of the word. It is important that we are operating here predominantly with such binary A-B systems in which both components have comparable values of σ_{sv} (on the boundary with the vapor).

In the local-coordination approximation, the system of equations describing the "layer-by-layer" distribution of the adsorbed component at the surface of the solid phase was formulated by Pines[28] and solved with a computer by V. S. Yushchenko of our laboratory. These calculations have shown that at $\sigma_{A-v} \approx \sigma_{B-v}$ the adsorption lowering of σ_{B-v} by introduction of small amounts of the component A is connected with positive deviations of the system from ideal, and usually does not exceed a value on the order of $\Delta\sigma \sim 10^2$ erg/cm², i.e., 10—20% of the initial value of σ_{B-v}. This rather obvious result agrees with data obtained by the zero-creep method[38] on the adsorption lowering of σ at low additive concentrations. It should be noted that adsorption of zinc (a component with a higher melting point and whose own value of σ is larger) on the surface of solid tin also results in such a relatively small lowering of the free surface energy.

A large decrease of σ following physical adsorption can be expected in binary metallic systems whose components have greatly differing values of σ. It must be emphasized, however, that under conditions of activated adsorption (chemosorption) on the surface of a metal, for example diphilic molecules of organic acids, the decrease in surface energy can be large, since the binding energy of the polar group corresponding to the formation of the surface compound (i.e., the degree of compensation of the surface bonds of the metal atoms) is large, whereas the free surface is now a layer of hydrocarbon chains with low surface tension (Sec. 4 of Chap. III). For nonmetallic solids, an example of strong adsorption lowering of σ is the adsorption of water on the surface of an ionic crystal (Sec. 3 of Chap. II).

2. Solids with covalent bonds. Crystals with covalent bonds, just like solid metals, can experience in the absence of chemical interactions a strong decrease of strength under the influence of molten metal. Thus, the strength of germanium single crystals decreases when it comes in contact with liquid gallium or copper[20,40,41]. A particularly pronounced example is the germanium-gold pair, the phase diagram of which is that of a simple low-melting-temperature eutectic.

With increasing temperature, germanium single crystals acquire an appreciable plasticity when tested in air; their strength increases accordingly. Under

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[3] As shown by Frumkin [39], these two states do not have a continuous transition in the presence of a finite wetting angle: with increasing amount of the easy-melting component, the adsorption layer reaches a certain limiting concentration, after which sections (drops) of a liquid phase, with a definite wetting angle, appear on the surface in equilibrium with the adsorption layer.

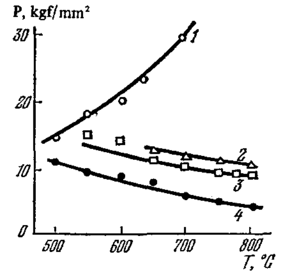


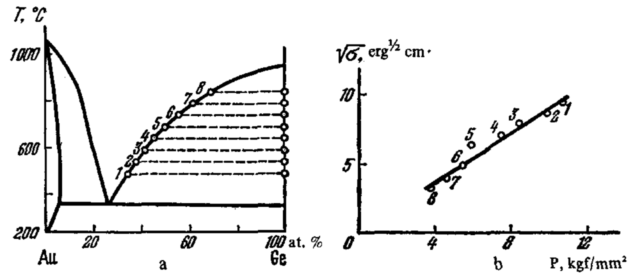
FIG. 5. Temperature dependence of the strength of pure germanium single crystals (1) and of those coated with a thin film of gallium (2), copper (3), and gold (4) [20,41].

these conditions, as shown by N. V. Pertsov and co-workers in our laboratory (Fig. 5, see[20,41]), contact with a drop of gold (saturated with germanium at the given temperature) again returns the crystal to the brittle state, and the rupture stress decreases. For this series of experiments—different temperature and accordingly different melt concentrations—V. S. Yushchenko calculated the interphase free energy on the boundary between the solid and liquid phases (in the local-coordination approximation, in accordance with the scheme represented by relations (1)—(3)). Both the results of this calculation and the measured strength, when plotted in the coordinates P_C and $\sigma^{1/2}$, fall on a straight line passing through the origin (Fig. 6). This confirms the validity of the Griffith relation (the failure at the contact with the melt has a brittle character) and at the same time the usefulness of the macroscopic parameter σ for describing the features of the interatomic interactions under the described conditions. We have reported above the decrease of the strength of indium-antimonide crystals acted upon by a liquid indium. These and similar phenomena can occur when semiconducting crystals are soldered and subjected simultaneously to mechanical stresses.

Extensive material on various influences of the medium is obtained by investigating the strength of graphite in contact with liquid metals[42]. In accordance with the character of the interatomic interactions (as reflected by the type of the phase diagram)[42], the following cases are observed[42]:

1) Tin, lead, gallium, and other metals that do not interact with carbon (and accordingly do not wet graphite) do not affect the strength of the graphite. 2) Iron, vanadium, molybdenum, tungsten, and other metals that form carbides and dissolve carbon lead to failure even in the absence of stresses as the cross sections of the samples are decreased. 3) In the case of very energetic carbide production, which leads to the formation of a strong carbide film resistant to the influence of the given melt, this film exerts a protective action and no decrease in strength is observed, for example in contact with molten titanium, zirconium, etc. 4) Finally, a "moderate" interaction that becomes manifest in the formation of weak carbides in a limited temperature interval (the case of contact between graphite and liquid aluminum) leads to an abrupt decrease in the strength precisely in this temperature interval. The strength of graphite is reduced even more strongly by alkali metals (at increased temperature, as the interaction with the carbon becomes stronger).

It is possible that the decrease of the free interphase energy determines to a considerable degree also the effect of iron on the mechanical properties of diamond; this is indicated both by the already observed contact eutecting melting of diamond in the presence of iron and by data showing that the strength of diamond grains decreases when they are used to work on steel and also directly under the influence of iron in a definite temperature interval[44].



a b

FIG. 6. Comparison of the experimental values of the strength P_C and of the calculated free interphase energy σ(b) for germanium single crystals tested at different temperatures (a) in the presence of a drop of gold (saturated with germanium) [20,41].

Under conditions of intense mechanical working and continuous uncovering of the juvenile sections of the surface, the number of solids that are affected by low-melting-point molten metals turns out to be much larger than heretofore assumed.

Thus, in the presence of molten metals, the effectiveness of grinding hard alloys (made of tungsten and titanium carbide with cobalt binder) with diamond wheels is increased[20,43]. Both the strength of the carbide grains themselves and the strength of their cohesion with the binder are decreased, and good wetting on the worked surface is observed at the same time. It must be emphasized that under these conditions the melt does not harm the tool, since the easy-melting metals are not surface-active with respect to diamond. Easy-melting metals, as established in our experiments with V. G. Bravinskii[46], can reduce appreciably (by a factor 1.5) the strength of aluminum oxide vacuum-tight ceramic. Under ordinary conditions, these metals do not wet aluminum oxide[47]. Nonetheless, tests of ceramic samples in a bath of molten metal have shown that the juvenile surface of the fracture is wetted by the melt; it is precisely then that the decrease in the strength is observed.

3. Solids with ionic bonds. a) Ionic single crystals and polycrystals. Glasses. Media that are related in chemical composition (in the character of the interatomic interactions) to ionic crystals are obviously molten salts, electrolyte solutions, and water itself[4)]. A typical example is the effect of molten aluminum chloride on the behavior of sodium-chloride single crystals. As is well known, these single crystals fracture in perfectly brittle fashion along the cleavage plane under tension at room temperature, but become sufficiently plastic at higher temperatures; at 400—450°C, the fracture is preceded by necking and the strength is increased. N. V. Pertsov and co-workers

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[4)] Here, as in the other sections, we assume (unless otherwise stipulated) that the medium is saturated by the given solid substance, and that in the absence of mechanical stresses the system is a thermodynamically-stable two-phase system with a stable interface.

Table II

Alcohol	$(P_0-P_A)/P_0$	$(P_0-P_A) \times P_0^{-1}(pd/M)^{-1}\cdot 10^{-18}$	Alcohol	$(P_0-P_A)/P_0$	$(P_0-P_A) \times P_0^{-1}(pd/M)^{-1}\cdot 10^{-18}$
Methyl	0.58	13.8	Butyl	0.23	12.8
Ethyl	0.52	17.3	Hexyl	0.20	16.0
Propyl	0.25	12.0	Heptyl	0.15	12 5

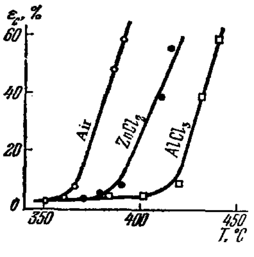


FIG. 7. Temperature dependence of the maximum elongation of sodium-chloride single crystals in air and in contact with zinc and aluminum chloride [48].

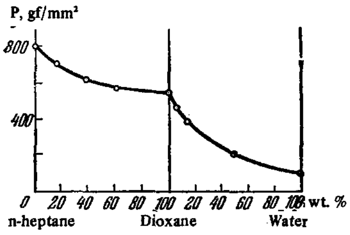


FIG. 8. Strength of polycrystalline potassium chloride samples vs. the composition of the medium, in n-heptane–dioxane and dioxane–water solutions [40].

have shown that in the presence of molten aluminum chloride, the sodium-chloride crystal returns to the brittle state at the same temperatures, and its strength decreases accordingly (Fig. 7).

