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SURFACE PHENOMENA IN THE DEFORMATION AND FRACTURE OF METALS

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1

In the deformation† and fracture of solid bodies an important part is played by small quantities of surface-active substances present in the surrounding medium or forming a component of the solid itself. The basis of this phenomenon, termed the Rebinder effect, is a decrease in the free energy of the new surfaces, formed and developed in the course of deformation and fracture of the solid, owing to reversible (physical) adsorption of surface-active molecules or atoms; this facilitates the development of such new surfaces and leads to a considerable reduction in the forces required to deform and fracture the body[1-17].

Adsorption may occur in various ways: adsorbed films may be formed on the external surfaces of the body by direct approach of surface-active material from the surrounding medium, or else such films may arise on internal micro-surfaces (on the walls of micro-cracks) as a result of rapid penetration of adsorption-active atoms inside the body by surface diffusion (migration) along defects in the crystal structure — the boundaries of blocks and grains, hollow dislocation centres, etc.[4,5,11,15,16,18]. Linear and two-dimensional structural defects, having an excess of free energy, serve as points for the selective adsorption of surface-active atoms arriving from the external surface or from the bulk of the material; in consequence, the behaviour of these defects during the course of deformation of the body is changed, e.g. their mobility is altered or their growth favoured, with the formation of a large free surface[15,19].

These changes in mechanical properties under the influence of adsorption have nothing to do with corrosion processes (including intercrystalline corrosion in polycrystalline solids), since they are produced by chemically inert media or by impurities present in extremely small amounts[5,11]; nor are these effects connected with dissolution, since the solids studied are either completely insoluble in the media or else (if a thin coating of molten metal acts as the medium) their solubility is low and, owing to the small mass of the coating, cannot lead to any substantial change in the specimen as a whole. Further, these effects relate to the surface of the metal itself, and are not due to the presence of oxide films, which can have only an incidental effect[5,20].

† In this review terms like deformation, strain, extension, etc. are often used synonymously (Ed. of Translation).

The development of a change in mechanical properties due to adsorption depends on several physicochemical factors, and primarily on the surface activity of the medium (or component) in relation to the given solid[6,11-14], i.e. on the absolute decrease in free surface energy resulting from adsorption. In addition, the experimental conditions — especially the temperature and the rate of deformation — profoundly influence the development on the effect[10,21-24]. Depending on these factors, the effect of surface-active substances on deformation and strength properties may take several quite different forms[13,14,24]. Thus an adsorption-active medium may soften the solid (metallic specimen); in such a case the yield point, and also the strain hardening in experiments with a constant rate of extension, is reduced or the rate of creep is increased in constant-load tests[5,23,24]. In other cases adsorption leads to the appearance of extreme brittleness in very plastic materials (single crystals of metals), accompanied by a sharp reduction in strength[11,12,22,25]. Under the influence of a strongly surface-active medium a solid may in certain circumstances show a tendency to disperse spontaneously into particles of colloidal dimensions[6,11-14].

Effects of the type under discussion find important practical application in the working of metals by pressure[26,27] and by cutting[28], in the find grinding of solids[7,8], etc. The study of these phenomena forms part of a new border-line science — the physicochemical mechanics of solids — developed by P. A. Rebinder and his collaborators, bordering on molecular physics, solid-state physics, physical chemistry, and the mechanics of continuous media. It has the aim of producing solids of specified structure and mechanical properties and of developing systematic methods for the mechanical working of solids by utilising physicochemical factors[6,29].

Single crystals of metals (including high-purity metals) provide the most interesting and also the simplest material for studying the effect of surface-active agents. In this case it proves possible to elucidate the most general and characteristic laws governing the observed phenomena, without complications due to grain boundaries, the presence of interfaces between different solid phases, and other subsidiary factors. At its present stage of development, the modern theory of the plastic deformation of crystalline solids — the theory of dislocations — which enables the mechanism of the action of the medium on the deformation and strength charaeteristics of a solid to be analysed[13-15,19,30], mainly in semi-quantitative terms, can be most usefully applied to materials of this kind. Such experiments will be examined in this survey.

2

The softening of metallic single crystals by organic adsorption-active media has been described in several papers[3-5,9]. Most authors have used dilute solutions of saturated and unsaturated aliphatic alcohols and acids and their substituted derivatives (i.e. substances whose molecules contain a polar group and a long hydrocarbon chain, such as oleic acid, palmitic acid, cetyl alcohol, etc.) in a non-polar hydrocarbon solvent (e.g. liquid paraffin). Experiments have been made on single crystals of tin, aluminium, and lead with extension both at a constant rate on a Polanyi type of apparatus and also under constant load. In the former case the effect of the medium is shown by a considerable decrease, almost to half, of the yield point (or crystal shearing stress) and of the strain-hardening (Fig. 1),

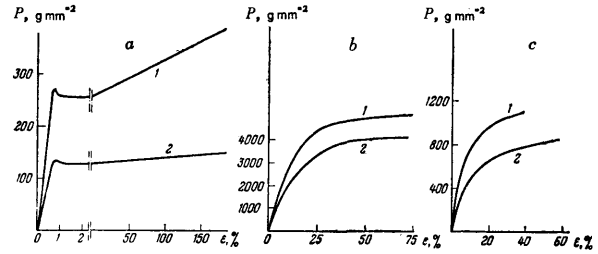


Fig. 1. Curves for the straining of single crystals: *a*) tin in an inactive medium (curve 1) and in a 0.2% solution of oleic acid (curve 2)[5]; *b*) aluminium in an inactive medium (curve 1) and in a 0.3% solution of cetyl alcohol (curve 2)[5]; *c*) lead in an inactive medium (curve 1) and in a 0.2% solution of palmitic acid (curve 2)[10].

TABLE 1. Values of the maximum softening effect and corresponding concentration of surface-active component for various organic surface-active media.

Medium	$\delta\epsilon_m$, %	c_m, moles kg^{-1}	Medium	$\delta\epsilon_m$, %	c_m, moles kg^{-1}
Octane as solvent			Dodecyl chloride	33	2.30
Propionic acid	123	0.59	Propyl sulphide	48	2.22
Octanoic acid	122	0.12	Aerosol OT	95	0.044
Stearic acid	126	0.0071	*Benzene as solvent*		
Oleic acid	190	0.0065	Propionic acid	120	3.90
Propyl alcohol	120	1.68	*Water as solvent*		
Dodecyl alcohol	118	0.20			
Octylamine	102	0.42	Propyl alcohol	49	4.10
Methyl laurate	38	1.50	Aerosol OT	no maximum	
			Aerosol MA		
			Sulfonol		

and in the latter case by a several-fold increase in the rate of plastic flow. Adsorption also changes the character of the slip lines on the crystal surfaces; this was particularly marked with single crystals of tin, which showed the characteristic phenomenon of a pronounced breaking up of the slip blocks on straining in an active medium[5].

The manner in which the magnitude of the softening effect depends on the nature of the polar group and the concentration of surface-active agent in the solution has been studied in detail in several investigations[5,31]. General rules were obtained governing the effect of surface-active substances on the deformation of metals as a function of the molecular properties and chemical structure of the former.

The external media used were the solvents octane, benzene and water, and solutions in them (concentration range 0–100%) of surface-active substances — aliphatic acids, alcohols, amines, ethers, halogenated and thio derivatives, soaplike colloidal electrolytes (sodium cetylbenzenesulphonate and dialkyl sulphosuccinate) and the wetting agents Sulfonol $C_{16}H_{33}.C_6H_4.SO_3Na$, Aerosol OT $C_8H_{17}OOC.CH_2.CH(SO_3Na).COOC_8H_{17}$, and Aerosol MA $C_6H_{13}OCC.CH_2.CH(SO_3Na).COOC_6H_{13}$. The hydrocarbons were carefully purified from polar impurities, and the surface-active substances were purified by repeated redistillation or recrystallisation.

The investigations were carried out on single crystals of tin and lead. The effect of the active medium was assessed from the relative increase in the deformation ϵ of the specimen in the surface-active medium compared with its deformation ϵ_0 in an inactive medium (the pure solvent) after the same periods of time, i.e. from the magnitude of $\delta\epsilon = [(\epsilon - \epsilon_0)/\epsilon_0] \times 100\% = f(c)$ during the creep of the single crystals, for solutions of different concentrations.

Solutions of surface-active substances in hydrocarbons (octane and benzene) exhibit in all cases a more or less sharply marked concentration optimum. As the concentration is increased, the effect rapidly reaches a maximum, and then gradually falls down to the lowest values in the pure surface-active component at $c = 100\%$.

Table 1 shows that the maximum effect $\delta\epsilon_m$ on single crystals of tin and the concentration c_m of surface-active component corresponding to this maximum are characteristically linked with the molecular properties of the active component. The magnitude of the effect in hydrocarbon media is determined solely by the nature of the polar groups in the surface-active molecules. The adsorption effect is most marked in solutions of aliphatic acids and alcohols in octane, its maximum value being almost the same, 120–125%, in the two homologous series.

