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V. I. LIKHTMAN, L. S. BRYUKHANOVA, I. A. ANDREEVA,

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## Abstract

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V. I. LIKHTMAN, L. S. BRYUKHANOVA, I. A. ANDREEVA,
Academician P. A. REBINDER

# LOWERING OF THE SURFACE TENSION OF SOLID METALS UPON ADSORPTION ON THEIR SURFACE OF ATOMS OF SURFACE-ACTIVE METALLIC MELTS

The work of our laboratory [1–3] established the basic regularities in the action of the thinnest films of surface-active metallic melts on the mechanical properties of more refractory metals. The presence of such films on the surface of refractory metals (mercury on zinc, or gallium on zinc and cadmium, etc.) leads (under conditions of tension at a constant rate of deformation) to a sharp decrease in the strength and plasticity of the base metal. The mechanism of these peculiar phenomena, which are not associated with corrosion or dissolution, nor with chemical interaction between the melt and the base metal, has always been explained by us as adsorption of atoms of the surface-active melt on internal interfaces—the nuclei of fracture, formed during deformation of the metal. The atoms of the melt penetrate into these embryonic cracks by irregular diffusion along structural defects. As a result of adsorption and the considerable lowering of the surface tension on the walls of the embryonic cracks associated with it, fracture of the solid is facilitated in accordance with the general law of brittle fracture of crystals that we found: $P_c\tau_c = \alpha\frac{E\sigma}{L}$, where $P_c$ and $\tau_c$ are, respectively, the limiting normal and shearing stresses at the moment of separation, and $\sigma$ is the surface tension of the metal, considerably reduced at the boundary with the given surface-active medium [4]. The regularities of the indicated phenomena studied by us give numerous indirect confirmations of the adsorption mechanism, but direct experimental confirmation of these ideas has been lacking.

In the present work we give the results of a direct experimental determination of the magnitude of the surface tension of solid zinc upon adsorption on its surface of various amounts of gallium. We also give the results of measuring the surface tension of zinc coated with a thin film of lead (of thickness $\sim 2\ \mu$).

At present there are several quite reliable methods for determining the surface

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

tension of solids. We used the "zero" creep method developed by Tammann and Udin [5,6]. The essence of this method is that, in the temperature range close to melting, under loads on the specimen greater than a certain limiting value $P_0$, the specimen elongates, whereas under loads smaller than $P_0$ the length of the specimen decreases as a result of the action of surface-tension forces. Consequently, the limiting value of the load $P_0$, corresponding to zero creep, just compensates the forces of surface tension $\sigma$. For foil this condition is: $P_0 = a\sigma$, where $a$ is the width of the foil.

Indeed*, the requirement of constancy of volume $v = lab$ during the process

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* The calculation given was proposed by E. D. Shchukin.

deformation gives: $lab = (l + \Delta l)(a - \Delta a)(b - \Delta b)$, where $l$ is the length, $a$ the width, and $b$ the thickness of the foil. From this expression we obtain: $\frac{\Delta l}{l} = \frac{\Delta a}{a} + \frac{\Delta b}{b}$. Assuming that, for a limited annealing time $\tau$, the cross section of the specimen remains self-similar, we have $\frac{\Delta a}{a} = \frac{\Delta b}{b}$. Then $\frac{\Delta a}{a} = \frac{\Delta l}{2l}$. The change in the surface of the foil $\Delta S$ during creep is:

$$\Delta S = 2la\left(1 + \frac{\Delta l}{l}\right)\left(1 - \frac{\Delta a}{a}\right) - 2la$$

or

$$\Delta S = a\Delta l,$$

if the product $\Delta l \Delta a$ is neglected in comparison with $\Delta l$ and $\Delta a$.

**Fig. 1.** Dependence of the relative elongation of zinc foil coated with gallium (coating thickness $\sim 0.1\,\mu$) on load at a temperature of 380° for different times of isothermal holding ($1a$—1 hour, $1b$—3 hours, $2v$—5 hours, $3g$—8 hours).

