A METHOD OF DETERMINING THE DIFFUSION COEFFICIENTS AND SOLUBILITY OF ADSORPTION-ACTIVE METAL MELTS AND POLYCRYSTALLINE METALS

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An account is given of approximate methods, based on the effect of adsorption reduction of strength, of evaluating the coefficients and activation energy of volume diffusion of a metallic melt into a solid metal, and also the limiting solubility of a liquid in a solid metal.

A considerable reduction in the strength and ductility of solid metals occurs [1–3] in the presence of small amounts of adsorption-active metal melts applied to the surface of the specimen in the form of a thin film or an individual drop. This very abrupt impairment of the mechanical properties is not connected with corrosion or solution, but is mainly due to a great reduction of the free surface energy of the new surfaces (e.g., ultra-microcracks) formed in the solid while subjected to strain [1]. The adsorption reduction of strength is a very specific effect: it appears, as a rule, only in cases when the liquid metal possesses a narrow but finite region of solubility in the solid metal, and also does not form intermetallic compounds with it [2]. Thus, mercury lowers the strength of tin and zinc, gallium that of tin, cadmium, and zinc, bismuth that of copper and indium, and cadium that of steel, etc. [1,3].

The reduction of tensile strength of metals in the presence of adsorption-active melts depends on a number of physical and chemical factors—temperature, strain rate, etc. The instantaneous strength p depends also on the time τ of prior exposure (to the beginning of strain) of the solid metal in contact with the adsorption-active melt [4].

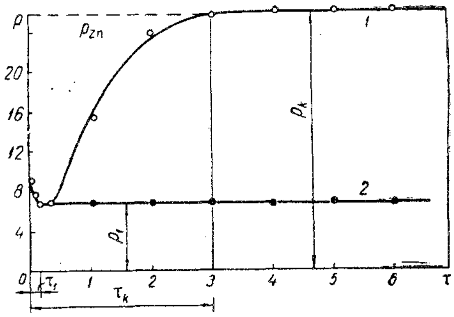

Fig. 1. Dependence of instantaneous strength p (kg/mm^2) of polycrystalline zinc on time τ of prior contact with mercury at various initial values of m_0/m_S (1 – m_0/m_S = 0.2%; 2 – 4%)

Analysis of the experimental curves $p = p(\tau)$ indicates that these data may be used to evaluate approximately the limiting solubility C_k of the liquid metal in the solid. The adsorption reduction of strength is kinetic in nature, i.e., for the effect to appear it is necessary to have well-timed and sufficiently rapid entry of the melt atoms into the incipient ultra-microcracks, which develop, as a rule, in the volume of the strained metal [1]. The melt in turn can propagate at quite high velocity if there is a layer of liquid metal on the specimen surface [5].

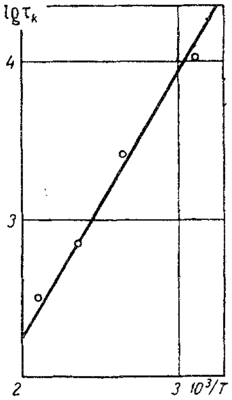

Fig. 2. Dependence of time τ_k (sec) for which the adsorption strength reduction effect is manifested in zinc on temperature T (°K) of prior exposure.

Let m_0 be the mass of liquid metal applied to the surface of the solid metal of mass m_S. If $m_0/m_S < C_k$, then given sufficient duration of prior contact (before tension) of the two metals, the entire amount of liquid metal is dissolved in the specimen, and the atoms of the melt will no longer possess enough mobility. As a result, no adsorption strength reduction will appear—the solid metal will yield at roughly the same tensile stresses as when the melt is absent. On the other hand, when $m_0/m_S > C_k$, the adsorption strength reduction effect will last indefinitely.

Plates of polycrystalline zinc (purity 98.7%, grain size 15 μ) of length 80, width 4, and thickness 0.5 mm were exposed in contact with mercury at room temperature, and extended at a rate of 24 mm/min on a tensile test machine (50 kg).

It follows from the results obtained (Fig. 1) that C_k = 4% by weight for the given zinc. The similarly determined limiting solubility of mercury in a zinc polycrystal of average grain size 50 μ was 0.3%, and in a single crystal—about 0.1%. To increase the measurement accuracy, one should use $m_0 \geqslant 20$ mg, when the error should not exceed ±25% of the mean value.

It can be seen from Fig. 1 that, during the initial period of prior exposure ($\tau < \tau_1$), there occurs a gradual reduction of instantaneous strength p of zinc, caused by diffusion of mercury along the intergrain boundaries [4]. Further exposure leads (when $m_0/m_s < C_k$) to a gradual increase of instantaneous strength due to diffusion of the melt into the grain volume. At exposure time $\tau > \tau_k$, when all the original mass m_0 has diffused, the adsorption strength reduction effect is no longer apparent.

If $m_0/m_s \ll C_k$, i.e., the concentration of the melt in the polycrystalline metal is very small, the volume diffusion coefficient will be practically independent of the concentration of diffusing melt [6].

Then, from the known equation [7]

$$m_0 = (2/\sqrt{\pi})\, c_0 \sqrt{D\tau_k}\, S \qquad (1)$$

the volume diffusion coefficient D may be determined. Here S is the area of contact between the film of melt and the specimen, C_0 is the concentration of melt in the surface layer of the metal (in gm/cm^3), and is close in order of magnitude to the limiting solubility of the melt in the given solid metal. The appropriate calculation from the data of Fig. 1 (e.g., for $m_0 = 3$ mg) gives a value of the diffusion coefficient of mercury into zinc grains of $D \approx 10^{-12}$ cm^2/sec at room temperature, with an error not exceeding the half order of magnitude.

This result agrees quite well with values of D for the same mercury-zinc pair determined by other methods, in particuler by that derived from the calculated influence of volume diffusion on the flow of a liquid metal over the surface of a solid [8].

For an identical mass m_0 and area S of a mercury film applied to a zinc plate, the time τ_k for which the adsorption strength reduction effect is maintained falls sharply with the temperature T of prior exposure, which is mainly due to the corresponding growth of the volume diffusion coefficient. Using the known equations $D = D_0 \exp(-U/RT)$ [6, 7], and transforming (1), it can be shown that

$$U = 2.3R[d \lg \tau_k / d(1/T)].$$

Having determined the quantity $[d\lg\tau_k/d(1/T)]$ from the experimental data as the slope of the line $\lg\tau_k = f(1/T)$, we can calculate the value of the activation energy. For the mercury-zinc pair (Fig. 2) $U = 8000 \pm 600$ cal/g-atom, which agrees satisfactorily with the results of other methods [8, 9].

It should be noted that when evaluating U by the technique described here, it is important that the limiting solubility c_k, in the whole range of temperature studied, should always remain far greater than m_0/m_s; otherwise, for values $m_0/m_s \approx C_k$, the volume diffusion coefficient depends not only on temperature, but also on the concentration of melt in the solid metal.

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