A considerable adsorption effect is exhibited also by Aerosol OT and octylamine, $\delta\epsilon_m = 95\%$ and 102% respectively; a far smaller effect is exerted by compounds having weakly polar groups — esters and halogenated and thio derivatives — for which the values of $\delta\epsilon_m$ are 38% with methyl laurate, 33% with dodecyl chloride, and 48% with propyl sulphide respectively.

Further, the maximum effect at the optimum concentration is completely independent of the length of the hydrocarbon chain of the surface-active molecules. Independently of the position of the homologue in the series of aliphatic acids, the value of $\delta\epsilon_m$ remains unchanged at 122–125%, as is also found in the aliphatic alcohols. This result is consistent with the fact that hydrocarbon solvents, and in particular octane, are inactive with respect to tin.

Although the length of the hydrocarbon chains has absolutely no influence on the maximum value of the adsorption effect, the concentrations c_m, at which the maximum effect occurs, obey laws similar to Traube's rule, but with a smaller coefficient. As can be seen from Table 1, in the series propionic, octanoic, stearic acids, these concentrations are 0.59, 0.12, and 0.0071 mole kg^{-1} respectively, decreasing by a factor of 1.3–1.4 for each CH_2 group.

The decisive role of the polar groups in the surface-active molecules is also supported by the increased effectiveness of an unsaturated compound, oleic acid. Compared with stearic acid, the value of $\delta\epsilon_m$ has increased from 126% to 190%. Similarly, introduction of a double bond into the chain of an alcohol molecule markedly increases its activity (from 120% for propyl alcohol to 182% for allyl alcohol).

The efficiency of the surface-active substances is substantially affected by the molecular properties of the solvent. Replacement of octane by benzene shifts the concentration c_m at which the additive (propionic acid) gives its maximum effect from 0.59 to 3.9 moles kg^{-1}, i.e. increases it by a factor of 6.5, while the magnitude of the effect remains unchanged. In aqueous solutions, e.g. of propyl alcohol, interaction of the polar groups results not only in a shift of c_m (from 1.68 to 4.10 moles kg^{-1}) but also

in a decrease in the magnitude of the effect (from 120% to 49%). In this case the effect includes that of the solvent, water, which is an active medium with respect to tin and itself produces an effect amounting to 16%.

Similar regularities are observed with lead.

The above experimental data, which establish that the softening of metals depends on the composition of the external medium, not only confirm the purely adsorptive nature of the effect but also show that the influence of surface-active substances is characterised by laws typical of adsorption at liquid interfaces. In adsorption from solutions in hydrocarbons at a boundary with water, the surface activity of organic molecules is determined mainly by the work required to expel their polar groups from the solution at the interface, and the length of the hydrocarbon chains, solvated by the hydrocarbon medium, has a very slight effect[32]. These measurements were carried out with water-insoluble higher homologues of surface-active substances, thereby avoiding their distribution between the phases and the possibility of any appreciable adsorption from the aqueous phase. The deformation behaviour of tin and lead in organic surface-active media is likewise characterised by complete insensitivity to hydrocarbon molecules. This provides the grounds for drawing an analogy between adsorption from hydrocarbon solutions at the boundary with water and at metal surfaces.

Comparison of the isotherms for the reduction in surface tension, $\Delta\sigma = f(c)$, at the interface between water and solutions in octane with $\delta\epsilon = f(c)$ isotherms for the active substances investigated on tin and lead indicate the complete similarity of the laws governing the effects of adsorption-active substances on the free energy of liquid interfaces and in facilitating the deformation of metallic single crystals.

These laws are as follows:

(*a*) The polar groups of surface-active molecules are arranged in the following sequence of effectiveness:

$$COOH \simeq OH > NH_2 \gg S \simeq COOR > Cl.$$

(*b*) The deformation activity in homologous series increases according to Traube's rule with the same low coefficient 1.2–1.3 as with the surface activity in octane, in which it is 1.1–1.2.[32]

(*c*) Double bonds in the hydrocarbon chains of surface-active molecules behave as weak polar groups, and therefore strongly increase the surface activity of the compound.

(*d*) In benzene, which is more strongly polarisable than octane, the surface activity of organic compounds is markedly depressed[33], and in conformity with this the deformation activity of solutions of surface-active substances is lower in benzene than in octane. In a polar solvent, water, the deformation activity of surface-active substances falls markedly. This reduction in the energy of interaction of adsorbed molecules with a metal surface is quite consistent with the fact that the polarisation of polar groups in water and their hydration[34] considerably depress the surface activity of organic substances in aqueous solutions.

These results show that attempts[35-37] to explain the influence of an external surface-active medium on the deformation of metals in purely chemical terms are quite unjustified. But the data cited are still insufficient to explain completely the occurrence of maxima in the isotherms for the softening of metals. Several papers[5,10,23,24] have also been concerned with the variation of the softening action of the medium with temperature and rate of deformation.

In analysing the mechanism of the softening action of organic surface-active media, the following facts must be taken into account[14]:

1. Since normal diffusion of large organic molecules within a metal is impossible, and since they can penetrate into a metal only along structural defects (walls of micro-cracks) by two-dimensional migration, the effect must be based on purely surface interaction between the specimen and the medium. This interaction is shown by a diminution in the free energy σ of the surface of the specimen, brought about by reversible adsorption from the surrounding medium.
2. Compared with the free surface energies of the metallic single crystals used ($\sim 500-1000$ ergs cm^{-2}), the decreases produced in these experiments by adsorption of organic substances are not very great; they are of the order of several tens of ergs cm^{-2}, i.e. they do not exceed 10% of the original value of σ.
3. The softening action is usually observed within definite limited ranges of temperature and rate of deformation[10], and is therefore due to some thermally activated process. At each temperature there is a corresponding optimum rate of deformation, producing a maximum effect (Fig. 2).

Since plastic flow of a crystal is a process of displacement of dislocations along slip planes and their emergence at the surface, while the softening effect is produced by purely surface phenomena, the fundamental cause of the observed effect must obviously be regarded as the interaction between the dislocations and the free surface of the crystal[13,14,16,19].

A dislocation, being a thermodynamically unstable defect (possessing an excess of free energy), tends to emerge at the surface of a crystal. Application of the theory of elasticity enables an estimate to be made of the force with which an edge dislocation situated parallel to the surface is attracted to the surface: this force (the so-called "mirror-image

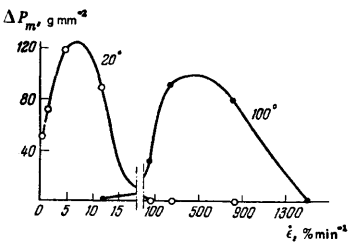


Fig. 2. Dependence of the magnitude of the adsorption effect on the rate of strain ϵ for single crystals of tin at different temperatures[10]. The magnitude of the effect ΔP_m is expressed as the difference between yield points in inactive and in active media.

force") is inversely proportional to the distance from the surface; i.e. it is determined by a slowly varying logarithmic potential[38]. Further, emergence of the dislocation (i.e. completion of its displacement in a given slip plane) is accompanied by the appearance of steps, the width of which at a given point on the edge of the slip plane is equal to the component of the Burgers vector lying in the slip plane normal to the edge. The creation of each new surface step requires work to be done $\leqslant b^2\sigma$, where b is the Burgers vector (unit translation). This potential barrier extends inside the crystal only to a distance of about half the width of the dislocation (of the order of a few b); i.e. it is quite steep, and in the immediate vicinity of the surface the force due to it, opposing emergence of the dislocation, may prevail over the expulsive "mirror-image force"[19].

Let us consider a point M on the edge of an active slip plane, at which the Burgers vector is perpendicular to the edge and the step reaches its maximum width of $\sim b$. During plastic flow of the crystal, v dislocations pass through this point per second, and passage of each of them creates in the region of M a new surface of $\sim b^2$, possessing a free energy of $\sim b^2\sigma$. In the absence of applied stresses, this quantity must apparently be regarded as the activation energy of the process.

The condition that the numbers of dislocations approaching and leaving the point M should be equal is then expressed by the equation

$$v = \nu \exp(-U/kT),$$

where $\nu \simeq 10^{12}-10^{13}$ sec^{-1} is the Debye lattice vibration frequency and the quantity U is equal to $b^2\sigma$ less the work A done by external forces. The temperature defined by this relationship, $T_1 = b^2\sigma/k \ln(\nu/v)$, then represents the "upper temperature limit" for the existence of this potential barrier: at $T \geqslant T_1$ emergence of dislocations at the crystal surface does not require the application of any considerable additional forces; at lower temperatures work must be done by external forces. Thus in the neighbourhood of T_1, when A is small, it can be expected that even a slight decrease in σ, reducing A to zero, will have the greatest effect on the plastic properties of the crystal; i.e. that the optimum temperature for the softening effect is $T_{opt} \simeq T_1$.

The parameter v introduced into the discussion is determined by the rate of deformation and its microheterogeneity (localisation of displacements in a series of slip lines), and for average orientations of the crystals can be approximately evaluated as follows[15,18,29]: $v \simeq \dot{\epsilon}hu/b$, where $\dot{\epsilon}$ is the rate of strain, h is the mean distance between the slip lines, and the deformation microheterogeneity factor u represents the ratio of the total number of slip lines to the number which are active at any particular instant (in general, the values of hu can vary within quite wide limits, e.g. from 10^{-1} to 10^{-3} cm).