Numerous observations of the decreased strength of ionic crystals in the presence of water, electrolyte solutions, and also when small additives of typically surface-active substances with diphilic molecules were described earlier[1,3,4]. It is precisely with ionic crystals, by fracture of calcite, rock salt, etc. along the cleavage plane, that the effect of adsorption embrittlement was first established and investigated[1]. We point out in particular the experiments with cleavage of mica crystals; in addition to the decrease of the cleavage force, a unique aftereffect is produced in the presence of water vapor or in liquid water, as shown by G. I. Logginov[49]. Namely, mica flakes, exhibit under load an elastic aftereffect that increases gradually in time (for several days). In accord with the pure adsorption nature of the effect, it turns out to be perfectly reversible in terms of the value of the strain, i.e., the strain vanishes just as slowly but fully after the load is removed.

Analogous phenomena take place in silicate glasses and in Fiberglas, as shown by M. S. Aslanova in our laboratory (see[50]). As is well known, in the presence of moisture, the "cutting" of glass, i.e., fracture after scratching with a diamond, becomes easier. The long-term strength of glass also decreases considerably under the influence of water. Accordingly, the hydrophobization of silicate-glass surfaces, i.e., its protection against the action of atmospheric moisture, can increase the strength appreciably.

Lowering the strength of minerals by water and by adsorbing substances dissolved in it ("hardness reducers") has been used to accelerate well drilling in hard rock[3] and at the same time to increase the lifetime of the drilling tool.

The significance of the "likeness" of the medium becomes clearly pronounced when the character of the medium is greatly varied. Thus, V. Yu. Troskin of our laboratory investigated the strength of polycrystalline potassium chloride samples in a continuous series of heptane-dioxane and dioxane-water solutions. The strength is highest in a nonpolar hydrocarbon (heptane, Fig. 8); following the adsorption isotherm, it decreases with increasing concentration of the polar molecules in the solution and reaches the lowest value in the most polar medium, water. The same regularity is observed also in experiments with saturated alcohols. Table II illustrates the influence of alcohols of the saturated series on the strength of polycrystalline samples of potassium chloride (p (cgs esu) is the dipole moment of the molecules, d (g/cm³) is the density, and M (g/mole) is the molecular weight of the liquid)[20,48,51].

Assuming that the conditions of brittle failure in such experiments follow the Griffith relation, i.e., $P_c/P_0 = (\sigma/\sigma_0)_{1/2}$, and combining this relation with the Gibbs equation in its simplified form (at small C):

$$\Gamma = -(RT)^{-1} d\sigma/d \ln C$$

we arrive at an equation relating the adsorption (mole/cm²) with the strength:

$$\Gamma = -2(\sigma_0/P_0^2)(RT)^{-1} P_c (dP_c/d \ln C).$$

The obtained relation makes it possible to estimate the adsorption by starting from the dependence of the strength on the concentration of the active component in the medium; on the other hand, the use of the maximum adsorption Γ_m yields an estimate of the maximum area a_m occupied by the active molecule on the newly formed surface of the deformed solid: $a_m = 1/N_A\Gamma_m$. Such a calculation leads to a correct order of magnitude of a_m, for example for adsorption of water from dioxane by KCl.

V. Yu. Troskin attempted an approximate estimate of the influence of the polarity of the medium on the strength of an ionic crystal at the "atomic level." The model for the calculation is the vertex of a wedge-like crack[4], into which a molecule having a dipole moment penetrates. By taking into account the interaction between this molecule and the positive and negative ions in front of it, it is possible to calculate the force component normal to the walls of the crack, which determines the decrease of the strength. Such tentative calculations, in agreement with experiment, show that the observed effect is proportional to the dipole moment per unit volume of the medium.

b) Disperse porous materials. Of great interest in

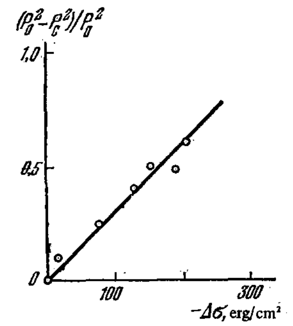


FIG. 9

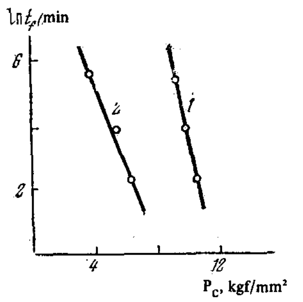


FIG. 10

FIG. 9. Comparison of independently obtained values of st.ength decrease and decrease of the free surface energy of magnesium hydroxide in the presence of water vapor [53,54].

FIG. 10. Logarithm of the time to failure vs the applied stress P for a magnesium-oxide catalyst: 1) in the absence of a reaction, 2) during the process of conversion of isopropyl alcohol [57,58].

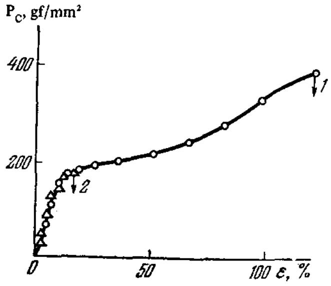


FIG. 11

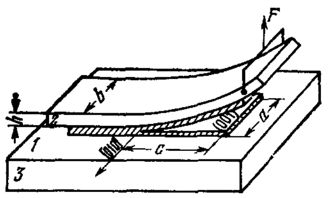


FIG. 12

FIG. 11. Strain properties of naphthalene single crystals in air (1) and in the presence of benzene (2) [59].

FIG. 12. Setup for the determination of the surface energy of a naphthalene crystal [60].

in the study of the irregularities and mechanism of adsorption embrittlement and also from the practical point of view, are disperse porous bodies, including bodies with ionic structure[52-58].

S. I. Kontorovich and co-workers of our laboratory (see[53]) used as a convenient model of a porous solid the crystallization structure of magnesium hydroxide obtained by hydratation hardening of magnesium oxide. Such structures have a large specific surface (tens of m²/g), making it possible to determine the adsorption Γ by a weight method: in the case of adsorption of water, one monolayer is already equivalent to a 1% increase in weight of the order. Series of such samples were placed in exsiccators over solutions of sulfuric acid of definite concentration, producing a specified water vapor pressure p. By determining the relation Γ = Γ(p) from the weight increase corresponding to moistening under such equilibrium conditions, it was possible to estimate the decrease of the surface energy of magnesium hydroxide following adsorption of water vapor

$$-\Delta\sigma=\sigma_0-\sigma=RT\int\limits_0^p\Gamma\, d\ln p$$

and to compare the obtained values of $-\Delta\sigma$ with independent measurements of the decrease of the strength P_c of these moistened samples, in comparison with the initial strength P_0 in the absence of water. Since such bodies experience brittle fracture, the Griffith relation is satisfied and the following relation should be obtained:

$$(P_0^2-P_c^2)/P_0^2=-\Delta\sigma/\sigma_0.$$

Indeed, in the corresponding coordinates, the experimental points lie on a straight line passing through the origin, and the perfectly reasonable value ~300 erg/cm² is obtained for σ_0 (Fig. 9)[54].

Special experiments performed jointly with V. F. Chuvaev by the magnetic nuclear resonance method have shown that the adsorbed water is indeed present in the form of an adsorption layer, and not in the liquid phase, since these experiments definitely showed no local dissolution of the stressed material in the vertex of the crack (in this case at the contacts between the crystallites).

We note that in the presence of a monolayer of water the strength of porous highly dispersed magnesium hydroxide decreases by one-half, corresponding approximately to a decrease of the free surface energy to one-quarter of its volume. This is due in the present case just to the adsorption, since the surface tension of the adsorbed component is small in comparison with the initial value σ of the solid adsorbent.

Similar results were obtained, for example, in the adsorption of ethanol by magnesium hydroxide[53] and in many other cases. It is precisely adsorption of water which causes the considerable decrease in the strength of all structural materials (which are usually hydrophilic) such as concrete etc. and others, particularly fine-grained gypsum dihydrate.

Even more prone to adsorption lowering of the strength are disperse structures with pointlike "atomic" contacts. Such structures are produced when the liquid phase and the adsorption layers are removed from coagulation structures. It is precisely these phenomena that cause grounds to have low endurance to water ("sinking," formation of quicksands, etc.)[55].

Adsorption of water vapor, ethanol, or benzene decreases the strength of synthetic sorbents such as granulated zeolites with a clay binder. In general, as shown by our investigations with L. Ya. Margolis[56,57], disperse porous materials such as sorbents, catalysts, and carriers, which are widely used in chemical technology, operate under "unfavorable" conditions: according to the very principle of heterogeneous catalysis, a lowering of the free surface energy of the catalysts is inevitable under the conditions of the reaction; the result is a considerable decrease of the life of the granules (Fig. 10). It is precisely the mechanical wear which limits in many cases the possibility of using a catalyst, particularly under intensive regimes. Taking these circumstances into account, methods for strengthening granules are being developed[58]. On the one hand, this calls for the formation of an optimal disperse structure, without internal stresses and with strong crystallization contacts between particles, using vibration molding, optimal heat treatment, etc. On the other hand, this involves protection of the contacts between particles against adsorption embrittlement, for example by introducing highly-dispersed additives that form at the contacts between the catalyst particles com-

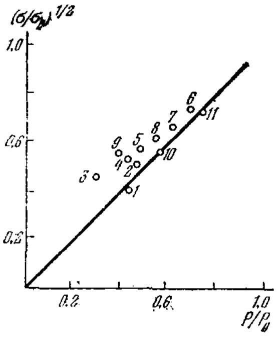


FIG. 13

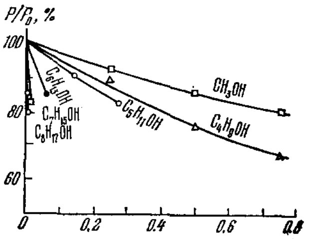


FIG. 14

FIG. 13. Comparison of the values of the relative lowering of the surface energy of naphthalene single crystals and of the relative lowering of the strength of polycrystalline samples of naphthalene in benzene (1), heptane (2), methylene chloride (3), chloroform (4), tetrachlormethane (5), and in methyl (6), ethyl (7), propyl (8), butyl (9), and tertiary butyl alcohol (10) as well as in 0.2M solution of butyl alcohol in water (11) [20,61].

