SPECIFIC FEATURES OF THE ADSORPTION-INDUCED REDUCTION IN STRENGTH OF POLYCRYSTALLINE ZINC IN THE PRESENCE OF GALLIUM


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The basic laws governing the deformation and fracture of metals in the presence of strongly surface-active substances (liquid metals) have been studied mainly on single crystal specimens. Investigations of this type have led to the conclusion that the sharp reduction in the strength and plasticity of solids under the action of adsorptive media is associated in most cases with a substantial reduction in free surface energy of the solid at the solid/liquid interface. The adsorption effects observed on single crystals are most conveniently explained in terms of the dislocation theory, which was used by Likhtman and Shchukin [1] to postulate an approximate mechanism of the action of surface-active media upon the mechanical properties of metals.

Fracture of polycrystalline metals in the presence of surface-active melts presents a different problem, the specific features of which are associated with the presence of grain boundaries. Under such conditions fracture usually takes place along the grain boundaries; this applies even to metals with close-packed hexagonal structures (zinc, cadmium, tin) which, when stressed in air or in an inactive medium, fail by intercrystalline fracture [2, 3]. This fact alone is sufficient to postulate that brittle fracture of polycrystalline metals under the influence of surface-active media is closely associated with the adsorption of an active liquid at the grain boundaries, i.e. at surfaces having excess surface energy [3].

Since the magnitude of the adsorption effect depends upon the concentration of the adsorbed substance, elucidation of the quantitative relationship between the quantity of an adsorbed liquid and the resulting reduction in strength of a polycrystalline metal was considered of sufficient interest to warrant the investigation described in the present paper.

The experimental work was carried out on polycrystalline zinc plates (measuring 70 x 20 x 1.8 mm) with an average grain size of 50 μ. Gallium, known to be able to diffuse rapidly along zinc grain boundaries [4], was chosen as the surface-active medium; it was deposited on zinc specimens (cathodes) by plating from an alkaline 5% KGaO₂ solution (a graphite rod serving as the anode) at a cathodic current density of 0.2 a/cm². The weight of gallium deposited, m, was controlled by controlling the plating time t with the aid of a previously determined calibration curve, described by m = 0.75 t (m in mg, t in minutes).

Three minutes after completion of plating each specimen was tested at room temperature* on a standard tensile testing machine at a strain rate of 2 cm/min. The results are reproduced in Fig. 1, where the tensile strength P of the specimen is plotted against the weight of gallium per unit surface area (q = m/S, where S is the total surface area of the specimen.

![Fig. 1. Tensile strength of zinc plotted against weight of gallium deposited per unit surface area.](image-url)

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*aGallium melts at 29.7°C, but can remain for a long time as a supercooled liquid at room temperature.
It will be seen that with increasing $q$ the tensile strength of zinc decreases linearly to a limiting value $P_m = 0.8$ kgf/mm$^2$, which does not change when $q$ is further increased.

Before carrying out a quantitative analysis of the relationship $P(q)$, let us discuss the main qualitative features of the fracture of gallium-coated zinc.

The first point to note is that a sharp reduction in strength of gallium-coated zinc was recorded even for specimens which, after plating, were held for 1 hr at 0°C and then tested at room temperature. Although by this treatment the possibility of gallium being adsorbed on the zinc surface in the form of a supercooled liquid was precluded, the values of $P$ obtained were not higher than for specimens tested immediately after plating. With single crystal specimens, however, the harmful effect of gallium was eliminated by such a treatment; the tensile strength of gallium-plated zinc single crystals held for 1 hr at 0°C was practically the same as that of gallium-free specimens.

If the propagation of a crack leading to fracture of a metal in the presence of a surface-active melt is to take place, it is usually necessary for the liquid to spread over the crack surface at a sufficiently fast rate. This was established by studies of propagation of macroscopic cracks of single crystals deformed in the presence of locally applied drops of active melts [11 and in many other instances in which the presence of a liquid phase at the crack surface was found to be necessary (on kinetic grounds) for the manifestation of the adsorption-induced reduction in strength [5].