With the above model, the optimum temperature for the softening effect thus proves to be related to the rate of deformation in the following fashion[14]:

$$T_{opt} \simeq \frac{b^2\sigma}{k \ln(\nu b/\dot{\epsilon}hu)}. \qquad (1)$$

When $\dot{\epsilon} = 10\%$ min^{-1}, the logarithmic term in the denominator is $\sim 20-25$, and substitution of $b = 3 \times 10^{-8}$ cm and $\sigma = 10^3$ ergs cm^{-2} gives a value of $\sim 0.5-0.6$ eV for the activation energy, which means that under these conditions $T_{opt} \simeq 300°$K; increasing $\dot{\epsilon}$ by a factor of 100 should raise T_{opt} to about 400°K.

This result is in good agreement with experimental data[10] for the reduction of the yield point of single crystals of tin (see Fig. 2), according to which the adsorption effect is a maximum at room temperature if the rate of straining $\dot{\epsilon} = 5-10\%$ min^{-1}, and at 100° if $\dot{\epsilon} \simeq 500\%$ min^{-1}.

Subsurface sources of dislocations (anchored at a single point) may play a significant part in producing the softening effect, as the force required to set them in operation is considerably less than with sources having two pinning points[39]. A thin polycrystalline film deposited on the surface of a single crystal, and also the alloying of a thin surface layer, can appreciably raise the yield point of a specimen, by impeding the operation of these sources[40-42]. On the other hand, a decrease in σ can naturally be expected to increase the activity of the subsurface sources and to lower the yield point. Since interaction of such a source with the surface is in effect a successive "drawing" of the second (unanchored) end of the section of the dislocation along the crystal surface, i.e. the formation of a step on the surface, relationship (1) remains valid; the parameter v retains the same order of magnitude, but acquires the sense of the number of turns per second of the subsurface source (the dislocation spiral in the Frank–Read mechanism[38]).

The above model cannot be directly applied, however, to the softening of metallic single crystals by molten metal coatings at elevated temperatures and very low rates of strain[23,24] (see below): in such a case the parameters entering into relationship (1) (activation energy, vibration frequency) evidently have a rather different physical meaning and magnitude. It is quite possible that interaction of dislocations with surface defects blocking individual points on the edge of the slip plane here plays an important role; the potential barrier then becomes higher and acquires a different expression, but remains as before short-range in effect and substantially dependent on σ.

The mechanism of the action of an adsorption-active medium may also be connected with a process of generation of dislocation sources. However, the question of the generation of sources is still not absolutely clear, and the influence of the magnitude of σ on this process is even less clear.

Thus the softening effect, which represents only one of the cases of the action of adsorptive-active media on the mechanical properties of a solid, is itself complicated and varied, being connected with the existence of a whole spectrum of activation energies, and can be observed over different ranges of temperature and rate of deformation.

3

Organic media are feebly surface-active: as was noted above, the decrease in free surface energy accompanying adsorption from such media is only several tens of ergs cm^{-2}. Rebinder and his collaborators have shown that melts of other, more readily fusible metals (and probably also of some salts and other compounds) are incomparably more active with respect to metals[6,11,12,22,25]. In this connection the work of Kishkin and Potak[43-46], in which the adsorption character of the reduction in strength of metals by readily fusible metallic melts is stressed, is of great interest.

The laws governing the action of such strongly surface-active media on the deformation and strength properties of single crystals of various metals have been studied in a series of investigations carried out during recent years in the Disperse Systems Section of the Institute of Physical

Chemistry of the Academy of Sciences of the USSR and in the Department of Colloid Chemistry of the Moscow State University. This work has shown that in the presence of strongly adsorption-active media a qualitative change in the mechanical properties of the metal may occur: a highly plastic metallic single crystal, capable of being deformed by several hundred per cent, will become brittle, its strength falling sharply. This type of effect is exerted by molten tin on single crystals of zinc and cadmium[11,12], by mercury on single crystals of zinc[22,47-50] and tin[21,22,24,51], and by liquid gallium on zinc[17,25], cadmium[25], and tin[52].

The single metal crystals which formed the subject of the investigations were grown by zone crystallisation[53] from extremely pure preparations (containing 99.99% and 99.999% of the main metal), and in a few cases, in order to study the effect of impurities, from technical materials, or from the pure metal containing a small admixture of another metal[49,50]. The specimens had a diameter of 0.5–1.0 mm and a wide range of crystallographic orientations. The adsorption-active metal was deposited on the surface of the specimens in the form of a thin coating (usually a few microns thick) either electrolytically[11,12], chemically (by displacement from a salt solution[22,47-50]), or mechanically[25,52].

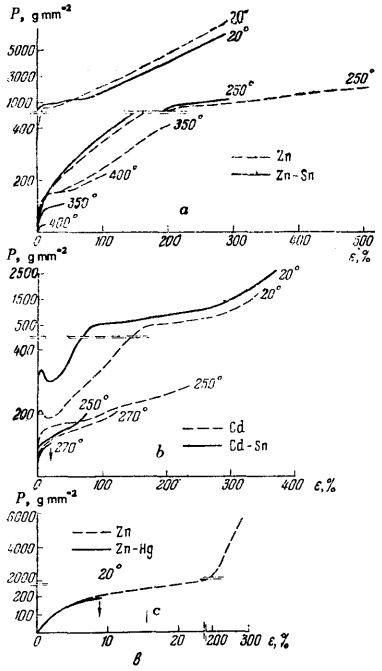


Fig. 3. Variation of true tensile stress P with strain ϵ: *a*) for single crystals of zinc with and without a tin coating; initial orientation of crystals $\chi_0 = 44°$ and rate of strain $\dot{\epsilon} = 15\%\ \text{min}^{-1}$;[12] *b*) for single crystals of cadmium with and without a tin coating; initial orientation of crystals $\chi_0 = 39°$ and rate of strain $\dot{\epsilon} = 15\%\ \text{min}^{-1}$;[12] *c*) for single crystals of zinc with and without a coating of mercury; initial orientation of crystals $\chi_0 = 48°$, rate of strain $\dot{\epsilon} \sim 15\%\ \text{min}^{-1}$.[15]

Coated and uncoated specimens were strained over a wide range of temperatures and rates of deformation both on a Polanyi type of apparatus and under constant load. The main results obtained in these experiments are indicated below.

At temperatures above the melting point of the metal–coating eutectic, the presence of a thin molten layer of surface-active metal leads to a great reduction in the plasticity and strength of the specimen (Fig. 3); the character of the fracture also changes: from being plastic in air it becomes brittle in the presence of a surface-active coating. Thus single crystals of zinc at room temperature can usually be deformed by several hundred per cent, stretched into a thin strip, and broken with the formation of a neck at stresses of $\sim 5\ \text{kg mm}^{-2}$; after amalgamation, the limiting deformation is reduced to 10% (or below) and fracture occurs at stresses of $\sim 200\ \text{g mm}^{-2}$ (and below), with a mirror-like cleavage on the (0001) plane[22,47-50]. Molten tin has a similar effect on the limiting deformation and the breaking stress of single crystals of zinc and cadmium; mercury acts in the same way on single crystals of tin at sufficiently high rates of deformation[21,22,24,51].

With respect to zinc, liquid gallium is evidently a still more strongly surface-active medium than tin and mercury: the limiting deformation in this case reaches only a few per cent or even fractions of one per cent[25]. A specially interesting case is provided by the cadmium–gallium system[25]: single crystals of cadmium are extremely plastic even at very low temperatures and high rates of deformation, and give no cleavage on the slip plane; on application of gallium, however, the same single crystals undergo brittle fracture at room temperature and relatively low rates of extension ($\sim 200\%\ \text{min}^{-1}$), with mirror-like cleavage on the basal plane.

The development of the embrittling action of a surface-active metallic melt depends greatly on the temperature and the rate of deformation[11,12,15,19,21,22,51]. When the temperature falls below the melting point of the metal–coating eutectic, the effect gradually disappears, obviously because the mobility of the adsorption-active atoms is reduced and their rapid migration along freshly developing surfaces becomes impossible. This is the lower temperature limit of the embrittling effect.

There exists also an upper temperature limit, whose position for a given metal–coating pair depends to a considerably greater extent on the rate of deformation. Thus in the case of amalgamated zinc at ordinary rates of strain ($\sim 10\%\ \text{min}^{-1}$) the plasticity and the normal strength are reestablished when the temperature is raised to $T_c \simeq 150°$ (Fig. 4); within a relatively narrow range of transition temperatures, $\Delta T \simeq 40°–50°$, a peculiar "partial embrittlement" is observed, in which the specimen, covered with deep, half-opened cracks, nevertheless shows considerable deformability. When the rate of deformation is decreased, the transition region between brittleness and plasticity is shifted to lower temperatures. The presence of alloying impurities in the single crystal acts in the opposite direction and raises the transition temperature T_c.