FIG. 14. Relative decrease of the strength of polycrystalline naphthalene samples in aqueous solutions of alcohols of the saturated series as a function of the concentration [61].

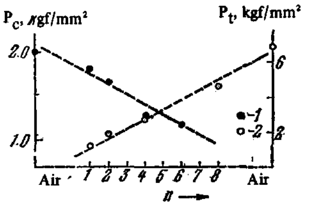


FIG. 15. Influence of alcohols of the saturated series $C_nH_{2n+1}OH$ on the strength P_c of polyethylene (1) and on the maximum stress P_t corresponding to a time t_f = 100 sec to failure for polymethylmethacrylate (2) [62].

pounds with respect to which the medium is not surface-active, while retaining the high catalytic ability of the entire effective principal surface of the catalysts.

4. Molecular crystals of organic compounds. Molecular crystals of organic compounds, and primarily hydrocarbons, are in a certain sense the opposite of ionic crystals. Here, in accordance with the general concepts of selectivity of the decrease of surface energy and of the strength under the influence of the medium, such related media should be nonpolar and low-polar organic liquids. Corresponding investigations on naphthalene, anthracene, urotropin, urea, and other organic compounds were made in our laboratory by N. V. Pertsov, E. A. Sinevich, and co-workers[19,20,59-61].

The results of the experiments with naphthalene single crystals are quite illustrative; we observe here exactly the same phenomena as with pure and amalgamated zinc single crystals. Under ordinary conditions, naphthalene single crystals are very plastic; if the initial orientation is favorable, the samples can be drawn into thin ribbons and, becoming noticeably strengthened, break only after very large elongations (up to 1000% and more!). On the other hand, in the presence of a drop of benzene or heptane saturated beforehand with naphthalene, or else in benzene vapor (after a certain exposure), the same single crystals turn out to be brittle and break along the cleavage plane at relatively small maximum deformation (Fig. 11).

For direct measurements of the surface energy of the naphthalene, we used the method of I. V. Obreimov (in Gilman's variant), namely the splitting of the single crystal along the cleavage plane[60]. The main difficulty in applying this method to molecular crystals, their softness, was overcome by a special method of securing the crystal (Fig. 12). The sample, in the form of a thin plate 1 (1.6–2 mm thick) was glued on one side to a much more rigid metallic plate 2, serving as the elastic element of the scheme, and on the other side to a thick glass plate 3, through which the position of the vertex of the crack in the slightly pierced crystal was determined by the interference lines. Here $\sigma = 3F^2c^2/Eab\hbar^3$, where F is the maximum force (at which the crack begins to grow rapidly) and E is the elastic modulus of the metallic plate 2.

In air, and also in water, which are inactive media, the free surface energy turned out to be the same and maximal: σ_0 = 60 erg/cm². The smallest value of the interphase energy, $\sigma \approx 10$ erg/cm², was observed in benzene, which is the liquid most closely related by chemical composition and structure (i.e., by the character of the intermolecular interactions). σ decreases to 15 erg/cm² in saturated hydrocarbons of the fatty series, namely pentane, hexane, and heptane, to 20 erg/cm² in butyl alcohol, and only to 30 erg/cm² in the more polar ethyl and methyl alcohols.

These data agree fully with the results of mechanical tests. Experiments performed with fine-grained polycrystalline samples of naphthalene in the presence of various organic liquids have shown a decrease in the strength by 30–50 and even by 70%—by a factor of 3 and more. The most effective turned out to be benzene and butyl alcohol; an appreciable effect is produced by saturated hydrocarbons with short chains. The more polar media with relatively larger functional groups exert a weaker action. In contact with water, is in the limit the least related medium, the strength of such a hydrophobic solid is not decreased, as expected. A typical decrease in the effectiveness of the action of the medium on the strength of naphthalene is observed in a series with increasing polarity: propyl alcohol—propylene-glycol—glycerine[19]. Thus, for nonpolar hydrocarbon crystals, the media exhibit just the opposite order in their activity on the surface energy and the strength, in comparison with the influence on the hydrophilic ionic crystals. Since the failure of the polycrystalline samples is brittle, it becomes possible again to verify the applicability of the Griffith relation (Fig. 13); the straight line corresponds to the Griffith equation and the observed small deviations of the experimental points may be connected with differences in the behavior of single-crystal and poly-crystalline samples.

Experiments with aqueous solutions of typical surface-active substances with diphilic molecules (alcohols and fatty acids) have shows that on going over to each succeeding homologue, the concentration corresponding to a given value of the lowering of the strength of the samples decreases by a factor of 3–3.5, in full agreement with the Traube rule that the surface activity increases with increasing length of the hydrocarbon chain (Fig. 14). At the same time, if the dependence of the lowering of the strength on the concentration of the surface-active component is available, it is possible to change over to the adsorption isotherm (since the Griffith relation is valid and permits such a transition, just as for ionic crystals). Then one can estimate, from the limiting adsorption, the smallest area on the active molecule in the monolayer; this value turns out to be $a_m = 20-25$ Å^2 and corresponds to the geometry of the adsorbent surface, the area of emergence of the unit cell of naphthalene on the basal plane[61].

5. **Polymer materials.** The concepts developed above can be extended also to the laws governing the failure of polymer materials in surface-active media, investigated by G. V. Karpenko and A. N. Tynnyĭ and co-workers, by G. M. Bartenev, Yu. S. Zuev, et al. It was established, for example, that propagation of the crack in organic glass is greatly facilitated by the presence of acetone; oils used in hydraulic systems and liquid fuels can greatly decrease the longevity and cause cracking of oil and fuel pipes made of different polymer materials, including teflon, which is known to be exceedingly inert to most media in the absence of mechanical stresses.

Organic polymer materials can be represented both by nonpolar hydrocarbons (in which case the surface is hydrophobic, for example polyethylene), and by compounds containing polar groups, in which case the surface has a "mosaic" character with a definite fraction of polar (hydrophilic) and nonpolar (hydrophobic) sections, such as polymethylmethacrylate. Failure can be accompanied, in principle, by breaking of either intermolecular bonds or the molecular chains themselves; in strongly surface-active media, however, the weakening of the intermolecular interactions can strongly predominate.

The specifics of the structure of polymers gives rise to a very close connection between the effects considered by us and such kinetic processes as penetration of the molecules of the medium into the investigated material (swelling), orientation of macromolecules, etc.

Investigating together with A. N. Tynnyĭ and co-workers (see[62]) the selectivity of the influence of the medium on polymer materials, we used as the main object polyethylene (PE) and polymethylmethacrylate (PMMA). For PE there is a clearly observed stronger embrittlement on going from polar media to nonpolar media that are related to this material. Thus, the tensile strength of the samples decreases 10% in methyl alcohol, 40% in hexyl alcohol, and 50—60% (by a factor 2—2.5) in hydrocarbons, compared with tests in air. The results for PMMA are somewhat more complicated and more varied, owing to the indicated mosaic structure of the damage surface in PMMA. At the same time, the results for substances of the same type are particularly interesting. Thus, for the homologic series of saturated alcohol, the lowering of the strength of PMMA samples decreases monotonically on going from methyl alcohol to octyl alcohol, i.e., in this case the observed dependence is the opposite of that obtained for PE (Fig. 15).

V. A. Kargin and P. V. Kozlov and co-workers (see[63]) have found that very small admixtures of surface-active substances that are not soluble in the given polymer (are incompatible with it) exert a plasticizing influence. These impurities, unlike ordinary molecularly soluble plasticizers, are obviously adsorbed on the internal surfaces of the phase particles in the disperse (microheterogeneous) structure of the polymer material and increase the mutual mobility of the phase elements of the structure.

III. INFLUENCE OF THE REAL STRUCTURE OF A SOLID AND OF THE EXTERNAL CONDITIONS ON THE EASING OF FAILURE AND DEFORMATION IN ADSORPTION-ACTIVE MEDIA

Thus, an analysis of the role of the chemical composition of the solid and of the surrounding medium shows, for the "moderate" (reversible) interactions considered by us, in which the two-phase system comprising the solid and of the medium is thermodynamically stable, that for practically all types of solids there exist media having a related chemical composition and structure and compensating, to a considerable degree, for the bonds that become exposed on the newly produced surface during the course of the failure (i.e., they decrease strongly the free energy of this new surface), leading by the same token to a strong decrease of the strength of the given solid. This is why these effects are so widely general and so distinctly selective.

At the same time, these physico-chemical conditions for the strong lowering of the interphase free energy σ, while making the strength-lowering effects possible in principle, are only the necessary but not the sufficient conditions. The degree and the very form of the influence of the medium on the mechanical characteristics of the solid depends also on many other circumstances; an important role among them is played by the real defect structure of the given solid.

