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Abstract

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ON THE SURFACE ACTIVITY OF LIQUID METALLIC COATINGS AND THEIR EFFECT ON THE STRENGTH OF METALS

S. T. Kishkin and Ya. M. Potak, with co-workers ([1,2]), studying the decrease in strength and the appearance of brittleness in a number of refractory and heat-resistant alloys under the influence of liquid metallic coatings and media, explained this influence by an adsorption effect ([3]). In our laboratory these effects were established in the tensile testing of single crystals of various metals coated with a thin film of a more fusible metal in the liquid state ([4,5]). These phenomena are explained by a lowering of the surface energy of the deforming solid metal on fracture surfaces developing on the basis of defects under conditions of adsorption from a liquid metallic coating as a result of two-dimensional diffusion of the adsorbed (surface-active) substance.

A detailed investigation of the influence of fusible coatings on the strength of metals showed that such influence possesses a clearly expressed specificity, manifested in the fact that one and the same coating causes a decrease in the strength of some metals and has no effect on others, and conversely, one and the same metal behaves differently depending on the chemical nature of the coating metal.

It should be noted that the decrease in strength cannot be attributed to the dissolving action of the molten coating, owing to the extremely small quantities of coating metal (less than 1 wt.%) and to the small, in any case limited, solubility of the base metal in the coating as a separate phase. The presence of very considerable effects in the case of metallic single crystals shows that such action of liquid metallic media should not necessarily be associated with selective action along grain boundaries.

Table 1

1. Decrease in the strength of the metal under the action of a molten coating	1. Decrease in the strength of the metal under the action of a molten coating	2. Absence of a decrease in the strength of the metal under the action of a molten coating	2. Absence of a decrease in the strength of the metal under the action of a molten coating
metal studied	metallic coating	metal studied	metallic coating

1. Decrease in the strength of the metal under the action of a molten coating	1. Decrease in the strength of the metal under the action of a molten coating	2. Absence of a decrease in the strength of the metal under the action of a molten coating	2. Absence of a decrease in the strength of the metal under the action of a molten coating
Cadmium	Tin	Cadmium	Mercury
Zinc	Mercury	Lead	Mercury
Zinc	Thallium	Copper	Mercury
Zinc	Tin	Copper	Tin
Copper	Bismuth	Copper	Zinc
Iron	(Hydrogen)	Zinc	Lead

Experimental data on the influence of fusible metallic coatings on the mechanical properties of metals fall into two sufficiently sharply delimited groups: 1) the presence of a sharp decrease in the strength of the metal under investigation and 2) the absence of a decrease in strength (see Table 1).

Comparing these data with the melting diagrams of the corresponding binary systems metal–metallic coating, it is easy to see that a decrease in the strength of a solid metal under the action of a liquid coating always corresponds to the presence on the melting diagram of a sufficiently narrow,

but within an entirely finite region of formation of the solid solution. This applies, of course, to that part of the diagram where the concentration of the coating metal is small, which corresponds to the case considered by us. Conversely, the complete absence of a decrease in strength corresponds to a broad region of formation of the solid solution of the coating metal in the metal under study.

From this point of view, the results obtained may appear trivial. Indeed, if the specified film thickness (of the order of a micron) corresponds to the ratio of the amounts of the low-melting and the more refractory metal within the region of formation of the solid solution, the strength of the system metal + coating will not be lower than the strength of the metal under study, and is usually somewhat higher (owing to the introduction of the impurity into the lattice). Of course, impurity atoms may, by diffusing within the volume of the solid-solution lattice, be adsorbed from the bulk onto surfaces developing at defective sites during deformation (if the impurity possesses a certain surface activity). However, the effects caused by this are small because of the low rate of volume diffusion in comparison with two-dimensional surface migration, and also because of the low impurity concentration. At high concentrations (corresponding to high solubility), however, the increase in strength due to the very formation of the solid solution predominates.