In the case of zinc–tin, the embrittling effect at strain rates of $\sim 10\%\ \text{min}^{-1}$ extends from the melting point of the coating right up to the melting point of zinc[11,12] (in other words, the transition temperature T_c would seem to be above the latter); furthermore, the effectiveness of the coating actually increases in this case when the temperature is raised (see below). When the rate of deformation is reduced to $\sim 10^{-4}\ \text{min}^{-1}$, however, the brittleness dis-

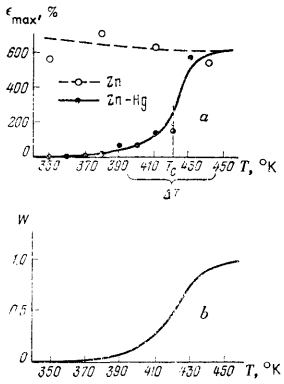


Fig. 4. *a*) Dependence of the limiting strain at fracture ϵ_{max} on temperature for single crystals of zinc with and without a mercury coating at $\chi_0 \sim 45°$ and $\dot{\epsilon} = 15\%\ min^{-1}$; *b*) theoretical curve for the temperature variation of the "probability of plastic flow" for amalgamated single crystals [15,22].

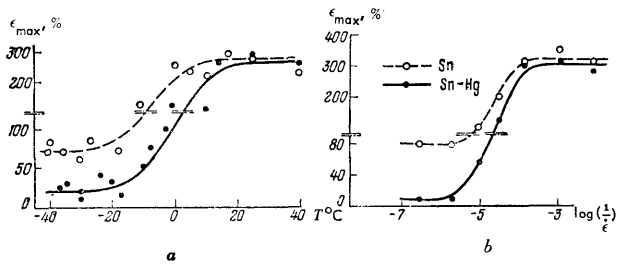


Fig. 5. *a*) Temperature dependence of the limiting strain at fracture ϵ_{max} for single crystals of tin with and without a mercury coating when $\dot{\epsilon}$ = const.; *b*) dependence of ϵ_{max} on rate of strain $\dot{\epsilon}$ when T = const. [21,51]

appears at all temperatures [22] (i.e. the transition temperature T_c falls below the melting point of the coating, but the coating is then already solid, and the effect is absent).

In the case of tin–mercury, the embrittling action of the coating on single crystals grown from extremely pure metal is distinct and reproducible at room temperature only at very high rates of strain (up to 10^5–$10^6\%\ min^{-1}$); but if the rate of deformation is low, the transition temperature T_c is around 0° or lower (see Fig. 5). Evidently this peculiar position of T_c is responsible for the fact that the development of the embrittling action of mercury on single crystals of tin at room temperature is very sensitive to the purity of the tin.

The following facts play a large part in elucidating the mechanism of the embrittling action of a molten coating:

1. The decrease in free surface energy at the interface between a metal and its saturated solution in another, liquid metal may be very considerable [6,11,12,14] — hundreds of ergs per cm^2.
2. Since we are concerned with the development of fractures within the crystal, this is a bulk effect and requires rapid penetration of adsorption-active atoms to the surface of the internal micro-voids by anomalous diffusion (migration) along structural defects in the crystal [14,15].
3. The effect appears practically immediately after application of the coating to the single crystal; consequently, normal (bulk) diffusion is not the decisive factor here.
4. With an appropriate rate of deformation, the effect is observed over a wide range of temperatures from the melting point T_m of the coating (more exactly, of the metal–coating eutectic) up to the melting point T_M of the main metal or the transition temperature T_c, and the magnitude of the effect is independent of temperature within this range. This suggests that the process of brittle fracture due to the presence of the coating is not by itself thermally activated†.
5. The transition from brittleness to plasticity in the presence of a coating is very similar (especially in the case of zinc–mercury) to the analogous transition in the absence of a coating occurring at lower temperatures; this latter transition may be termed the "threshold of natural cold-shortness", in contrast to the threshold displaced to higher temperatures, that of "imposed cold-shortness", due to the action of the adsorption-active medium. It may be assumed that, other things being equal, the position of this threshold is determined primarily by a single parameter — the magnitude of the free surface energy σ. [21]

Thus an elucidation of the mechanism of the embrittling action of a strongly adsorption-active medium on metallic crystals must start from an analysis of the mechanism of the brittle fracture of these crystals in the absence of such a medium; a description of the conditions for the transition from brittleness to plasticity in the presence of a coating must likewise be correlated with the analogous phenomenon for the pure metal.

At the present time the most detailed data are available for zinc–mercury [22,42,47-50], and they will be mainly used in discussing the mechanism of the embrittling action of the medium.

It has been shown convincingly in several papers that, even at very low temperatures, brittle fracture of single crystals of zinc along a cleavage plane is not perfectly brittle, in the sense that it is always preceded by some plastic deformation [47-50,54,55]. At the temperature of liquid nitrogen and normal rates of deformation of $\sim 10\%\ min^{-1}$, the limiting

† The increase in the effect with temperature in the case of zinc–tin (at ordinary rates of extension and relatively high temperatures) is evidently associated with a sharp increase in the solubility of zinc in tin, and hence with a further fall in the free surface energy at the metal–melt boundary; indeed, when the concentration of the main metal in the liquid metallic coating becomes high, conditions at the phase boundary approach those at the metal–melt boundary in a single-component system, and in this case the free interfacial energy may be only several tens of ergs cm^{-2}.

displacement a_c in the a_0 direction for specimens of diameter $L_0 \simeq 1$ mm is within the range from several to several tens per cent, depending on the initial orientation of the crystal [the angle χ_0 between the axis of the specimen and the slip plane (0001), which in this case coincides with the cleavage plane]. The relation between a_c and χ_0 for the fracture of single crystals of zinc at liquid-nitrogen temperature is exactly opposite in character to that observed at ordinary temperatures (without any coating): in the former case a_c falls abruptly with rise in χ_0, whereas in the latter case a greater crystallographic displacement a_c corresponds to greater angles χ_0 (Fig. 6).

Zonke's law, which states that single crystals with different orientations undergo brittle fracture when the stresses normal to the cleavage plane reach a definite value p_c = = const., proves to be completely inapplicable to the fracture of single crystals of zinc at the temperature of liquid nitrogen. With increase in the angle χ_0, in fact, the values of p_c increase sharply (Fig. 7*a*), while the values of the shearing stresses τ_c reached at the instant of fracture decrease substantially (approximately in inverse proportion to the increase in p_c). Exactly similar regularities are observed for the fracture of amalgamated single crystals of zinc at room temperature (Fig. 7*b*), but the values of p_c and τ_c are then less than half. The fracture of single crystals of zinc and cadmium in the presence of liquid gallium follows analogous rules[22].

The actual breaking stresses p_c in the cleavage planes are smaller by several powers of ten than the so-called "theoretical" value, $p_{theor} \simeq (E\sigma/b)^{\frac{1}{2}}$, calculated on the basis of some model of the interatomic forces for an ideal crystal lattice containing no imperfections; here E is Young's modulus, σ the specific free surface energy, and b a lattice constant. This discrepancy is usually related to the presence in a real crystal of various structural defects, primarily micro-cracks. The fact that Zonke's law is not obeyed, and the observed dependence of a_c, p_c, and τ_c on χ_0 for the brittle fracture of single crystals of zinc, enable us to make the following step towards explaining the mechanism of brittle fracture and specifying the role of p and τ more exactly[30].

It is reasonable to assume that, in plastic flow under the action of shearing stresses τ, defects arise and develop, and then, on reaching certain dimensions and with an appropriate value of the normal (tensile) stress p_c, become "dangerous", i.e. lead to the appearance of macroscopic cracks, which spread throughout the cross-section of the crystal. In such a case at least two main stages are to be distinguished in the process of fracture:

Stage *A*: Plastic deformation preceding the appearance of dangerous cracks (which in turn can evidently be divided into several different substages).

Stage *B*: A more or less rapid spreading throughout the specimen of one or several dangerous cracks which are close together and merge into one another.

In the case of brittle fracture, the start of stage *B* is very clearly marked, and itself occurs with extreme rapidity.

In stage *A* the shearing stresses and the resulting plastic deformation play the principal role. It is highly significant here that the plastic deformation of a crystal always develops with great inhomogeneity, both in space (in the body of the crystal) and in time. Spatial inhomogeneities consist in the localisation of deformation in

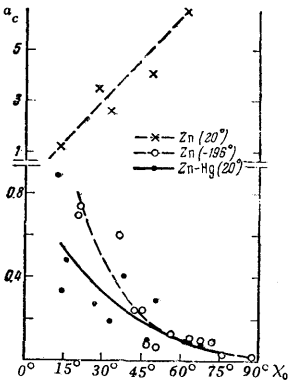


Fig. 6. Dependence of the limiting displacement of a_c on orientation for single crystals of zinc with and without a mercury coating, χ_0 being the initial value of the angle between the basal plane and the axis of the specimen[47–50].