1. **Influence of real (defect) structure.** a) Specific role of grain boundaries. The grain boundaries in a polycrystal are the most pronounced example of the effect of a real defect structure on the degree of adsorption embrittlement.[5)] Having an excess free energy σ_g, the grain boundaries sometimes become the preferred manner of crack propagation even in the external medium has no effect, viz., when the failure is brittle and σ_g plays an important role in the general balance of the energy loss. Consequently, under conditions when the work of producing the failure is greatly reduced, the role of the "margin" of σ_g becomes particularly important when contact with a strong surface-active medium exists, namely, preferred intercrystalline failure of polycrystalline materials is observed (Fig. 16)[18], leading sometimes to complete fracture along the grain boundaries. Whereas low-temperature brittle failure of polycrystalline zinc is predominantly of the transcrystalline type, brittle failure of the same polycrystalline zinc by the action of liquid gallium or mercury proceeds exclusively over the gain boundaries.

[5)] Taking the contents of the preceding sections into account, we use the terms "surface active" or "adsorption active medium" in a broad sense, having in mind a medium that reduces appreciably the free surface energy of the solid both when the solid is in contact with a "related" liquid phase and when an active component is adsorbed; accordingly, the concept "adsorption lowering of the strength" (or "adsorption embrittlement") is used in all these cases.

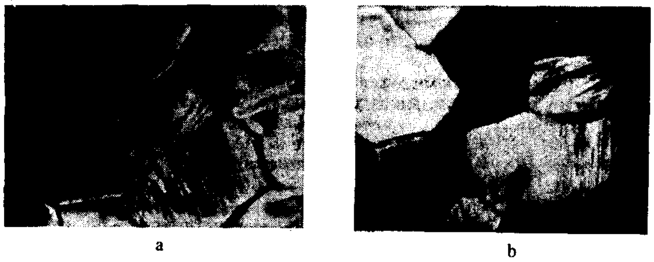


FIG. 16. Failure at zinc grain boundaries in the presence of gallium after 0.63% (a) and 0.83% (b) elongation of the sample [18].

At the same time, if the plasticity of the solid (for example, metallic single crystal) is very high in the initial state, then a transition to a brittle state with a noticeably decreased strength may not set in under conditions when σ is sharply decreased; thus, liquid bismuth does not embrittle copper single crystals as a rule. On the other hand, in the polycrystalline state, the grain boundaries act as a strengthening factor and at the same time as a factor that decreases the plasticity (owing to the slowing down of the dislocation motion in the slip planes, stress concentration, etc.). Therefore under the same conditions, but in the case of polycrystals of the solid, a lowering of σ can already suffice for a transition to the brittle state, for example in the same copper-bismuth pair.

There may, however, be an exactly opposite cause for a greater decrease in the strength of a polycrystal in contact with an active medium than in a single crystal, if the latter is very brittle already in the initial state, without the given medium, as is the case for sodium or potassium chloride at room temperature. In addition to other causes, an important factor that cancels out the action of the medium in this case is the high speed of the cracks over the cleavage plane (which exceeds the speed of the active molecules of the medium).

Having an excess free energy, the grain boundaries act as places where surface-active impurities are adsorbed, both during crystal growth from melts and solutions[6] and as a result of diffusion[23,64]. Different cases are possible here. An easy-melting impurity with low proper surface tension can be strongly surface-active and be energetically adsorbed both on the outer surface and on the grain boundaries, for example phosphorus in iron. Then adsorption over the grain boundaries causes strong embrittlement, for the surfaces with greatly decreased free energies are uncovered as the failure progresses. However, as noted by Glikman[65], the impurity can become adsorbed on grain boundaries but cannot be strongly surface-active on the free surface if the impurity has a high melting point and its own surface energy is high (for example, carbon in iron). Alloying of steels with such elements, not being dangerous, can even be beneficial by forcing harmful impurities out from the grain boundaries, in accordance with the concepts developed by V. I. Arkharov and S. T. Kishkin (see[8]).

b) Certain laws of crack development. The structure defects in solids, which cause strengthening, increased hardness, and long life (under the usual conditions) lead at the same time to a decrease in the thermodynamic stability, owing to the accumulation of excess free energy of these defects in the body. Accordingly, very frequently a solid that has been strengthened with respect to ordinary conditions turns out to be particularly prone to the harmful influence of a medium[9,11].

To the contrary, in those cases when high strength is due to the absence of defects (approach to the ideal state) one can expect the effect of the medium to become weaker, as the case of whisker crystals. Indeed, Rozhanskiĭ [66] has found that mercury weakens zinc whiskers when the diameter of the latter is decreased. Similar phenomena were observed by A. Westwood[15] for large zinc single crystals having no noticeable faults (however, a decrease in the strength took place when the surface was damaged, and also in bicrystals). Investigations performed in our laboratory on large zinc single crystals that were carefully grown and prepared, enabled us to observe (in amalgamated samples) a typical transition from the plastic state to the brittle state following an increase in a specially introduced "rationed" defect, such as pricking by a diamond indentor with a definite force (Fig. 17).

An example of a quantitative analysis of the joint influence of a medium and of defects on the strength is the scheme developed by us and by V. I. Likhtman[16-18], describing the features of failure of single crystals with different initial orientations in the presence of a more or less noticeable strain prior to fracture.

An analysis of the experimental results obtained with metallic as well as with ionic, covalent, and molecular single crystals has shown that to understand correctly the adsorption-influence mechanism it is necessary to consider two stages of the crystal failure process: (1) gradual nucleation and development of "equilibrium" microcracks on the basis of a local strain and stress concentration determined by the initial structure defects and microinhomogeneities of the plastic deformation, which are connected with its dislocation nature, and (2) the relatively rapid propagation of cracks, once they lose equilibrium, over the entire cross section of the crystal[7].

Crack growth during the first stage governed by the flow of plastic strains, and consequently by the action of shear stresses τ, can be approximately described by the relation

$$c = \beta\tau^2L^2/G\sigma, \tag{4}$$

---

[6] It is this which makes it possible to use in casting modifiers that contribute to the production of fine grain by selective slowing down of the growth rate (modifiers of type I, unlike modifiers of type II, which increase the number of crystallization centers).

[7] Unlike the Griffith microcracks, which are cavities of elliptic cross section with a specific surface energy that is constant over the cross section, we consider throughout cracks wtih sharp tip edges at which σ drops rapidly to zero from a constant (maximum) value in a sufficiently broad part of the crack [4]. The theories of such cracks were subsequently developed by Barenblatt [69], Panasyuk [70], and others.

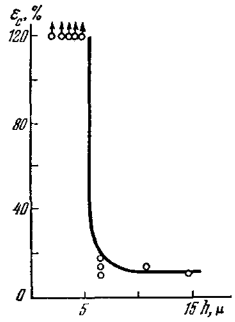


FIG. 17. Defects produced in undamaged zinc single crystals by indentations of different depths h vs. the appearance of enbrittlement, viz., the decrease of the maximum strain ϵ_c in the presence of a mercury film (the samples could be elongated to only 120% with the employed apparatus) [67].

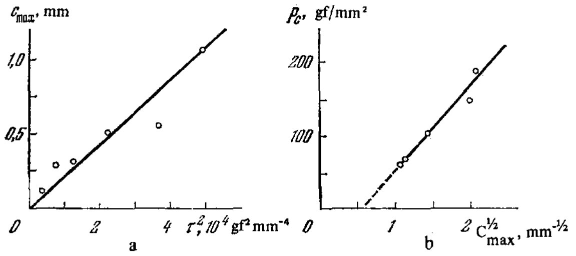


FIG. 18. Plots of c_{max} against τ^2 (a) and of p_c against $c_{max}^{(-1/2)}$ (b) for amalgamated zinc single crystals [18].

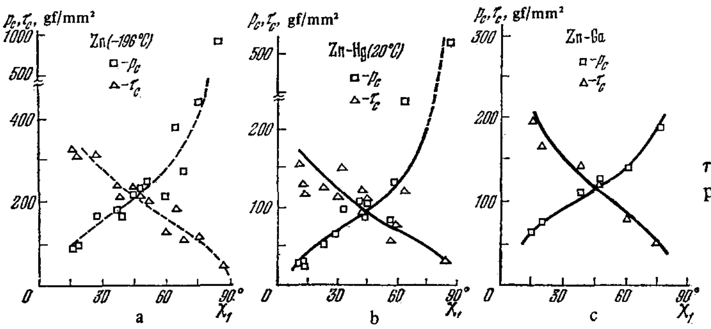


FIG. 19. Limiting values of the normal and shear stresses p_c and τ_c in brittle fracture of differently oriented zinc single crystals: a) pure, b) mercury coated, c) gallium coated [18,24].

where c is the maximum length of the crack under the given conditions, G is the shear modulus, L is a structure parameter that corresponds to the maximum distance within which dislocation microinhomogeneities are produced in the slip plane (the diameter of the single crystal, the grain dimension, etc.), and β is a dimensionless coefficient characterizing the fraction of elastic energy accumulated in the region of the produced microinhomogeneity and serves during the development of the cracks as the work of formation of the new surface. Under brittle failure conditions (more accurately, at a relatively low value of the plastic deformation preceding the failure), the coefficient β approaches unity in order of magnitude, whereas on going from brittle failure to plastic failure it can decrease to $\sim 10^{-3}$ and less (see below). The indicated relation $c = c(\tau)$ agrees with results of a direct observation of crack dimensions on microsections of amalgamated zinc single crystals (Fig. 18)[18].

The onset of the second stage, of the failure proper, can be described as a transformation of a crack of length c into a non-equilibrium crack, when the tensile stress p (normal component) reaches a critical value

$$p_c = \alpha\,(E\sigma/c)^{1/2} = \alpha\,(G\sigma/c)^{1/2}, \qquad (5)$$

where α and α' are dimensionless coefficients that do not differ greatly from unity. Thus, σ plays an important role in both stages.