If, on the other hand, the region of formation of the solid solution is so narrow

that the system metal + coating lies outside this region, deformation of the metal is carried out in the presence of the liquid phase of the coating, which has time to become saturated with the substance of the metal being deformed. Upon crystallization of the melt (metal + coating), these ratios correspond to an equilibrium system consisting of separate crystallites of the solid metallic phase, separated by interlayers of the coexisting melt and possessing zero strength or, at any rate, low strength corresponding to the formation of a coagulation structure. In the phenomena under consideration, however, the question is not one of equilibrium systems formed at temperatures above the melting point of the eutectic, but of the deformation behavior (mechanical properties) of a solid, initially one-component metal—which may also be a single crystal—coated with a liquid film of a low-melting metal.

The decrease in the strength of a solid body (metal) is explained by the adsorption action of the molten metallic coating—by its ability to lower the surface or interphase tension at the metal/gas or metal/thin layer of liquid phase boundary from the value σ_0 to σ, and to ensure rapid penetration, owing to the high two-dimensional pressures $\sigma_0 - \sigma$, of atoms of the low-melting metal into the prefracture zone by the mechanism of two-dimensional migration.

The dependence of the magnitude of the effect of lowering the strength of metals, as a consequence of the lowering of surface tension, on the solubility in them of the coating metal proves to be entirely analogous to the increase in the surface activity of organic surface-active substances in aqueous solution as their solubility in water decreases. Liquid coatings that are only slightly soluble in the base metal prove to be the most surface-active in the sense of their ability to lower the surface tension of the base metal owing to the formation of an adsorption layer on the surfaces being formed. The greatest decrease in surface tension, and consequently also in strength, with sharply expressed brittle fracture, corresponds to the formation of a new liquid phase or of a polymolecular layer transitional to it.

Using the theoretical calculations of E. D. Shchukin ([6]), from the experimentally found dependence of the strength of zinc single crystals $P_c = f(c)$ on the concentration of tin in the lead + tin coating ([4]), one can find, in the region of brittle fracture, the dependence $\sigma(c)$, and from this, by the approximate Gibbs equation, estimate the magnitude of adsorption Γ and the course of the isotherm

adsorption $\Gamma = \Gamma(c)$ on the surfaces being formed. The approximate calculations shown in Fig. 1 lead to the value $\Gamma_m = 1.3 \cdot 10^{-9}$ mole/cm^2, which agrees well with a monatomic layer of tin, and to a further increase of $\Gamma(c)$ into the region of polymolecular layers, which corresponds, as is known, to complete wetting, i.e., to a continuous transition to a wetting film of the liquid phase.

In the case of a polymolecular layer—the transition to a film of the liquid phase on the surface (in the limiting case, the formation, upon rupture, of new zinc surfaces in liquid tin saturated with zinc)—the work of formation of such rupture surfaces (i.e., σ) will be the lower, the greater the mutual solubility (in the limit

Fig. 1

Figure 1: Fig. 1

$\sigma \to 0$ for unlimited mutual solubility).

Fig. 1. $P(c)$—experimental isotherm ([4]) of the reduction in the strength of single-crystal zinc as a function of the concentration of tin in the liquid coating Pb + Sn; $\sigma(c)$—calculated in the region of brittle fracture from ([6]) from $P(c)$, the surface-tension isotherm; $\Gamma(c)$—the corresponding adsorption isotherm.

The absence of a noticeable reduction in strength when the coating is practically completely insoluble in the base metal (zinc coated with lead) is connected with the preservation of a fairly high value of the surface tension at the phase boundary.

Ya. M. Potak ([2]) emphasizes that the decrease in the strength of iron (steels) under the action of hydrogen dissolved in it is likewise an adsorption effect (internal adsorption). Hydrogen in the metal, forming a solid interstitial solution, has high mobility, which, together with the surface activity of atomic hydrogen with respect to iron ([7]), causes the formation of a monatomic hydrogen layer on the surfaces being ruptured; this in turn causes a sharp decrease in the surface tension of iron and leads to hydrogen embrittlement ([8]).

Complex multicomponent alloys with an increased concentration of impurities at grain boundaries give a considerably more complex picture of the adsorption action of low-melting coatings (for example, the reduction in strength of heat-resistant alloys coated with a molten film of tin ([1])).

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