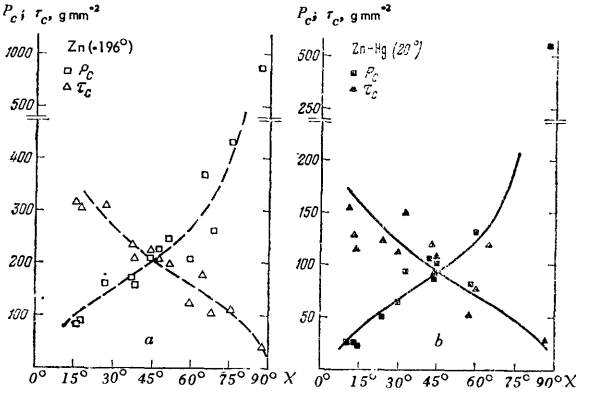


Fig. 7. Orientation dependence of normal (p_c) and shearing (τ_c) stresses at fracture for single crystals of zinc: *a*) without coating at temperature of liquid nitrogen; *b*) with a mercury coating at room temperature. The angle χ is that between the basal plane and the axis of the specimen at the instant of fracture. Purity of the material 99.999% and 99.99% Zn.[15,30,49,50]

narrow slip lines (or bands), the propagation of these lines to only part of the edge of the slip plane (i.e. the accumulation of incomplete, local displacements in the crystal), fragmentation and block formation in the crystal, the appearance of deformation and kink bands (fault formation), the occurrence of twin boundaries, etc. The temporal inhomogeneity of deformation is shown, for example, by slip lines appearing at different times, and by various advances and delays in the process, right up to clearly defined sudden changes in deformation, etc.

Micro-heterogeneities in deformation are closely connected with the dislocation nature of plastic flow. Local deformations may reach very high relative values and lead to considerable local disturbance of the crystal lattice, a marked weakening of the bonds in the lattice over a more or less appreciable distance (i.e. to the appearance of centres of disintegration with some effective dimensions c), and also to the formation of new barriers opposing slip — sub-boundaries (dislocation networks), pinned dislocations, stacking faults, twin boundaries, etc. Furthermore, certain kinds of micro-heterogeneities in the deformation, including incomplete slip which has not spread over the whole cross-section of the crystal (i.e. dislocations piled-up in a single slip plane, or in several closely adjacent planes against various obstacles), lead to the appearance of marked local stress concentrations, many times greater than the applied shearing stress τ [15,19,30,56,57]. These high local stresses may in turn lead to the formation and gradual extension of micro-cracks, which are equilibrium centres of breakdown (the term "equilibrium" is understood to mean here that the magnitude c of a given defect, with the existing level of applied normal stress, has not yet reached at stage A the critical value at which the defect becomes dangerous and spreads over the whole crystal in the form of a fracture)†.

The character of the centres of disintegration and the extent of their development (the effective quantity c) at different substages of stage A depend essentially on the nature of the crystal and the conditions under which deformation occurs. In the case of pure basal slip in single crystals of zinc at low temperatures, as well as at ordinary temperatures, the following scheme can be used for the initial substages of deformation — i.e. for not very high values of displacement a and shear stress τ — when the process of relaxation of local deformations and high stresses is not sufficiently effective††.

Let us suppose that a shear stress τ has caused a displacement Δ in a slip plane, and that this displacement has not extended over the whole cross-section of the crystal owing to the presence of some sufficiently strong ("insurmountable") obstacle O in the slip plane (Fig. 8)†††. The main region of localisation of the displacement is then the distance $MO = s$ along the slip plane.

The magnitude of s obviously depends on the initial slip Δ, which in turn is determined by the overall plastic strain a reached by that instant. From the point of view of elucidating the cause of fracture of the crystal, we are primarily interested in the greatest possible value, $s_{max} = L$, under the given conditions. In a well annealed crystal $L = 0$. It may be assumed that, during the first substage of stage A, the quantities Δ and L increase monotonically with increase in the displacement a, at first very rapidly, then more slowly. This substage (A') is characterised by a high value of the strain-hardening factor and the accumulation in the crystal of the relatively large elastic energy of the heterogeneities which are formed. At some value of the crystallographic displacement $a = a_0$, corresponding to the shear stress τ_0 on the deformation curve, limited slip ceases, since the elastic strain field thereby set up, which opposes displacement along the given slip plane, becomes so intense that, at the given level of shear stress, further slip can proceed more readily in other sections of the crystal, which do not contain such strong obstacles. It is evident that L may then reach values of the same order of magnitude as the diameter L_0 of the single crystal.

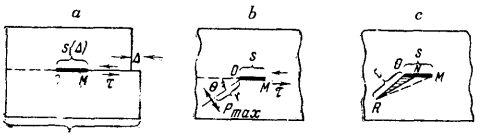


Fig. 8. a) Appearance of limited slips; b) concentration of normal stress near region of limited slip; c) appearance of a micro-crack in the region of maximum concentration of tensile stress [30].

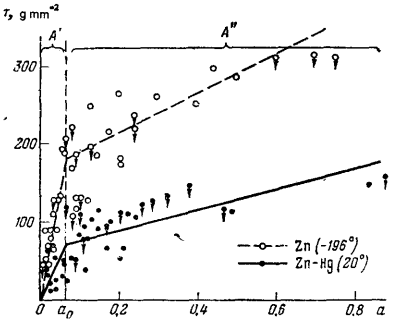


Fig. 9. Dependence of shear stress τ on the crystallographic displacement a for differently oriented single crystals of zinc without any coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature). The arrows indicate the points corresponding to the instant of fracture; the broken lines correspond to the averaged form of the τ (a) curves. Purity of material 99.999% and 99.99% Zn. [49,50]

The displacement a_0 at which substage A' finishes corresponds to a characteristic break in the deformation curve for the single crystal (Fig. 9). The next substage A'', during which the maximum variation in the displacement changes considerably more slowly, is characterised by an appreciable decrease in the strain-hardening factor.

The stress field around the defect of extent $MO = s(\Delta)$ may be likened to the elastic field of a notch of length s parallel to the applied shear stress τ. The theory of

† An "equilibrium" crack in this sense of the word is not, of course, reversible; when the tension is removed, the crack generally remains.

†† It is essential that this should occur even if in only a single slip band; it is just here that a centre of breakdown will then develop to a dangerous size.

††† In the present case, where we have several horizontal dislocations lying in a single slip plane, or in a few such planes close together, the obstacles may be pinned dislocation, vertical wall dislocations (tilt boundants with a small angle of disorientation), etc.

elasticity shows[57,66] that the maximum tensile stress then arises along a line inclined at an angle θ to the plane of the notch, reaching a value $p_{max} \sim \tau(s/r)^{\frac{1}{2}}$, r being the distance of the point from the apex of the notch.

Let a crack NOR of length c (see Fig. 8) be formed in the region of maximum stress concentration. These high stresses will then be relaxed over an area of $\sim cs$. In the absence of a crack, the density of elastic energy in the region of the gap MO would be $w = p^2/2E \simeq \tau^2 s/2Er = w(r)$. The decrease in energy entailed in opening the crack (per unit length in a direction perpendicular to the plane of the paper) is roughly $(\tau^2 s^2/2E) \ln(c/r_0)$; here the lower limit of integration r_0 (of the order of a few b) is determined by the inapplicability of the relationships of the theory of elasticity in the immediate vicinity of point O, and b is the repeat distance of the lattice.

At the same time, formation of the crack requires that work of $\sim 2c\sigma$ should be done to produce the new free surface. The net increase in energy is $\Delta W = 2c\sigma - (\tau^2 s^2/2E) \ln(c/r_0)$. The function $\Delta W(c)$ has a minimum at $\partial(\Delta W)/\partial c = 2\sigma - \tau^2 s^2/2Ec = 0$. Hence accumulation of limited slip over a distance of $s = s(\Delta)$ in the slip plane may produce an equilibrium V-shaped crack of magnitude $c \simeq \tau^2 s^2/4E\sigma$ in the crystal. Since we are interested in the maximum possible length c, the value $s_{max} = L(a) \leqslant L_0$ must be substituted in the resulting expression.

A completely analogous expression for c may be obtained in terms of the theory of dislocations, since the limited slip Δ is obviously the same as a set of $n = \Delta/b$ dislocations. Actually $n \simeq \pi(1 - \mu)L\tau/Gb$, where G is the shear modulus and μ is Poisson's ratio[58]; the coalescence of n dislocations produces a crack of length[57]

$$c \simeq n^2 Gb^2/8\pi(1 - \mu)\sigma, \text{ i.e. } c \simeq \{\pi(1 - \mu)/8\}(\tau^2 L^2/G\sigma).$$

It can thus be assumed that application of a shear stress τ in a slip plane in a crystal may produce an equilibrium crack up to $c = \beta\tau^2 L^2/E\sigma$ in size, where the dimensionless coefficient β does not differ greatly from unity, and L increases monotonically during the first substage of stage A from zero to some final value approaching the diameter L_0 of the crystal, which is greater, the greater the displacement a_0 in the given substage A'. †

The actual start of an incipient micro-crack having as yet no fully developed free surface may be imagined as a process of combination of the primary (leading) dislocations of the set to form a narrow, hollow dislocation nucleus[15,19,65]. Such hollow nuclei can evidently be formed at very low values of τ and a, and play a large part in the penetration of adsorption-active atoms inside the crystal. With increase in τ an equilibrium micro-crack of size $c = c(\tau)$ gradually develops. In the case of zinc the fissures in the basal plane then alternate with those in the prismatic plane; ultimately, the direction of extension of the crack is close to the basal plane[14,15,30].