Comparison of the expressions for $c(\tau)$ and $p_c(c)$ leads to the condition that the product of the normal and shear components of the stress be equal

$$p_c\tau_c = \text{const} = K^2, \quad K = (\alpha'/\beta^{1/2})^{1/2}(G\sigma/L)^{1/2}, \qquad (6)$$

which is also the condition for brittle failure of single crystals, a condition invariant to their orientation[68] and with allowance for two stress components, unlike the known conditions p_c = const (Sohnke's law) and τ_c = const (Schmid's law).

The condition $p_c\tau_c$ = const is most clearly manifest in single crystals in which the only pronounced slip plane coincides with the cleavage plane. Then, if the angle between the slip plane and the longitudinal axis of the sample is equal to χ, we have

$$p_c = K\,(\operatorname{tg}\chi)^{1/2}; \quad \tau_c = K\,(\operatorname{ctg}\chi)^{1/2}.$$

Indeed, these relations are satisfied in failure of differently oriented zinc single crystals under conditions of embrittlement by an active liquid metal (gallium, mercury) and of low-temperature brittleness (Fig. 19). This uncovers a possibility of comparing the values of the surface energy: in the former case K is smaller by a factor 2–2.5 than in the latter; this corresponds to an approximate fivefold decrease of σ upon contact with the molten metal.

2. Influence of deformation and failure conditions. a) Role of temperature and strain rate. The influence of the temperature is manifest in different ways. Of course, the effects vanish when the medium solidifies; this may be accompanied by some strengthening as a result of formation of a hard surface film[18].

At the same time, a weakening and vanishing of the strong influence of the surface-active medium on the strength of a solid is frequently observed also when the temperature is raised to definite critical values; we have named this phenomenon the threshold of in-

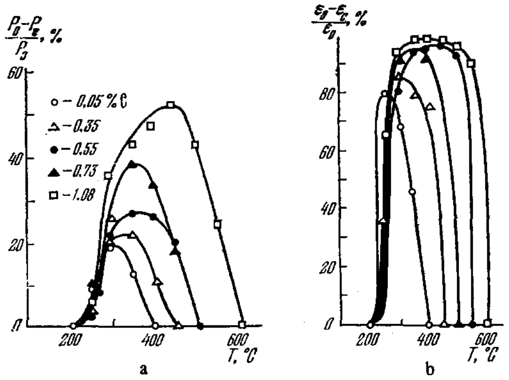


FIG. 20. Temperature dependence of the relative decrease of strength (a) and of plasticity (b) of carbon steels in the presence of tin [18].

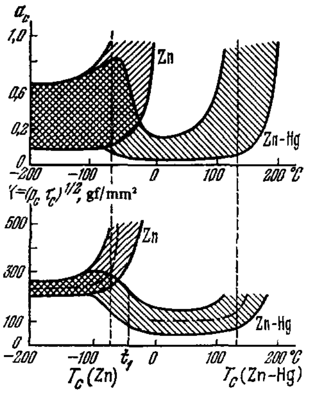


FIG. 21. Temperature dependence of plasticity (maximum crystallographic shear) a_c and of the strength $K = (p_c\tau_c)^{1/2}$ of zinc single crystals with and without mercury coating [71].

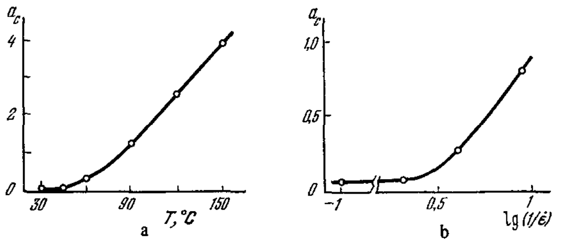
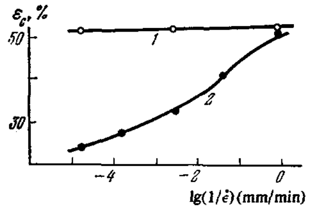


FIG. 22. a) Temperature dependence of the plasticity of gallium-coated zinc single crystals at a constant strain rate 30%/min; b) dependence of the plasticity of gallium-coated zinc single crystals on the strain rate (%/min) at a constant temperature 50°.

FIG. 23. Dependence of plasticity (maximum elongation) of silver chloride single crystals on the tension rate in the case of deformation in air (a) and in solution of aluminum chloride (b) [19,48].



duced cold brittleness, in analogy with the "natural" low-temperature cold brittleness observed when the medium has no effect but when the temperature is sufficiently lowered (Fig. 20, and also 21, where the shaded regions indicate the experimental data for samples of different purity and orientation, the dash-dot lines correspond to the theoretical function K(D); $t_1 = -30°$C is the freezing point of mercry)[16-18].

Such a transition from brittleness to plasticity is due principally to the easier flow of the plastic deformation (dislocation motion) and to the overcoming of various kinds of obstacle defects in the slip planes, i.e., to the gradual disappearance of the deformation microinhomogeneities and to healing of the microcracks with increasing temperature. As a result, the plasticity is restored at sufficiently high temperature even under conditions when the surface energy is decreased[70,72]. The approximate scheme of competition between the influx of dislocations into the growing crack and the gradual removal of the accumulating dislocations (the overcoming of the obstacles by them) leads to the following expression for the strength of single crystals on going through the threshold for both the low-temperature and the "induced" brittle fracture threshold[18,71]:

$$(p_c\tau_c)^{1/2} = K = (\alpha'/\beta^{1/2}(T))^{1/2}(G\sigma/L)^{1/2} = K_0[\beta(T)/\beta_0]^{-1/4};$$
$$K_0 = (\alpha'/\beta_0^{1/2})^{1/2}(G\sigma/L)^{1/2};\quad \beta(T) = \beta_0\exp\{-\exp[Uk^{-1}(T_c^{-1}-T^{-1})]\};$$

Here K_0 is the constant strength level at temperatures below the brittle-fracture threshold, i.e., the minimum value of the strength, and T_c is the temperature of transition from brittleness to plasticity:

$$T_c \approx U\,[k\ln(\nu\lambda b/\dot{\varepsilon}hu)]^{-1};$$

λ is the number of points in which the dislocation segment can "break through" the obstacle (in accordance with the Stroh scheme[73]), ν is the frequency of the atomic oscillations, b is the lattice parameter (the Burgers vector of the dislocations), $\dot{\varepsilon}$ is the strain rate, and U is the activation energy needed by the dislocations to overcome the obstacles, i.e., the activation energy of plastic flow with allowance for the acting stresses and for the possible additional slowing down of the dislocations by the atoms of the surface-active component, say by their adsorption on the dislocations. The product hu represents the spatial and temporal inhomogeneity of the strain: its localization in slip lines spaced on the average a distance h apart, the number of active slip lines at each instant being smaller by a factor u than their total number. On the whole, the factor hu can fluctuate in a wide range, for example from 10^{-3} to 10^{-1} cm. At ordinary strain rates, the logarithmic term in the denominator is approximately 30—35. In accordance with (4)—(6), the sharp decrease of β with increasing temperature in a definite temperature interval means that only a small fraction of the elastic energy of the deformation microinhomogeneities is converted in this case to the work of breaking the bonds and producing a new crack surface, and the overwhelming part becomes dissipated by the thermal fluctuations. The indicated β(T) dependence was observed directly in measurements of crack lengths on microsections of amalgamated zinc single crystals[71].

The threshold of induced cold brittleness is observed not only in metals but also in other types of solids such as covalent crystals (the germanium-gold system[20,41], etc.), ionic compounds (for example, sodium chloride in molten aluminum-chloride[48]), or molecular crystals (naphthalene in a hydrocarbon medium[61]). In other

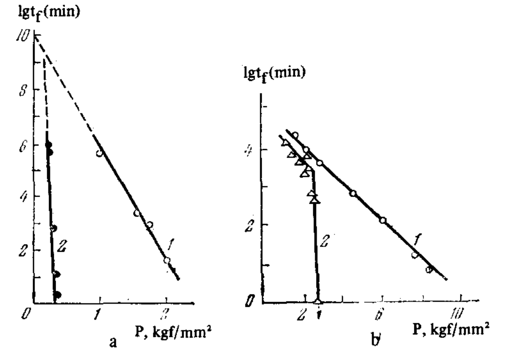


FIG. 24. a) Dependence of the endurance time t_f (sec) on the stress P at 20°C of uncoated zinc single crystals (1) and of amalgamaged samples (2) [18,75]; b) dependence of t_f(sec) on the stress P at 100°C of uncoated polycyrstalline cadium (1) and of galliumcoated samples (2) [18,75].

words, there is usually a limited temperature interval in which the considered effect becomes most clearly pronounced. The effect is hindered at low temperature by the excessive initial brittleness of the given solid (see above) or by solidification of the medium, and at high temperature by the exceeding plasticity of the same body.

The influence of temperature is not limited to these forms. Thus, with increasing temperature, the rate of penetration of the atoms of the medium into the prefailure zone at the vertex of the grown crack increases, and this should strengthen the influence of the medium. With increasing temperature, however, the diffusion "spreading" of the atoms of the medium in the volume of the solid also accelerates (if the amount of the medium is limited and if it has a noticeable solubility in the solid phase); this weakens the influence of the medium. The higher the temperature, the lower the interfacial tension between the solid and the melts, and accordingly the greater the decrease in strength. At the same time, with increasing temperature a decrease takes place in the adsorption of the active component from the solution or from the vapor. Then the action of the medium weakens. Heating can also influence strongly the initial structural (and consequently mechanical) properties of solids, giving rise to recrystallization, phase transitions, etc., which in turn influence the degree of the adsorption effects.

