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## Abstract

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## ON THE INFLUENCE OF TEMPERATURE ON THE DIFFUSION OF MERCURY IN ZINC

*(Presented by Academician P. A. Rebinder on March 30, 1963)*

Studies of the mechanism and regularities of the adsorption-induced reduction in the strength and plasticity of metals under the action of an adsorption-active melt ($^1$) have shown that this phenomenon is based on a decrease in the interfacial surface energy, caused by adsorption penetration of atoms of the melt into the deformed metal along structural defects (grain boundaries, blocks, hollow dislocation cores, etc.). In this connection it was necessary to establish the principal regularities of the spreading of a liquid adsorption-active metal over the surface of a solid and to clarify the role of volume and surface diffusion in these processes.

Work in our laboratory has shown that mercury is a very strong adsorption-active medium for zinc; this pair was therefore used as a model in most of the investigations carried out. The data available in the literature on the temperature dependence of the coefficient of volume diffusion of mercury into zinc are qualitative in character ($^2$), or were obtained indirectly ($^3$). The temperature dependence of the coefficient of surface diffusion of mercury over zinc has not been determined at all by direct methods. The aim of the present work was to determine, by direct methods, the temperature dependence of the diffusion coefficient of mercury in zinc, both volume and surface.

### 1. Determination of the temperature dependence of the coefficient of volume diffusion of mercury in zinc.

For the work we used the mercury isotope $Hg^{203}$ ($\beta$-radiation energy 0.21 MeV, $\gamma$-radiation 0.28 MeV, half-life $T$ = 47 days). Diffusion was followed by the method of S. N. Kryukov and A. A. Zhukhovitskii ($^4$). The object of study was zinc of grade TsO (99.96% Zn) in the form of foil 71 $\mu$ thick. Specimens 15 × 15 mm in size were annealed at 200° for one hour and cooled together with the furnace; the average grain size proved to be 120 $\mu$. A mercury film was applied to the surface of the zinc, freed from the oxide film (under a previously applied drop of 10% nitric acid solution*), by the contact method from a solution of mercurous nitrate labeled with $Hg^{203}$. The thickness of the mercury film obtained under these conditions was 1.5 $\mu$, and its area was 0.3-0.4 $cm^2$. With this method of local application of the mercury film, the possibility of surface diffusion of mercury over the zinc is excluded, since the remaining surface of the specimen remains covered with an oxide film. Only after prolonged holding of the specimens at 200° does the mercury begin to spread, despite the presence of the oxide film.

The intensity of $Hg^{203}$ radiation was measured on a B-2 apparatus using an end-window counter with a thin mica window (1.2 mg/cm$^2$). Immediately after application of the mercury film, the initial activity was measured from the side of the film, $I_{01}$, and from the opposite side of the specimen, $I_{02}$; subsequent measurements were carried out at hourly intervals over the course of 5–10 h. The experiments were performed at temperatures of 21, 110, 150, and 200°. The thermostat temperature was controlled with an accuracy of ±0.5°. To avoid evaporation of mercury at temperatures of 110, 150, and 200°, the specimens were thermostated under a layer of vaseline oil. In these cases, before measuring the activity, the specimens were washed with petroleum ether.

The diffusion coefficients, determined from the slope of straight lines on plots of $\lg \frac{I_1 - I_2}{I_1 + I_2} = f(\tau)$, are given in Table 1. The values of the activities $I_1$ and $I_2$ were taken from the $\beta$-radiation of $Hg^{203}$. At 200° a violation of the rectilinear dependence was observed after two hours of holding, owing to the onset of mercury spreading. The values of the diffusion coefficients for a temperature of 200° given below were calculated from the initial rectilinear portion of the plots.

The temperature dependence of the coefficient of volume diffusion of mercury in zinc is presented in Fig. 1; the value of the activation energy of this process (in accordance with the slope of the straight line) is $E = 3200$ cal/g-at. The experimental straight line satisfies the equation

$$D = 5.8 \cdot 10^{-10} \exp\left(-\frac{3200}{RT}\right).$$

**Table 1**

**Values of the coefficients of volume diffusion of mercury in zinc $D_v$ ($10^{-11}$ cm$^2$/sec) at different temperatures**

| Experiment No. | 20° | 110° | 150° | 200° |
|---|---|---|---|---|
| 1 | 0.26 | 0.95 | 1.35 | 1.74 |
| 2 | 0.20 | 1.18 | 1.25 | 2.00 |
| 3 | 0.25 | 0.86 | 1.68 | 2.38 |
| 4 | 0.15 | 0.67 | 1.07 | 1.41 |
| 5 | 0.28 | 0.96 | 0.76 | 1.78 |

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[*] The change in specimen thickness as a result of etching was taken into account in calculating the diffusion coefficient.

| Experiment No. | 20° | 110° | 150° | 200° |
|---|---|---|---|---|
| 6 | 0.33 | 1.18 | 1.74 | 2.35 |
| 7 | 0.13 | 0.72 | 0.67 | 1.76 |
| 8 | 0.26 | 0.72 | 1.75 | – |
| Average | 0.23 | 0.90 | 1.28 | 1.92 |

**2. Determination of the temperature dependence of the coefficient of surface diffusion of mercury on zinc.** As was established in works ($^5$), two forms of propagation of mercury over a zinc surface free of an oxide film are possible: 1) spreading in the form of a sufficiently thick phase film over a rough surface, and 2) surface diffusion—migration of atoms—over a smooth surface.