We have thus considered stage A, preceding fracture, the main part in which is played by the shear stress and the inhomogeneity of plastic deformation.

In stage B, which is extremely short-lived in the case of brittle fracture, the normal stress has the decisive role. Stage B ensues when the displacement a_c is such that the stress p normal to the plane of the crack [in this case the (0001) plane] is sufficient to make the crack dangerous and non-equilibrium, i.e. when $p_c(c) = \alpha(E\sigma/c)^{\frac{1}{2}}$, where α is some dimensionless coefficient which differs little from unity[15,59].

On substituting the value found for the maximum possible size of crack $c(\tau)$ in the expression for $p_c(c)$, we obtain the following relationship[29] instead of Zonke's law:

$$p_c\tau_c = K^2; \quad K = \gamma'\sqrt{E\sigma/L} = \gamma\sqrt{G\sigma/L}, \qquad (2)$$

where the dimensionless coefficients γ' and γ are close to unity in magnitude, and K is constant at stage A'' and increases when $a_c < a_0$. The resulting relationship may be called the "condition of constant product of normal and shear stresses" during brittle fracture.

In combination with the "geometrical" conditions $\tau_c = P_c \sin\chi \cos\chi$, $p_c = P_c \sin^2\chi$, and $p_c/\tau_c = \tan\chi$, where P_c is the true tensile stress and χ is the angle between the basal plane and the axis of the specimen at the instant of fracture, we find that

$$p_c = K\sqrt{\tan\chi}; \quad \tau_c = K\sqrt{\cot\chi}; \quad P_c = K \sin^{-3/2}\chi \cos^{-1/2}\chi. \dagger \qquad (3)$$

The relations (3) are well satisfied both for the fracture of single crystals of pure zinc at the temperature of liquid nitrogen††, and for the elongation of amalgamated single crystals at room temperature (Fig. 10)[14,15,30,47-50]. The values of $K = (p_c\tau_c)^{1/2}_{av} \equiv (P_c \sin^{3/2}\chi \cos^{1/2}\chi)_{av}$ obtained from the experiments are 209 g mm^{-2} in the former case and 95 g mm^{-2} in the latter, which according to (2) correspond to a decrease in the free surface energy of zinc in the presence of mercury roughly by an amount

$$\sigma_{Zn-Hg} = \sigma_{Zn}/(K_{Zn}/K_{Zn-Hg})^2 \sim 10^3/(209-95)^2 \sim 200 \text{ ergs cm}^{-2}$$

The good agreement of experimental values of P_c for differently oriented single crystals with condition (3) shows

† An extremely rough estimate of a_0 may be obtained as follows. Since $\Delta/s \sim \tau/G$, the maximum value Δ_{max} for $s \sim L_0$ is $\sim L_0\tau/G \sim 10^{-5}$ cm (the accumulation of several hundred dislocations); on the other hand, at the end of substage A', the value of Δ_{max} is evidently not very much greater than that of $a_0 h$, where h is the distance between the slip lines. Assuming that $a_0 \sim \Delta_{max}/h$, we find that when $h \sim 10^{-3}$ cm, $a_0 \sim 10^{-2}$, which is roughly of the same order of magnitude as that given by the experimental data (see Fig. 9).

† In this scheme the dimensions of the slip plane are identical with the diameter of the single crystal, which is actually merely the minor axis of a slip plane in the shape of an ellipse; this means, in essence that relationships (2) and (3) relate to the propagation of strain inhomogeneities along the minor axis of an ellipse, i.e. to groups of screw dislocations. In the case of edge dislocations the maximum size of the region of localisation of the strain inhomogeneities must be taken as the major axis of the ellipse. Conditions (2) and (3) are then written in the form

$$p_c\tau_c = K^2 \sin\chi_0; \quad p_c = K \operatorname{tg}^{1/2}\chi \sin^{1/2}\chi_0 \text{ and } \tau_c = K \operatorname{ctg}^{1/2}\chi \sin^{1/2}\chi_0.$$

This fact may be linked with some observed deviations from the condition that $p_c\tau_c$ should be constant, especially at small angles χ, as well as with the considerable scatter of the experimental results. Comparison with experiment shows, however, that the condition $p_c\tau_c = \text{const.}$ is quite acceptable as a first approximation.

†† According to (2) $K \propto L^{-\frac{1}{2}}$; since at stage A'' the value of L approaches the order of magnitude of the diameter L_0 of the single crystal, and for a given degree of purity of the material is apparently a definite fraction of L_0, it may be assumed that $K \propto L_0^{-\frac{1}{2}}$. In fact, this is confirmed both in our own experiments[47,50] and by comparison with the data of other workers[54,55] on the brittle fracture of single crystals of zinc at low temperatures[49,50].

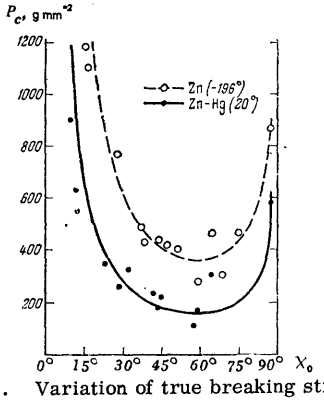


Fig. 10. Variation of true breaking stress P_c with orientation for single crystals of zinc without a coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature); the curves correspond to the condition $P_c\tau_c$ = const. Purity of material 99.999% and 99.99% Zn.[49,50]

TABLE 2. Experimental values of the quantity K and of the strain a_0 corresponding to the yield point in the $\tau(a)$ curve for single crystals of zinc of differing purity without a coating (at the temperature of liquid nitrogen) and with a mercury coating (at room temperature)[49].

Purity of zinc	Diameter of specimens L_0, mm	$K=(P_c \sin^{1/2}\chi \cos^{1/2}\chi)_{av}$, g mm^{-2}: non-amalgamated, at -196°	K: amalgamated, at 20°	a_0, %	$\frac{a_0}{a'_0}$	$f=\frac{K^2L'_0}{K^2L_0}$ at -196°
Zn 99.999% / Zn 99.99%	$0.9=L'_0$	$209=K'$	$\frac{92}{91}$	6 to 7 $=a'$	1	1
Zn +0.2%Cd	0.54	316	153	3	~0.5	0.72
Zn technical	0.9	263	124	2 to 3	~0.4	0.63
Zn +0.5%Cd	0.54	361	230	2	~0.3	0.5

that in these experiments fracture has occurred with $a_c > a_0$, when the process of forming inhomogeneities is in the main already complete, and L is approximately constant. Actually, the stress–strain curves exhibit in nearly all cases a more or less well developed stage A''. But if fracture takes place at very small strains $a_c < a_0$, as occurred in experiments[55] with single crystals of zinc of diameter 6 mm at extreme orientations $\chi \leqslant 60°$, stage A'' is not reached; the stresses P_c then prove to be greater than would follow from condition (3), and the values of $(p_c\tau_c)^{1/2}$ increase monotonically with decrease in a_c.[49,50]

Study of the laws of the brittle breakdown of alloyed single crystals of zinc[49,50] has shown that in this case the condition $p_c\tau_c$ = const. remains valid over a wide range of orientations, for the fracture both of specimens without a coating at -196° and of amalgamated specimens at room temperature (in both cases fracture generally occurred at stage A''). The strength increases to about the same extent with increasing content of impurity in the two cases (see Table 2); furthermore, the value of the strain a_0 corresponding to the yield point in the deformation curve (i.e. the extent of stage A') falls.

With other conditions the same, alloyed crystals are deformed more uniformly than are pure crystals, and their strain-hardening factors are considerably higher. Hence growth of local strains takes place less intensively in alloyed crystals, and ceases at lower values of a_0, than in the case of pure crystals. Thus at the same diameter alloyed crystals are characterised by a lower value of L at stage A'', as is confirmed by the data in Table 2.

Even in the case of alloyed specimens, where there is a general increase in K, values of K for amalgamated crystals fractured at room temperature prove to be roughly half (or somewhat lower) the values for uncoated specimens strained at -196°.

Thus, the concept of a considerable reduction in the free energy of new surfaces developed in the process of fracture explains, in good agreement with the experimental data, the sharp decrease in the plasticity and the strength of amalgamated single crystals of zinc. The above scheme is obviously applicable to the analysis of other metal–coating pairs, such as zinc–tin, cadmium–gallium, etc.

From a comparison of the metal–coating pairs investigated with the binary melting-point diagrams, a semi-empirical rule has been established, indicating whether or not a given metal M_1 is strongly surface-active with respect to a more refractory metal M_2.[17] This is that a reduction in strength due to adsorption, corresponding to a considerable decrease in σ, is observed when M_1 has a small but finite range of solubility in metal M_2 in the solid state. On the other hand, no effect is generally observed if this range is very wide, or if it is altogether absent.