In analogy with the increase of the temperature, a decrease can take place in the strain rate, since after a long time the thermal vibrations ensure a more complete flow of the plastic deformation (Figs. 22 and 23). To the contrary, when the rate of loading is considerably increased, the cracks begin to branch out strongly, the active melt is intensively absorbed by the large new surface, and the propagation of the principal crack is hindered. On the other hand, if the cracks are forced to grow at large strain rates so rapidly that the active melt does not have time to penetrate into their vertices, then the effect stops[9,20]. The joint action of thermal vibrations and mechanical stresses as a rule shortens the time to failure of the sample with increasing load; these irregularities were established for different types of solids by S. N. Zhurkov with co-workers[74]. Under conditions of contact with an active medium, for example a solid metal with a melt, at large stresses, the durability may decrease very rapidly, but at low stresses it remains practically unchanged[18,23,75,76]. A kink appears on the long-term strength curve, and is connected with the same mechanism of the transition from brittleness to plasticity under active tension at a specified strain rate (Fig. 24).

b) Laws governing the propagation of the active medium. Under conditions when the strength is increased by a surface-active medium, the rate of crack propagation is limited by the supply of atoms (molecules) from this medium, i.e., by the rate of surface diffusion or flow over the crack walls to its vertex. Yu. V. Goryunov, B. D. Summ, and the authors (see[77-79]) have compared the crack growth rate in bent metallic plates, on which drops of liquid metal were placed locally, with the propagation rate in the same metals over the free surfaces of the plates (in the absence of oxide films); it turned out that these processes indeed exhibit similar irregularities.

After penetrating into the cracks, the molten metal spreads by different mechanisms during different stages. Over an appreciable area of the cracks (with the exception of the sections directly adjacent to its orifice and vertex), the propagation process can be regarded in a number of cases as a quasistationary flow of a thin layer of the liquid phase over a free surface under the influence of surface-tension forces that are determined by the gain in the total surface energy due to wetting of the solid surface by the liquid. It is the presence in the crack of a liquid phase, the deformation of which does not require noticeable stresses, which makes it possible to realize this gain when one part of the body breaks away from the other; this gain is connected with the lowering of the free energy on the interphase boundary in comparison with the free surface energy of the given solid in vacuum (if $\sigma_{lv} \approx \sigma_{sv}$, then this lowering is not provided by the adsorption layer (see Sec. 1 of Chap. II). Near the vertex (at the tip) of the crack, two-dimensional diffusion, namely surface migration of the active atoms, seems to predominate. A quantitative description of the growth kinetics of the crack can be based on the concepts of the competition of two processes—the propagation of the medium along the walls of the cracks, and the absorption of the atoms of the medium by the volume of the solid adjacent to the crack, as a result of diffusion, especially over the structure defects. Thus, the principal stage of viscous flow of a drop of liquid metal of mass m in the form of a thin film along a "track" of width a over the free surface of the solid is described approximately by the expression

$$x(t) \approx [(3m/2a)(f/\eta\delta\varkappa)]^{1/3}t^{1/3},$$

where x is the distance traversed by the front of the

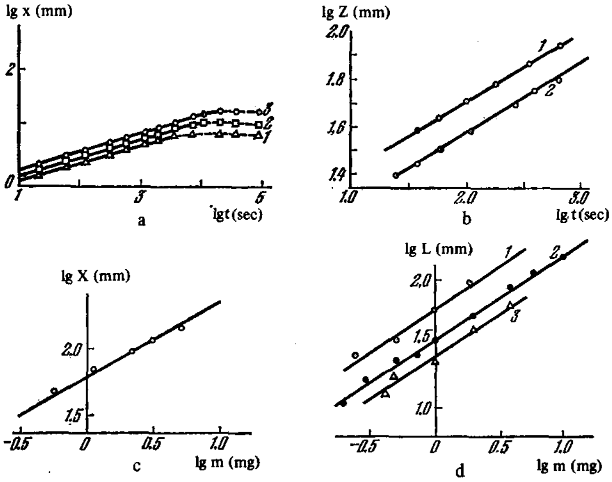


FIG. 25. a) Distance x (in mm) over which mercury spreads on zinc along a track of width a = 1 mm (to one side of the deposited drop), vs the time t (in seconds) at mercury–drop masses m = 1, 2, and 3 mg; b) growth of crack length l (mm) in a zinc plate d = 1.85 mm thick with time t (sec) during the main stage of its development (in one direction away from the point of initiation) at mercury-drop masses m = 40 (1) and 10 (2) mg; c) dependence of the final distance X (mm) over which mercury spreads on zinc in a track of width a = 1 mm (to one side of the point of deposition of the drop) on the mercury-drop mass m; d) dependence of the total final crack length L (mm) on the mercury-drop mass m (mg) in zinc plates of thickness d = 0.8 (1), 0.85 (2), and 3.0 mm (3) [78].

liquid film by the instant t, η and δ are respectively the viscosity and the density of the liquid phase, $\kappa \approx 10$ is a dimensionless coefficient that takes into account the profile of the layer near its front, $f = K\sigma_{sv} - (\sigma_{lv} + K\sigma_{sl})$ is the decrease of the total surface energy of the system following the wetting of 1 cm^2, i.e., the moving force of the considered surface-flow process, and K is the surface roughness coefficient. The final distance reached by the front of the spreading film, and the time t_m of termination of this process, are equal to

$$X \approx 1{,}3\,(C_0 D^{1/2})^{-2/5}(f/\eta\delta\kappa)^{1/5}(m/2a)^{3/5};$$
$$t_m \approx 0{,}7\,(C_0 D^{1/2})^{-6/5}(f/\eta\delta\kappa)^{-2/5}(m/2a)^{4/5},$$

where C_0 is the largest concentration of the absorption-active component in the surface layer of the solid phase and D is the coefficient of volume diffusion.

Accordingly, the kinetics of crack growth in a plate of thickness d following the deposition of a molten drop of mass m, and the final length crack L, are given by

$$l\,(t) \approx [(3m/2d)\,(f/\eta\delta\kappa)]^{1/3}t^{1/4};$$
$$L \approx 2.56\,(C_0 D^{1/2})^{-2/5}(f/\eta\delta\kappa)^{1/5}\,(m/2d)^{3/5}.$$

These relations are in good agreement with the experimental data (Fig. 25). Relations of this type hold also for another form of medium propagation, namely surface diffusion of adsorption-active atoms over the free surface of the solid, and along the walls of the crack.

In addition to the kinetics of medium propagation, a very important factor in the adsorption lowering of the strength is the establishment of a reliable primary contact between the liquid phase and a certain section of the bare surface of the given solid, i.e., the wetting of a surface that is free of oxide and other films. This is added by various types of fluxes and etchants: even a trace of alkali is sufficient to permit a drop of mercury to wet a small area on the order of several square millimeters of a zinc plate, and this initiates propagation of cracks whose newly formed surfaces then absorb the entire drop[78-79]. At the same time, local contact is frequently made possible by mechanical removal or damage of the surface film[11].

The other side of the question is the influence of the very process of formation (directly during the course of bond breaking) of juvenile surfaces during the failure, which favors the wetting. Confining ourselves to the examples already presented (wetting of aluminum-oxide ceramics and carbides by easy-melting metals), we note that under these specifically non-equilibrium conditions an important role can be played by mechano-chemical phenomena.

The relatively rapid penetration of appreciable amounts of adsorption-active components into the interior of a solid can be observed also in the absence of external mechanical action, in migration along the grain boundaries.[8] The adsorption due to such intergranular penetration weakens the solid initially, so that subsequent tests in contact with the given medium show it to be weaker then when loaded immediately after the wetting. Characteristic examples of the influence of such a penetration are: the behavior of polycrystalline zinc after a sufficiently long contact with mercury or with liquid gallium (Fig. 26), of polycrystalline naphthalene in contact with benzene, of polycrystalline sodium chloride in water (previously saturated with NaCl), etc.[20,80]. Nonetheless, even these concrete cases obviously do not provide grounds for specially singling out a third "diffusion" influence of the melt on the strength of the solid from the two main mechanisms of such an influence, corrosion in its various manifestations and adsorption effects (in the broad sense of the influence of lowering the surface energy), including intermediate phenomena. Indeed, some form of transport of the active component is an obligatory condition of either corrosion or of adsorption embrittlement, but taken by itself such a transport of foreign atoms can still not be regarded as the direct reason why it becomes easier to break the bonds in the solid.

Finally, in this brief list of the main conditions that determine the degree and manifestation of the effect of

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[8] The possibility of the limiting case, the penetration of a liquid phase along the grain boundaries, can be formulated, as is well known, as a condition for the formation of a "zero dihedral angle": $\sigma_g > 2\sigma_{sl}$; "spreading" of this kind over the grain boundaries is observed, for example, in contact between gallium and zinc or between bismuth and copper at sufficiently high temperatures, etc.

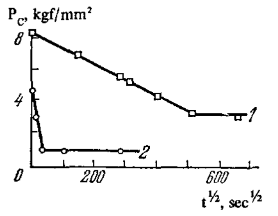


FIG. 26. Dependence of the strength of polycrystalline zinc on the time of contact with mercury (1) and with gallium (2) prior to application of the load [20,80].

the medium on the strength, we must emphasize once more the role played by the stressed state. As already noted, the joint action of the medium and mechanical stresses constitutes a unified common base for the considered adsorption effects. In this case, a characteristic feature of the given group of phenomena is the preferred influence of stressed states, with predominance of the tension components, whereas under conditions of compressive stresses, especially in surface layers, the action of a very active medium may not come into play. Accordingly, in contact with a surface-active medium, a favorable, i.e., very dangerous, effect is frequently produced by various stress concentrators, recesses, threads, etc.[10].