**Fig. 2.** Dependence of the relative elongation of zinc foil coated with a layer of gallium of various thicknesses on load at a temperature of 380° and an isothermal holding time of 3 hours: 1—zinc foil without coating, 2—coating thickness $\sim 0.005\,\mu$, 3—$\sim 0.02\,\mu$, 4—$\sim 0.1\,\mu$.

The work performed by the load $P$ in the process of stretching the foil is

$$A = P\Delta l = Pl\dot{\varepsilon}\tau.$$

This work is expended on the formation of a new surface $\Delta S\sigma$ and on the established viscous flow $\eta\dot{\varepsilon}^2\tau v$, where $\sigma$ is the surface tension and $\eta$ is the viscosity. Consequently,

$$Pl\dot{\varepsilon}\tau = \Delta S\sigma + \eta\dot{\varepsilon}^2\tau v = al\dot{\varepsilon}\tau\sigma + \eta\dot{\varepsilon}^2\tau lab,$$

whence, under the condition of zero creep rate ($\dot{\varepsilon} = 0$), we obtain

$$P_0 = a\sigma.$$

We used zinc foil of thickness $\sim 7 \cdot 10^{-3}$ cm and width 0.2 cm. The length of the working part was 2 cm. Creep tests were carried out in a helium atmosphere at a temperature of 380°. A gallium film of different thicknesses (from $5 \cdot 10^{-7}$ to $1 \cdot 10^{-5}$ cm, as calculated from $h \simeq m/\rho \cdot 2S_0$, where $m$ is the mass of gallium deposited on the surface $2S_0$, and $\rho$ is its density) was deposited electrolytically from an alkaline solution of $GaCl_2$.

Figure 1 gives the results of a preliminary study of the creep of zinc foil coated with a gallium film $1 \cdot 10^{-5}$ cm thick. The graphs are plotted in coordinates: relative elongation during the given experiment time $\frac{\Delta l}{l_0} \cdot 10^3$ versus the parameter $P/a$, which assumes a value equal to $\sigma$ at the point of intersection with the abscissa axis. It is seen from this figure that experiment durations of 1 and 3 hours give coincident results, whereas a longer pro—

the duration of the experiment leads to a distortion of the results, caused by the tendency of the foil to decrease in size even under very high loads (this is especially pronounced at $\tau = 8$ h). A similar phenomenon was first observed by A. A. Zhukhovitskii and G. I. Belashchenko in other systems (7), and its nature has not yet been definitively established. (In pure metals this effect is absent.) It was important for us to establish that an isothermal holding time of the specimens from 1 to 3 h corresponds to a quasi-equilibrium state of the zinc—gallium system.

Figure 2 presents the results of measurements of the surface tension $\sigma$ at $\tau = 3$ h for pure zinc foil and foil with different amounts of deposited gallium. For pure zinc, $\sigma$ was found to be 830 erg/cm$^2$, which agrees well with measurements of $\sigma$ for the melt ($\sigma_{Zn} = 810$ erg/cm$^2$ at $\sim 450°$). The greatest decrease in the surface tension of zinc, by 600 erg/cm$^2$, was found by us for a gallium layer of thickness $\sim 10^{-5}$ cm, whereas smaller amounts of gallium lead to a smaller decrease in the surface tension of zinc.

The results obtained make it possible to construct an adsorption isotherm of gallium on zinc. However, it is first necessary to estimate the depth of diffusion penetration of gallium into zinc at the given temperature and experimental time.

The literature contains no data on the diffusion coefficient $D$ of gallium in zinc at comparatively high temperatures or on the solubility of gallium in zinc. If it is assumed that over 3 h diffusion penetration of the deposited amount of gallium takes place through the entire thickness of the foil, then for $D$ we obtain an order of magnitude $D \sim h^2/\tau \sim 1 \cdot 10^{-9}$ cm$^2$/s. This value is smaller than those usually obtained for other pairs of metals at the corresponding temperatures, and therefore it may be assumed with sufficient justification that during the experiment (3 h) gallium actually has time to diffuse into the zinc foil, and only an adsorption layer of gallium remains on the surface, corresponding to the given equilibrium bulk concentration $C$, apparently within the solubility of liquid gallium in solid zinc at the given temperature. To calculate the adsorption isotherm one may use the Gibbs equation in the approximate form

$$\Gamma = -\frac{C}{RT}\frac{\Delta\sigma}{\Delta C}.$$

Table 1 gives the values of the surface tension $\sigma$ and adsorption $\Gamma$ in accordance with the concentration of gallium in zinc.