4

As was noted above, the presence of a molten, strongly adsorption-active coating shifts the threshold of cold-shortness to substantially higher temperatures. With unamalgamated single crystals of zinc and normal rates of straining, the transition from brittleness to plasticity is observed at about -50°.[60] At this temperature the relaxation of inhomogeneities in the deformation (dislocation pile-ups) and of high local stress concentrations is sufficiently effective to decrease the size c of the equilibrium disintegration nuclei at the same level of sheer stress τ; K begins to increase. Furthermore, as a result of the decrease in the strain-hardening factor, the quantity $(p\tau)^{1/2}$ now reaches its dangerous value (a new and larger value of K) only at very large deformations†, the deformability increases sharply, and brittle fracture proves impossible.

In the presence of a strongly adsorption-active medium (amalgamated zinc), the size $c(\tau)$ of the incipient micro-cracks increases for the same value of τ, and the level of dangerous normal stress $P_c(c)$ falls for the same value of c. According to (2), both result in a decrease in K (proportional to the square root of σ). The quantity $(p\tau)^{1/2}$ can now reach a dangerous level (a new, much lower value of K), and brittle fracture can occur, even at ordinary and elevated temperatures, during the early stages of deformation (while the shear stress is insufficient to diminish substantially the activation energy required to overcome obstacles to movement of dislocations). With further rise in temperature (in the case of zinc–mercury to ~150° at a

† It is important that the shear stress then becomes large: relaxation of deformation in homogeneities is then very rapid (the activation energy required to overcome obstacles to movement of dislocations is substantially decreased by the work done by the applied stress).

TABLE 3. Steady rate of creep of single crystals of zinc without a coating ($\dot{\varepsilon}_0$) and with a tin coating ($\dot{\varepsilon}$).[23]

Temperature °C	P, g mm^{-2}	$\dot{\varepsilon}_0$, min^{-1}	$\dot{\varepsilon}$, min^{-1}	$\dot{\varepsilon}/\dot{\varepsilon}_0$
200	76	$0.7\cdot10^{-4}$	$0.2\cdot10^{-4}$	0.3
280	51	$1.7\cdot10^{-4}$	$10\cdot10^{-4}$	6.0
350	19	$1.0\cdot10^{-4}$	$15\cdot10^{-4}$	15.0

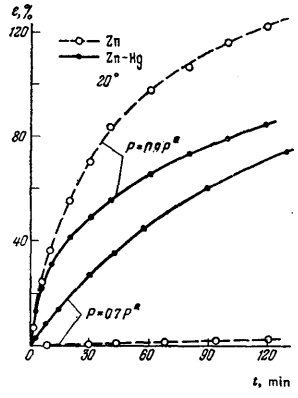


Fig. 11. Curves for the creep of single crystals of zinc at room temperature with and without a mercury coating under stresses of 0.7 and 0.9 of the yield point; $\chi_0 \sim 45°$.[24]

strain rate of $\sim 10\%$ min^{-1}), however, relaxation is already so effective and the strain-hardening factor so small that, even with a sharply reduced value of σ, the equilibrium disintegration nuclei are formed too late and are too small to become dangerous during the early stages of deformation. The value of K becomes somewhat larger again, and, owing to the very low strain-hardening factor, this new increased value is reached only after very great extension: the amalgamated crystal becomes plastic. A rough quantitative analysis has been made[15,19] of the conditions for transition from brittleness to plasticity in the absence and in the presence of a strongly adsorption-active medium; it is based on a model of the formation of dislocation pile-ups taking into accoun the obstacles to be overcome, and an expression has been obtained for the condition of deformability of a single crystal as a function of T, $\dot{\varepsilon}$, and σ. The resulting estimates for the transition temperature T_c and the transition range ΔT are fully consistent with the experimental data (see Fig. 4).

Thus, both the intrinsic and the imposed thresholds for cold-shortness are evidently of the same nature, and it is only the marked difference in the parameter σ that determines their relative positions on the temperature scale†.

The pair cadmium–gallium is of special interest in this connection, as no intrinsic threshold for cold-shortness is observed in this case.

The specific effect of the molten coating is displayed also after crossing the threshold of imposed cold-shortness (at sufficiently high temperatures or very low rates of strain) and can appear in two substantially different forms.

Thus in the case of zinc–tin[23] the presence of a molten coating is found to increase appreciably very low rates of creep of $\sim 10^{-4}$ min^{-1} (see Table 3), this softening effect being similar to the analogous action of organic surface-active media (see above); under other conditions of deformation it is masked by the effect of embrittlement. A similar phenomenon is observed at low rates of creep in the case of zinc–mercury[24] (Fig. 11).

At rather greater rates of creep (as before, in the absence of embrittlement), mercury has a hardening effect on single crystals of zinc, and raises the strain-hardening factor (Fig. 11). Such an effect is obviously connected with the normal alloying action of mercury, and for a given rate of deformation has its own upper temperature limit (determined by the activation energy for the interaction of dislocations in zinc with mercury atoms); hence at a given temperature the hardening effect is observable only when the rate of strain is not too low: in the contrary case, the softening effect predominates.

The alloying action of mercury on single crystals of zinc also appears to some extent below the threshold of imposed cold-shortness (in this case increase in the strain-hardening factor merely contributes to the development of the embrittlement). The hardening action of mercury is observed particularly clearly at low temperatures, however, when the coating is solid and adsorption effects vanish[19,42].

5

Rebinder has shown that, when there is a very marked reduction in the free surface energy of a solid with a low true solubility in a given medium, spontaneous dispersion into particles of colloidal dimensions $\delta_m = 10^{-6}$ cm, i.e. of the same order of size as the structural micro-blocks, may be detected. Development of these ideas shows that the magnitude of σ must be diminished to a few ergs of a few tenths of an erg per cm^2, and then the increase in free energy of the system due to the creation of a large area of new surface may be balanced by the gain in configurational entropy of the system[13,14]†. Kinetic and thermodynamic criteria are given for the spontaneous dispersion of a solid, and the process is shown to be considerably facilitated (to require a smaller decrease in σ) if account is taken of the free energy of the internal interfaces in the solid in its original state — the elastic energy of the sub-boundaries (dislocation lattices) and other structural defects.

Let us consider a body with a linear dimension L. Neglecting small numerical coefficients, we find its surface area to be $A_0 \sim L^2$ and its volume $V_0 \sim L^3$. The total number of micro-blocks in the surface is roughly L^2/δ_m^2, and the

† Evidently the alloying action of mercury is an additional factor. On passing from room to elevated temperatures the strain-hardening factor of amalgamated single crystals falls considerably more slowly than that of non-amalgamated crystals. This in turn contributes to the embrittling action of the coating.

† Voner's papers[62] in the theory of lyophilic colloids are of interest in this connection. He analyses (for the case of emulsions) the possibility of forming thermodynamically stable colloidal systems at extremely low values of the interfacial energy.

probability of detaching any of them is proportional to $\nu \exp(-U_A/kT)$, where U_A is the activation energy of the process and ν the thermal-vibration frequency of the block.

During one second $q \simeq (L^2/\delta_m^2)\,\nu \exp(-U_A/kT)$ particles leave the surface. Let us assume arbitrarily that the solid is able to disperse if its comminution is completed in time $t^* \simeq 1$ year $= 3 \times 10^7$ sec. The mean number of particles leaving per second should then be $q^* \simeq L^3/\delta_m^3 t^*$.

The probability of the dispersion process, or more exactly a "measure of the dispersibility of the solid", may then be defined as the ratio

$$M_D = q/q^* = (\nu t^* \delta_m / L) \times \exp(-U_A/kT).$$

A tendency to dispersion obviously corresponds to the condition $M_D \geqslant 1$ or, what is the same, the condition $\mathrm{Di} \leqslant 1$, where the dimensionless quantity Di is

$$\mathrm{Di} = U_A/kT \ln(\nu t^* \delta_m / L). \qquad (4)$$

The activation energy U_A of the process is in general defined as the work of formation of the new surface minus, firstly, the work done by external forces (or internal elastic fields due to local concentrations of stress around defects) and, secondly, the term $T\Delta S$, where ΔS is the increase in entropy of a particle on passing into the colloidal solution. Let us suppose, however, that dispersion is occurring in the absence of external forces (spontaneously); let us neglect also the work of the internal elastic fields and the gain in entropy, which leads to an overestimate of the quantity U_A, which may be written in this case in the form $U_A \sim \sigma\delta_m^2$. The condition for spontaneous dispersion is then approximately

$$\mathrm{Di}_0 = \sigma\delta_m^2/kT \ln(\nu t^* \delta_m / L) \leqslant 1. \qquad (5)$$

It is not difficult to estimate the logarithmic term in the denominator on the basis of the following considerations. The vibration frequency ν is determined by the order of magnitude of the dimension δ_m and the velocity of sound c_{sd}: $\nu \sim c_{sd}/\delta_m$. Hence

$$\ln(\nu t^* \delta_m/L) = \ln(c_{sd} t^*/L) = \ln(10^5 \times 3 \times 10^7/1) \simeq 30^{13}.$$

Choice of the numerical value of t^* is obviously not very critical, and the same applies to the quantity L.