Finally, in this brief list of the main conditions that determine the degree and manifestation of the effect of the medium on the strength, we must emphasize once more the role played by the stressed state. As already noted, the joint action of the medium and mechanical stresses constitutes a unified common base for the considered adsorption effects. In this case, a characteristic feature of the given group of phenomena is the preferred influence of stressed states, with predominance of the tension components, whereas under conditions of compressive stresses, especially in surface layers, the action of a very active medium may not come into play. Accordingly, in contact with a surface-active medium, a favorable, i.e., very dangerous, effect is frequently produced by various stress concentrators, recesses, threads, etc.[10].

Thus, the degree of manifestation of adsorption lowering of the strength depends strongly on very many factors and can vary in a very wide range. This is the main reason for the apparent contradictions in the published data on the presence or absence influence of a medium in various cases.

Consequently, in those cases when the contact with the adsorption-active melt cannot be eliminated, protection against adsorption embrittlement requires that at least one of the indicated conditions not be satisfied[26]. On the other hand, for a useful application of the effects in question it is necessary to choose the most favorable combination of conditions: a polycrystalline metal should be subjected to a complicated stressed state with high concentration of the shear and tensile stresses following repeated actions at sufficiently large rates (frequencies), but such that any exposed juvenile surface has time to become covered with a thin layer of the active medium. Such conditions can be realized, for example, in cutting of different metallic and nonmetallic materials, particularly drilling in the presence of a medium that is strongly surface-active relative to the given material (Fig. 27)[20,81-83].

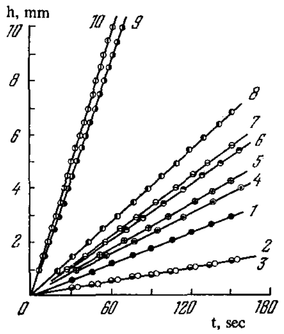


FIG. 27. Dependence on the time t, of the depth of penetration h of a drill into stainless steel 1Khl8N9T: 1) dry, 2) in petroleum oil 3) in emulsion, and in the following molten metals: 4) Wood's alloy, 5) tin, 6) gallium, 7) indium, 8) In-Ga-Sn eutectic, 9) Sn-Pb eutectic, 10) Sn-Zn eutectic [83].

3. **Spontaneous dispersion of solids following a very strong decrease of the free interphase energy. Easing of mechanical dispersion.** We now consider a special limiting case of the manifestation of adsorption effects—without participation of mechanical stresses; this case of very strong decrease in the specific free surface energy on the boundary between condensed phases (in the absence of unlimited molecular solubility, i.e., in the presence of thermodynamically stable interphase boundaries), when spontaneous dispersion of one of these phases into the other with formation of a lyophilic colloidally-dispersed system is possible. Such thermodynamically stable systems can occur if the increment of the free energy of the system, due to the development of the interphase surface upon dispersion, is offset by the growth of entropy of the system following uniform distribution of the produced particles in the volume of the dispersion medium, due to the Brownian motion of the particle[7,16]. The increase of the free energy of the system following dispersion of a unit volume of the future dispersed phase into n particles with linear dimensions δ in ν moles of liquid (containing $N = \nu N_A$ molecules) can be approximately estimated by the following relation[16,18]:

$$\Delta F = n\alpha\delta^2\sigma + kT\ \{n \ln [n/(n+N)] + N \ln [N/(n+N)]\},$$

where the dimensionless coefficient α, which is close to unity, takes into account the shapes of the particles. Since the dimensions of the colliodal particles ($\delta \approx 10^{-6} - 10^{-5}$ cm) greatly exceed the molecular dimensions ($b \approx 10^{-8}$–10^{-7} cm) and the condition $N \gg n$ is satisfied, the expression for ΔF takes the form

$$\Delta F = n\alpha\delta^2\sigma - kTn\,[\ln (N/n) + 1],$$

or, since $n \approx 1/\delta^3$,

$$\Delta F = \alpha\sigma\delta^{-1} - \beta kT\delta^{-3},$$

where the coefficient β ranges from several units to several dozen. The condition $\Delta F \leq 0$ means that the dispersion is favored energywise, but the particle dimensions for which this dispersion takes place is important: only if the quantity $\delta = \delta^*$ determined from the equation $\Delta F(\delta) = 0$ exceeds noticeably the molecular dimensions b can a colloidal phase actually be present. In other words, the condition for spontaneous dispersion can be written in the form

$$\delta^*/b = (\beta kT/\alpha b^2\sigma)^{1/2} = (\gamma kT/b^2\sigma)^{1/2} \gg 1$$

at room temperature, this condition is satisfied if the

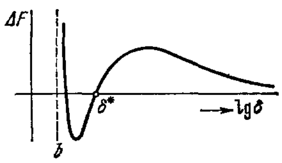


FIG. 28. Diagram illustrating the dependence of the change of the free energy ΔF of the system on the particle dimension δ in spontaneous dispersion of a body into particles of colloidal dimensions, under conditions when the free surface energy at the boundary with the dispersion medium is greatly decreased, in the absence of true (molecular) solubility or if the latter is small [18].

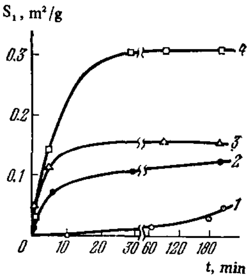
interphase energy σ drops to values not exceeding several tenths of an erg/cm^2.

This condition, while necessary, is however not sufficient to form a stable colloidally-dispersed system: it is necessary also that the dispersion not continue down to molecular dimensions, i.e., that the free energy of the system again increase abruptly as δ approaches b (Fig. 28). This requirement reflects the conditions formulated above with respect to the limited true (molecular) solubility, or, equivalently, the preservation of thermodynamically stable interphase surfaces at small but finite positive values of σ[18,84].

A simple example is the case of highly-dispersed porous structures with point contacts between the particles. The dispersion of the body into component particles then causes (even at not a very great decrease of the interphase energy) a relatively small increment of the free energy of the system, since only the contact cross-section area becomes exposed, and this area is small in comparison with the total surface of the particles. Once the porous body is broken up into the colloidal particles of which it is made up, further pulverization is greatly hindered by the sharp growth of the free energy of the system, occurring when the new surface is produced by crushing the particles themselves. It is thus obviously possible for the curve $\Delta F = \Delta F(\delta)$ to have a minimum, and furthermore at negative values of ΔF, i.e., it is possible for a perfectly stable colloidal system resulting from spontaneous dispersion to exist. Of course, strictly speaking, in the general case we have here only relative thermodynamic stability, since it is assumed that the practical absence of molecular solubility makes the gathering together of the particles by recrystallization impossible.

An example of complete thermodynamic stability of a spontaneously produced colloidally-dispersed system can be the process of micelle production in aqueous solutions of soap-like surface-active substances, for example, non-ionogenic soaps of the type of polyethylene glycol esters with long hydrocarbon chains. In this case the abrupt growth of ΔF at small δ is determined by the relation $\sigma = \sigma(\delta)$. Indeed, the breaking up of the micelles, which have a shell of polar groups, and accordingly a very low value of σ on the boundary with the water, can lead to an uncovering of the hydrocarbon nuclei and to formation of new interfaces between the hydrocarbons and the water, with high values of σ, i.e., to a rapid growth of the effective value of σ with decreasing δ; this growth can be quantitatively estimated on the basis of an approximate geometrical model (A. V. Pertsov)[84].

FIG. 29. Specific surface of powder S_1 vs the grinding duration t for pure zinc (1) and following introduction of gallium in amounts of 1% (2), 3% (3), and 10% (4) [19,86].



Similar phenomena were observed also in spontaneous swelling in water and in the melting (colloidal dissolution) of certain minerals such as bentonite clay, with characteristic layer structure and mosaic surface of particles, or of graphite in liquid sodium. One of the most characteristic cases of spontaneous formation of lyophillic colloidally-dispersed system is the formation of critical emulsions (with limited mutual solubility of components) near the mixing temperature[85].

Cases of this kind are sufficiently widespread in nature and can play an important role (particularly also in biological processes), but we encounter more frequently conditions such that while the surface energy of the solid is strongly decreased on the boundary with the medium, the decrease is still insufficient for spontaneous dispersion to set in; the process of mechanical dispersion, namely the pulverization of a great variety of materials, is then greatly facilitated.

For example, when an attempt is made to break up a plastic metal such as zinc in an ordinary vibrating ball mill, the granules are merely "burnished" and it is practically impossible to pulverize them, whereas the presence of 1% of gallium leads to a 200-fold increase of the pulverization rate (Fig. 29). Gallium exerts a similar action also on the pulverization of tin, cadmium, aluminum, and bismuth[9)]; an appreciable acceleration is observed also in a number of organic media and in aqueous solutions of typical surface-active substances (especially graphite)[10)].

In general, fine pulverization cannot be in principle a purely mechanical process. Since it requires the formation of a tremendously large new surface, it must require the interference of physico-chemical factors in order to control the phenomena on the interphase boundaries[26,55]. The role of the adsorption lowering of the strength consists here not only in the facilitation of the breakup into possibly smallest particles without strengthening (without deep amorphization), but also in

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[9)] When gallium interacts with tin, deep structural changes are observed also in the absence of external mechanical stresses (on as a result of internal stresses, structure-defect energy, or the formation of a solid solution) [18,84]: a tin single crystal coated with a thin film of liquid gallium is transformed spontaneously and gradually into a polycrystal, and the reflections produced by the single crystal vanish from the x-ray pattern and give way to the picture typical of a polycrystal.