Table 1

Values of $\sigma$, $C$, and $\Gamma$ for the zinc–gallium system

| Concentration of gallium in zinc $C \cdot 10^4$, g-at/cm$^3$ | Surface tension of zinc $\sigma$, erg/cm$^2$ | Adsorption of gallium on the surface of zinc $\Gamma \cdot 10^8$, g-at/cm$^2$ |
|---:|---:|---:|
| 0 | 830 | 0 |
| 0.12 | 660 | 0.16 |
| 0.5 | 480 | 0.27 |
| 2.5 | 200 | 0.38 |

Figure 3 gives plots of the change in surface tension $\sigma$ and adsorption $\Gamma$ as functions of the bulk concentration of gallium in zinc. From this figure it is seen that for the limiting adsorption $\Gamma_m$ one may take $\Gamma_m = 0.4 \cdot 10^{-8}$ g-at/cm$^2$, whereas calculation of the close packing of gallium atoms on the zinc surface for a monolayer gives $\Gamma_m = 0.2 \cdot 10^{-8}$ g-at/cm$^2$.

The work of adsorption of gallium on zinc was calculated by us from the equation

$$W = RT \ln \frac{\Gamma}{\delta C}$$

for the value $C = 0.12 \cdot 10^{-4}$ g-at/cm$^3$ ($\delta \sim 10^{-8}$ cm). The value of the work of adsorption obtained in this case was $W = 13000$ cal/g-at. Such a considerable value of the work of adsorption may be connected with the circumstance that adsorption of gallium proceeds at high temperature.

Of note is the experimentally obtained considerable decrease in the surface tension of zinc in the presence of a monolayer of gallium (by 600 erg/cm$^2$), since the surface tension of gallium itself is about 700 erg/cm$^2$. However, the very large limiting decrease in surface tension obtained in our experiments, substantially exceeding $RT\Gamma_m$, indicates the possibility of formation of a polyatomic layer of gallium in the near-surface layer of solid zinc. Evidently, with a further increase in the amount of deposited gallium, it forms on the surface an independent film phase, with the appearance of a second surface tension: gallium (saturated with zinc)–gas medium, which experimentally should be expressed in a sharp increase in the measured total surface tension. The deposition of such phase amounts of gallium is impossible, since it leads to spontaneous destruction of the foil specimen ([2]).

Fig. 3 Fig. 4

Fig. 3

Fig. 4

**Fig. 3.** Change in the values of surface tension $\sigma$ and adsorption $\Gamma$ as a function of the concentration $C$ of gallium in zinc

**Fig. 4.** Dependence of the relative elongation of zinc foil on load at a temperature of 380°:
1 –without lead coating after isothermal holding for 3 hours,
2 –with a lead coating (coating thickness $\sim 2\,\mu$) at different times of isothermal holding ($a$ –1 hour, $b$ –3 hours, $v$ –8 hours)

In Fig. 4 is shown a creep curve at 380° for zinc foil coated with a thin lead film of thickness $\sim 2 \cdot 10^{-4}$ cm (lead is practically insoluble in zinc). At all observation times from one to eight hours the same result was obtained: the surface tension of the foil with the lead film is $\sim$ 1200 erg/cm$^2$. If one takes into account that the surface tension of molten lead is $\sim$ 450 erg/cm$^2$, then the decrease in the interfacial surface tension at the zinc–lead melt boundary is about 100 erg/cm$^2$. This result is in good agreement with the circumstance that lead is only very weakly surface-active on zinc according to the data of mechanical tests.

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Institute of Physical Chemistry
Academy of Sciences of the USSR

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*Note: Figure translations are in progress. See original paper for figures.*