At room temperature Eqn. (5) leads to the condition $\sigma \leqslant 4 \times 10^{-14} \times 30/\delta_m^2$, or more roughly $\sigma \leqslant 10^{-12}/\delta_m^2$ erg cm^{-2}. This means that, in the sense we have adopted, a solid can disperse into particles with $\delta_m \sim 10^{-6}$ cm if σ is reduced to 1 erg cm^{-2} or below.

The above condition, however, relates to the kinetics of the process only if it is thermodynamically possible: if the process of dispersion is thermodynamically advantageous, it will occur sufficiently rapidly provided that the inequality (5) is satisfied.

Let us now examine qualitatively the change ΔF in the free energy of the system when a solid is dispersed in a liquid into particles of colloidal dimensions: $\Delta F = \sigma\Delta A - T\Delta S$, where ΔA is the increase in free surface area of the particles and ΔS the increase in entropy of the system. Neglecting, as before, small numerical coefficients, we can write ΔA in the form $\Delta A \sim n\delta_m^2$, where $n \doteq V_0/\delta_m^3$ is the number of colloidal particles in the solution.

Let N_1 moles of the solid be dissolved in N_2 moles of liquid, when the entropy of mixing will be

$$\Delta S = -kN_A(N_1 + N_2)\{[N_1/(N_1+N_2)] \ln[N_1/(N_1+N_2)] + [N_2/(N_1+N_2)] \ln[N_2/(N_1+N_2)]\},$$

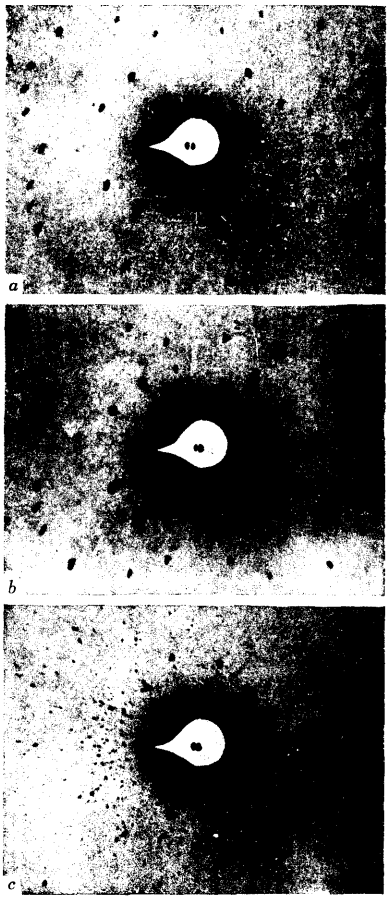


Fig. 12. Laue photographs of the same portion of a single crystal of tin: *a*) before application of coating to the specimen; *b*) 5 h after application of gallium coating; *c*) 316 h after application of gallium coating[52].

where N_A is the Avogadro number. When $N_1 \ll N_2$, we have $\Delta S = +kN_AN_1\{\ln(N_2/N_1) + 1\}$. The product N_AN_1 is in this case the number of particles n of the solid phase, and the logarithmic term is not very critical, being about 10–15. Hence $\Delta S \simeq (10 \text{ to } 15)nk$.

For the change in free energy we have $\Delta F = n\sigma\delta_m^2 - n(10 \text{ to } 15)kT$, which becomes negative if

$$\sigma \leqslant (10 \text{ to } 15) \times kT/\delta_m^2, \qquad (6)$$

giving at room temperature, approximately, $\sigma \leqslant 0.5 \times 10^{-12}/\delta_m^2$ erg cm^{-2}. Consequently in order to ensure that it is thermodynamically advantageous for dispersion into particles of $\delta_m \sim 10^{-6}$ cm to occur, the value of σ should be reduced at least to a few tenths of an erg per cm^2. The greater rigour of the resulting condition compared with criterion (4) warrants writing the latter in the approximate form (5).

Nevertheless, even the more rigorous condition (6) is still not sufficient for the process to be possible. Indeed, at extremely small values of δ_m the picture is changed sub-

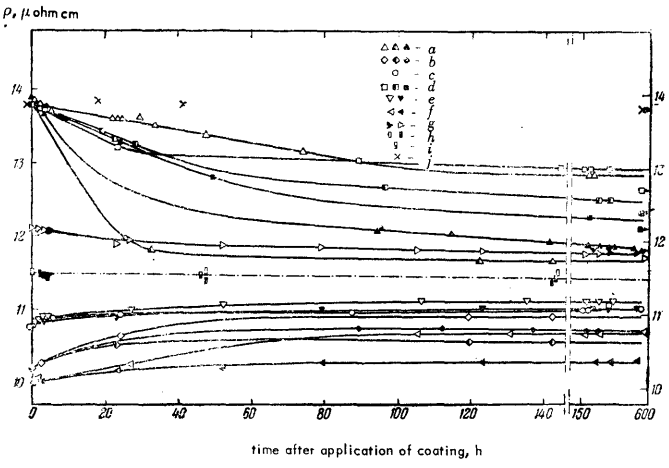


Fig. 13. Change in the electrical restivity ρ of differently oriented single crystals of tin after application of a gallium coating. Points indicated by arrows were obtained after 1800–2100 h. [52]

	Crystal	λ[001]°	Diameter, mm		Crystal	λ[001]°	Diameter, mm
a	Sn — I/1,2,3	18	0.520	*f*	Sn — XI/11.12	80	1.04
b	Sn — II/1,2,3	75	0.615	*g*	Sn — XII/11.12	~45	1.04
c	Sn — III/3	62.5	~0.8	*h*	Sn — XIII/1.2	polycrystalline	~0.6
d	Sn — V/1,2,4	20	0.583	*i*	Sn — XIV/5	polycrystalline	~1.0
e	Sn — X/11,12	63	1.04	*j*	Sn — V/3	20	0.533

Length of specimens 21 — 24 mm. (not coated with gallium)

stantially if account is taken of the equilibrium between colloidal particles and the material which is in a state of true solution, as well as of the presence of a charge on the surface of the particles. As δ_m decreases, the quantity ΔF again begins to increase. It may possibly have no minimum at all, and then the colloidal state is unrealisable under the given conditions. Alternatively, in spite of the condition $\Delta F = 0$ not being satisfied, there may still be a minimum, but a positive one; then the colloidal state is metastable. Only if the condition $\Delta F = 0$ is satisfied will the quantity ΔF have a negative minimum, corresponding to a stable colloidal state, at some still smaller value of δ_m.

The microstructure of a given solid also imposes substantial restrictions on the possibility of its dispersion: the process will hardly occur at all if this structure is too coarse compared with the thermodynamically possible dimension δ_m, or if the nature of the defects between the blocks of the microstructure does not allow adsorption-active molecules to penetrate even to a small depth. In the latter case, however, it is possible to consider the successive development of the surface δ_m^2 of the particle cell by cell[63]. It must be emphasised that the microstructure of crystalline solids is a dislocation structure; its character is determined by the conditions under which the single crystal or polycrystalline aggregate was grown and by the plastic deformations which it has undergone. On the other hand, allowing for the liberation, on disintegration of the solid into colloidal particles, of the elastic energy associated with the existence of the microstructure (dislocation arrays, etc.), makes it easier to satisfy conditions (4) and (6).

Actually, in metals which have been work-hardened to the limit, the density of the dislocations may reach a value of $\sim 10^{11} - 10^{12}$ cm^{-2}, and the corresponding stored elastic energy $\sim 10^8$ ergs cm^{-3} and above. This means that every unit of the material with a linear dimension $\delta_m \sim 10^{-6}$ cm is associated with up to 10^{-10} erg. If the whole of this elastic energy could be used to produce a new surface, dispersion would prove possible even at the relatively high values of σ of ~ 10 ergs cm^{-2} and above.

The extremely interesting specific phenomena observed with the pair tin–gallium[24,64] may approach the case of a very marked diminution in σ.

Several days after application of gallium, single crystals of tin completely lose their strength and plasticity, and are easily crushed to a powder. The original spots on the Laue photographs of such specimens (in the absence of any external mechanical constraints) gradually disappear, and the picture approaches the X-ray diffraction pattern given by a polycrystal (Fig. 12), the single crystal disintegrating into individual, sharply disoriented blocks. This is supported also by measurements of the electrical resistivity of gallium-plated single crystals of tin (Fig. 13): with specimens which are oriented in such a way that their initial resistivity is low (i.e. at large angles $\lambda_{[001]}$ between the tetragonal axis and the axis of the specimen), the resistivity increases in the course of time, whereas with single crystals having a high initial resistivity (when the tetragonal axis is close to the axis of the specimen), the resistivity gradually falls after application of the coating; in both cases the resistivity tends to the value corresponding to polycrystalline tin.

At low temperatures, at which the disoriented blocks are firmly soldered together by thin layers of solidified gallium, such specimens become considerably stronger than the original material[52,64].

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PROGRESS IN METHODS FOR THE SEPARATION OF RARE-EARTH ELEMENTS

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