[10)] Gurwitsch [87] observed a transition (peptization) of lead into a colloidal dispersion following addition of oleic acid to non-polar kerosene in which lead shot was shaken. In this case, however, the decisive role is played by the chemical reaction, namely formation of a soft film of lead oleate, which can be easily removed by friction. In pure form, this case represents the technique of chemical polishing of metals and glass subsequently perfected by I. V. Grebenshchikov.

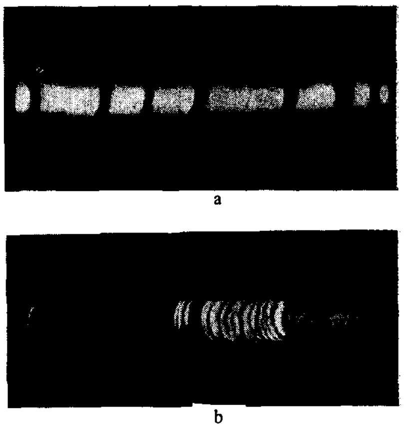

FIG. 30. Slip traces on the surface of tin single crystals following tension in air (a) and in a solution of oleic acid in petroleum oil (b).

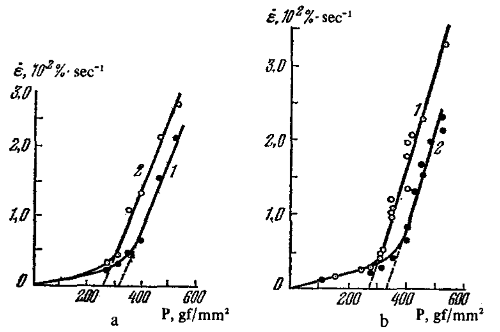

FIG. 31. Dependence of the plastic strain rate $\dot{\epsilon}$ of lead single crystals in the initial region of the creep on the applied stress P in a 0.01-N solution of H_2SO_4 (a) at a null-charge potential $\varphi_0 = -0.70$ V (1) and at a potential $\varphi = -0.87$ V (2) and in air (b) for pure samples (1) and for those coated with an oxide film 0.25 thick (2) [88,91].

the prevention of aggregation, in the destruction of coagulation contacts that are produced again between the particles. Such a destruction of the developed structure is essential also in the subsequent operations with the obtained finely-dispersed material, particularly to facilitate mobility, to obtain maximally dense and homogeneous packing of the particles, in casting of various parts, for example in powder metallurgy or in the production of structural materials.

4. Easing of plastic deformations in solids under the influence of an adsorption-active medium. The very manifestation of the adsorption effects can vary. with the character of the interatomic interactions, with the real structure of the body, and with the deformation conditions. If none of the conditions necessary for an abrupt decrease of the strength and for embrittlement are satisfied, and a decrease in the surface energy on the interface does take place, then an effect that in a certain sense is the opposite can occur, namely easing of plastic flow of a crystal, or plasticization.

A typical example of the plasticizing action of a medium can be the lowering of the yield point and of the strengthening of metallic single crystals in solutions and vapors of organic surface-active substances, accompanied sometimes by a clearly pronounced breaking up of the glide lamellas (Fig. 30), which were investigated in detail by A. B. Taubman and E. K. Venstrem, and by V. I. Likhtman and co-workers (see[2,6,18]).

We have posited that the observed facilitation of plastic flow should be regarded as a result of the lowering of the potential barrier that is overcome by the dislocations as the points of their emergence to the crystal surface move[16,18,72]. The existence of this barrier is connected with processes of realignment and breaking of the interatomic bonds, which accompany the formation of new elementary cells of the surface upon formation and development of the slip lines. Lowering of the free surface energy upon adsorption of surface-active molecules corresponds to a decrease in the work consumed in these processes. Under suitable conditions, the increase of the mobility of points where the dislocations emerge facilitates the displacement and multiplication of dislocations in a definite layer of metal adjacent to the surface, at least in a depth commensurate with the average length of the dislocation segments in the crystal. In relatively thin single crystals of plastic metals with low dislocation density, the entire volume of the sample begins to "feel" the surface, especially near the yield point, where small changes in the resistance to deformation lead to a noticeable acceleration of the flow[88].

In the examination of the relation between the rates of the dislocation-accumulation process in the surface layer and the process of their overcoming the surface potential barrier, we have shown that the dependence of the optimal temperature T_{opt} of the plasticization effect on the strain rate $\dot{\epsilon}$ can be represented in the form

$$T_{opt} \approx U_a \, [k \ln (\nu b/\dot{\epsilon} h u)]^{-1},$$

where the activation energy U_a is close to the work required to produce a unit cell of the surface, i.e., $U_a \approx b^2\sigma$. The parameters h and u, as above (Sec. 2a of the present chapter) take into account the spatial and temporal inhomogeneity of the deformation (its localization in slip lines); the product hu can amount to $10^{-3}-10^{-1}$ cm. Putting $\nu \approx 10^{12}$ sec^{-1} and b on the order of several Å, we have $\ln(\nu b/hu) \approx 12-17$.

The presented relation can be compared, for example, with the data on the influence of the temperature and strain rate on the facilitation of plastic flow of tin single crystals in solutions of surface-active substances in nonpolar petroleum oil[18]. According to these data, at room temperature the effect is maximal at $\dot{\epsilon} \approx 10^{-3}$ sec^{-1}, whereas at 100°C the maximum manifestation of the effect is observed at $\dot{\epsilon} \approx 10^{-1}$ sec^{-1}. Substitution of these values in the indicated relation leads to the following estimates: $\ln(\nu b/hu) \approx 15$ and $U_a \approx 0.9 \times 10^{-12}$ erg; these agree in order of magnitude with the quantities in the scheme under consideration; indeed, $b^2\sigma \approx 10^{-15}$ cm$^2 \times 10^3$ erg/cm$^2 \approx 10^{-12}$ erg.

The surface barrier that the dislocations overcome can be modified also by other physico-chemical methods; thus, the surface energy can be lowered by electrically charging the surface (in accordance with the known equation $\partial\sigma/\partial\varphi = -e_s$, and the laws of the electrocapillary effect investigated by A. N. Frumkin and his school of electrochemists.[89] As shown by Likhtman and Venstrem (see[6,18,90]) and recently by L. A. Kochanova (see[19,91]), a complete analogy is observed between plasticization due to adsorption of surface-active substances and that resulting from electrically charging the surface (Fig. 31).

Adsorption plastification is a very universal effect and occurs in all types of solids. Different organic media, for example hydrocarbons with relatively large molecules, accelerate the plastic flow of naphthalene single crystals, if the masking action of the lowering of the strength and plasticity is eliminated. Gypsum single crystals have a clearly pronounced creep in water vapor[11)]. Moreover, even perfectly elastically-brittle materials such as inorganic glasses reveal an irreversible creep in the presence of water upon indentation, when compressive stresses predominate[92]. In general, the conditions for microindentation, when the deformation takes place only in the sections of the body that are immediately adjacent to the surface, are very favorable for plastification and make it possible to reveal it by observing the penetration of the indentor or from the geometry of the dislocation rosette, both for metals[93] and for ionic crystals, upon adsorption of active molecules[82,94] or application of an electric field[95]. In ionic crystals and semiconductors, an important role can be played here also by the interaction of the surface with the charged dislocations, if the interaction is sensitive to the adsorption of the ions on the surface or to the adsorption-induced changes in the surface energy levels[82].

The plasticizing influence of surface-active substances is used in die casting of metals[96].

Surface-active components of lubricants play an important role in friction joints, helping automatically to regulate the wear conditions[97].

Under intensive and repeated action, the easing of plastic deformation in a surface layer, as shown by T. Yu. Lyubimova of our laboratory, can lead at a definite stage also to an opposite result, to additional strengthening by accelerated accumulation of distortions in the metal structure. Direct electron-microscope observations by B. I. Kostetskiĭ and co-workers have shown that in this case the dislocation density in the surface layer increases appreciably. Under suitable conditions (temperature, stress, velocity, etc.), such a unique "conditioning" can be used to improve the structure and the mechanical properties of the surface layer. At the same time, we find ourselves already at the borderline of the manifestation of adsorption fatigue, which was exhaustively studied by G. V. Karpenko and co-workers[6,10], who have shown that at a suitable stress level the adsorption-induced accelerated accumulation of defects in the surface layer, in the case of periodic action, can lead after a definite number of cycles to a premature development of cracks and to spoiling of the part.

* * *

The foregoing examples do not exhaust all the varied effects produced by surface-active media on the mechanical properties of solids, and the concepts advanced concerning the nature and mechanism of these phenomena are still far from explaining the observed irregularities completely. Among the urgent problems in this field are both the development of comprehensive experimental research, especially in "pure" reproducible conditions, and further theoretical analysis, primarily of the mechanism of the elementary acts of the fracture and realignment of the bonds when foreign atoms or molecules take part. At the same time, it is advisable to give maximum coverage to such "intermediate" phenomena as the effect of chemical adsorption on the mechanical characteristics, mechanical finishing under conditions when chemical, electro-chemical, and mechano-chemical reactions and corrosion under stress take place on the surface of a solid. It is undoubtedly important to study the influence of active media on the adhesion strength at the interphase boundaries in various macro- and microheterogeneous materials, i.e., processes of "adsorption lowering of cohesion strength"). Finally, in addition to continuing research on structural materials, appreciable interest attaches to the transition to new (geological and biological) objects.

[11)] The solvent can increase the plastic deformation in brittle bodies for another reason, not by lowering the resistance to plastic flow but by increasing the strength as a result of dissolving a surface layer that contains defects—cracks (the Ioffe effect); in this case the influence of the medium becomes strong only to the extent to which it is not saturated by the given substance.

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