We considered it possible, by using a vertical arrangement of the specimens, to study surface diffusion from the rate of rise of the mercury front not only on smooth but also on rough surfaces, assuming that, because of the high density of mercury, the force of gravity would rapidly balance the driving force $\Delta\sigma$ causing spreading of the mercury film, as a result of which spreading would cease and the mercury would propagate only by the mechanism of surface diffusion. The quadratic time dependence of the height of rise of mercury, characteristic of diffusion processes, established by our measurements confirmed the validity of the procedure we chose.

The experiments were performed at temperatures of 0, 20, 35, 45, 60, 75, and 90°. To prepare the specimens, wire of technically pure zinc with a diameter of 1 mm was used. Specimens 10 mm long were annealed at 200° for one hour. The oxide film formed on the zinc surface in this process is an almost anhydrous zinc oxide ($^6$), which dissolves with difficulty at ordinary temperature in alkalis and, still more, in ammonia. With increasing temperature, however, the solubility of ZnO in alkalis and ammonia increases. To remove and subsequently prevent formation of the oxide film, the experiments were carried out in a 5% KOH solution. To achieve the same degree of cleaning of the zinc surface from the oxide film, the specimens were preliminarily etched in 5% KOH at 90° for 3 min, after which they were transferred into graduated tubes located in a thermostat at the temperature under study and containing a fresh portion of the alkali solution.

of the same concentration, and on the bottom—a drop of mercury weighing 5 mg. After holding to equalize the temperature, the specimen was brought into contact with the mercury, and the rate of rise of the sharply outlined boundary of the mercury film was determined visually with the aid of divisions marked on the tubes. As already indicated above, the propagation of the mercury front is described by the power function $h \sim t^{0.5}$, characteristic of diffusion processes. The values of the surface-diffusion coefficients of mercury over zinc, calculated from the mean values of several parallel experiments, for temperatures of 0, 21, and 35° are, respectively, $1.88 \cdot 10^{-2}$, $2.48 \cdot 10^{-2}$, and $2.93 \cdot 10^{-2}$ cm$^2$/s. Beginning at 45°, the quadratic dependence $h = f(t)$ is violated, which should be explained

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

mainly by the increasing role of volume diffusion of mercury into zinc, leading to a decrease in the distance over which mercury is able to spread along the surface of zinc. In addition, a significant change in temperature also affects the factors governing the spreading of mercury—surface tension, viscosity, and density. The conditionally calculated surface-diffusion coefficients for temperatures of 45, 60, 75, and 90° are, respectively, $2.69 \cdot 10^{-2}$, $6.21 \cdot 10^{-3}$, $2.56 \cdot 10^{-3}$, and $1.63 \cdot 10^{-3}$ cm$^2$/s.

**Table 2**

Values of the coefficients of surface diffusion of mercury over zinc $D_s$ ($10^{-2}$ cm$^2$/s) as a function of the character of preliminary etching of the specimens

| Etching duration, min | In 5% KOH solution, at 35° | In 5% KOH solution, at 90° | In 10% $NH_4OH$ solution, at 35° |
|---:|---:|---:|---:|
| 1.5 | – | 2.37 | – |
| 3 | 1.87 | 2.93 | – |
| 6 | 2.17 | 3.05 | – |
| 12 | 2.89 | 2.94 | – |
| 30 | 2.60 | – | 1.10 |
| 60 | – | – | 1.85 |

Because the spreading of mercury over the surface of zinc depends strongly on the degree of its oxidation, it was necessary to determine whether removal of the oxide film occurs sufficiently completely under the etching conditions selected by us. For this purpose, studies were carried out of the surface diffusion of mercury at room temperature on specimens etched in 5% KOH at 90 and 35° and in 10% $NH_4OH$ at 35° for various periods of time (Table 2).

**Fig. 1**

**Fig. 2**

As follows from the data of Table 2, the value $D_s = 2.9 \cdot 10^{-2}$ cm$^2$/s attained with three-minute etching practically does not change with increasing etching time. This gives us grounds to believe that the zinc surface is completely freed from the oxide film. Profilograms taken from the surface of specimens etched in 5% KOH at 90° for various times showed no visible change in the microrelief, which corresponded approximately to cleanliness class 7.

When etching is carried out at 35°, the limiting value of $D_s$ is also reached, but after a longer time—12 min. In 10% $NH_4OH$ at 35°, even after etching for one hour, only the value is reached

$D_s = 1.85 \cdot 10^{-2}$ cm$^2$/sec, which in 5% KOH at 35° we obtain in 3 min.

This difference in the action of 5% KOH and 10% $NH_4OH$ should also be taken into account when removing the oxide film, consisting of zinc hydroxide and basic carbonate[6], which forms on the surface of zinc when it is stored in air containing moisture and carbon dioxide, since only freshly precipitated zinc hydroxide with a high water content dissolves readily in alkalis and ammonia.

Figure 2 presents the temperature dependence of the coefficient of surface diffusion of mercury over zinc. In accordance with the slope of the straight line in the temperature range 0–35°, the activation energy of the surface diffusion of mercury over a zinc surface free of oxide film is $E = 2150$ cal/g-atom. At higher temperatures (above 40°), the linear dependence of $\lg D_s$ on $1/T$ is sharply disrupted: the values of $D_s$ begin to decrease rapidly. This is associated with the increasing role of volume diffusion, leading to enhanced absorption of the mercury spreading over the surface by the bulk of the specimen.

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