The results of experiments, in which gallium-plated zinc was given a preliminary treatment at 0°C show that, under such conditions, a reduction in strength and ductility is observed even in the absence of liquid gallium on the specimen surface. This fact, correlated with the corresponding data on the behavior of single crystals, leads to the conclusion that the reduced strength of gallium-coated polycrystalline zinc is associated mainly with a reduction in free energy of the grain boundaries caused by adsorption of gallium atoms. What is particularly significant is that adsorption of gallium at the grain boundaries occurs before the application of a load. This rapid adsorption of gallium in the bulk of the specimen, which is practically completed at the end of the plating operation, is possible only because of the fast rate of diffusion of gallium atoms along the zinc grain boundaries. That this rapid diffusion does actually take place is indicated by the fact that no increase in strength of a gallium-plated zinc specimen is attained on grinding the specimen down even to half its original thickness; it is significant that in the case of mercury-coated polycrystalline zinc the strength and ductility of the latter can be fully restored by removing a surface layer 0.1-0.2 mm thick.

It follows therefore that the bonds in the grain-boundary regions, i.e., in the potential paths of fracture, of gallium-plated polycrystalline zinc are weakened in the very early stages, long before the load is applied.

Having elucidated the qualitative characteristics of the fracture of gallium-coated polycrystalline zinc, we can now approach this problem in a qualitative manner. The following assumptions are made.

1) After plating, all the gallium is uniformly distributed in the grain-boundary regions, practically no gallium is present in the grain bodies owing to the very low solubility of gallium in zinc [6]. By "grain boundary region" in this context we understand the zone of distorted crystal structure whose width $\Delta$ can reach several hundred A[7, 8].

2) Each gallium atom adsorbed in the grain-boundary region causes the same reduction of forces which bind the neighboring zinc atoms. For the sake of simplicity it is assumed that the grains are of cubical shape, the cube edge being $d$; the number of grains in a volume $V$ enclosed by the gallium-plated surface $S$ is therefore $V/d^3$, and their total surface area ($V/d^2$) $6d^2 = 6V/d$. The total volume of the grain-boundary regions in the specimen part under consideration is $(6V/d) \Delta/2$, and the average concentration of gallium in the grain-boundary region $C = (m/V)(d/3 \Delta) = (q/h)(d/3 \Delta)$, where $h$ is the specimen thickness.

The propagation of the principal (i.e., fracture) crack is directly assisted only by those gallium atoms which are situated in the immediate vicinity of the crack surface. In the first approximation it can be assumed that these atoms are concentrated in a layer the thickness of which is close to the atomic diameter $\delta_{Zn}$ of zinc. Their total number then is $n_{Ga} = \delta_{Zn} ah N/A_{Ga}$, where $ah$ is the crack surface area, $a$ the specimen width, $N$ Avogadro's number and $A_{Ga}$ the atomic weight of gallium.

Let us assume that $\alpha$ is the number of interatomic bonds weakened by the action of one gallium atom. Then the proportion of bonds weakened near the crack surface is $\varphi = n_{Ga} \alpha/n_{Zn}$, where $n_{Zn} \approx ah/\delta_{Zn}^2$ is the total number of bonds destroyed during crack formation. Substituting the values for $n_{Ga}$ and $n_{Zn}$, we obtain

$$\varphi = d(\delta_{Zn}^2/N/A_{Ga}) \cdot (d/3 \Delta) \cdot (q/h).$$

(1)

On the other hand, it can be assumed (also in the first approximation) that the experimentally recorded breaking stress $P$ is a sum of the strength of bonds of pure zinc ($P_{Zn}$) and bonds weakened by the action of gallium ($P^*$). Then

$$P = P_{Zn}(1-\varphi) + P^* \varphi.$$

(2)