Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1961

SovietRxiv

Fig. 1. Dependence of the height of rise of the mercury spot on time

Figure 1: Fig. 1. Dependence of the height of rise of the mercury spot on time

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1961. Volume 137, No. 6

PHYSICAL CHEMISTRY

B. D. SUMM, Yu. V. GORYUNOV, N. V. PERTSOV, and E. D. SHCHUKIN

ON THE SPREADING OF MERCURY OVER THE FREE SURFACE OF ZINC IN CONNECTION WITH THE STUDY OF ADSORPTION LOWERING OF STRENGTH

(Presented by Academician P. A. Rehbinder, 9 XII 1960)

A substantial condition for the lowering of the strength of metals under the action of molten adsorption-active metallic coatings is the rapid penetration of melt atoms into the prefracture zone by two-dimensional migration along defects of the crystal structure and along the walls of incipient microvoids ([1], [2]). In one of our recent communications we described the development of macroscopic fracture cracks in zinc plates under the action of locally applied small drops of mercury ([3]). These experiments made it possible for the first time to reveal directly the role of mercury migration in crack development and to relate the kinetics of its growth to a distinctive competition between two processes: the spreading of mercury along the crack walls toward the prefracture zone (surface migration) and the absorption of mercury by the crack walls along its entire length (bulk diffusion).

In the present work, the spreading of mercury over the free surface of zinc (in the absence of mechanical stresses) was studied*. The experiments were carried out on plates of technical zinc (98.7% Zn) 1.85 mm thick at room temperature. To remove the oxide film, the specimens were etched in 12% nitric acid, then washed with water and immersed in a bath with a 10% solution of ammonia, in which they remained for the entire duration of the experiment.

Fig. 1. Dependence of the height of rise of the mercury spot on time

The first series of experiments was carried out on vertically arranged plates 2.0–2.5 cm wide and up to 30 cm long. The lower end of the plate was brought into contact with mercury, which wetted the entire lower edge of the zinc. The

Fig. 2. Dependence of the radius of the mercury spot on time. Mercury mass $m = 10$ mg. The vertical dashed line corresponds to the moment of disappearance of the liquid phase of mercury at the center of the spot

Figure 2: Fig. 2. Dependence of the radius of the mercury spot on time. Mercury mass $m = 10$ mg. The vertical dashed line corresponds to the moment of disappearance of the liquid phase of mercury at the center of the spot

mercury was taken in a sufficiently large quantity so that the mass of the source practically did not decrease during the experiment ("linear source with infinite capacity"). Immediately after zinc comes into contact with mercury, a readily visible light matte spot with a sharply outlined front begins to spread upward over the surface of the plate. At the initial moment—a small fraction of a second—the spot front moves with a relatively high velocity (of the order of a centimeter per second); thereafter the rate of its spreading rapidly decreases. Visual readings of the position of the spot front were made through the wall of the bath (a glass beaker) by means of scale marks applied in advance to the specimen. A series of such experiments made it possible to establish good quantitative reproducibility of the results. It turned out that the height of rise of the spot h is a power function of time t (Fig. 1).

The second series of experiments was carried out on square horizontally placed plates. A small drop of mercury—from several tenths of a milligram to several tens of milligrams—was applied to the center of the plate (a "point," or, strictly speaking, a "source with finite capacity" having a small finite radius). In this case the spreading process

---

* G. I. Varicheva took part in the work.

the mercury over the surface of zinc breaks down into three successive, clearly distinguishable stages. The first, shortest stage (fractions of a second) is the spreading of the drop. The drop turns into a "puddle" with a shiny mirror-like surface; its dimensions naturally depend on the mass of the mercury. For 10 mg samples, the radius of the circle occupied by the mercury at the end of the spreading stage is 3-4 mm.

Fig. 2. Dependence of the radius of the mercury spot on time. Mercury mass $m = 10$ mg. The vertical dashed line corresponds to the moment of disappearance of the liquid phase of mercury at the center of the spot.

Immediately after the drop has finished spreading, the second, principal stage begins, similar to the process described above for the propagation of mercury along a vertical plate. Namely, from the edge of the mirror-like "puddle" a light matte spot of regular circular shape begins to spread; at the first moment the velocity of displacement of the front reaches ~ 1 cm/s; then it decreases regularly. After several minutes (depending on the mass of the initial drop

Fig. 3. Dependence of the final radius of the mercury spot on the mass of mercury

Figure 3: Fig. 3. Dependence of the final radius of the mercury spot on the mass of mercury

of mercury), the evidently liquid mercury phase remaining in the central part of the circle is exhausted—the mirror shine disappears; the third stage of the process begins. The spot grows very slowly; in this case the characteristic linear dependence of the logarithm of the spot radius on the logarithm of time, which existed in the second stage, is violated. After several hours the growth of the spot ceases completely. (It should be noted that, in the presence of a strongly textured layer on the surface of the plate, the rates of propagation of the spot along and across the fibers differ somewhat, and as a result the spot assumes the shape of an ellipse.) The growth of the spot radius with time for a drop of mass 10 mg is shown in Fig. 2 (readings were begun a few seconds after the onset of the second stage). Fig. 3 gives the dependence of the final radius of the spot R (2 hours after application of the drop) on the initial mass of mercury.

Fig. 3. Dependence of the final radius of the mercury spot on the mass of mercury.

A series of experiments was also carried out with an imitation, on a horizontal plate, of a "point source of infinite capacity" : in this case, as the mercury in the central part of the circle was exhausted (before the end of stage II), it was added successively in small portions. Finally, several experiments were set up for observing the vertical propagation of mercury from a "point source of infinite capacity" : in this case the specimens were plates cut in the form of sectors with an angle of about 60°. The sector was placed with its vertex downward, and the vertex was brought into contact with a sufficiently large mass of mercury. The experiments showed that the course of the process (with the exception of stage I) is practically independent of whether the plate is positioned horizontally or vertically.

In all cases, when using a "source of infinite capacity" (and also in stage II for a source of finite capacity), the propagation of the mercury front is described by a power function of time: $r \sim t^n$; depending on the experimental conditions, values of the exponent n approximately from 0.3 to 0.4 are observed.

The results of these experiments reveal a close similarity to the data on the propagation of cracks in zinc plates under local application of mercury [3]: here the same stages are observed—spreading of the drop, propagation of mercury by surface migration from a source containing an evidently liquid phase of mercury, and, finally, slow migrational re-···

···determined by the mercury still present in the thinnest surface layers, when the source is already absent. It is obvious that in the experiments described, with the spreading of mercury over the surface of zinc in the absence of mechanical stresses, the kinetics of the process is likewise determined by competition between surface migration of the mercury and its absorption (diffusion) into the bulk of the zinc. In this connection the following circumstance is of interest: if, soon after the end of stage II, a new portion of mercury is placed at the center of the spot, this addition proves to be "additive" : the spot then assumes the same final dimensions as if the total mass had been taken at once. However, when a second drop is applied after 2–3 hours, when stage III has already completely ended, there is no longer additivity of action: if the second portion is equal to the first, the dimensions of the spot practically do not change; if the second portion is larger, then the final radius of the spot approximately corresponds to the action of only one larger drop.

Mechanical tests also confirm the substantial role of bulk diffusion (absorption) of mercury in the kinetics of its spreading over the surface of zinc. We previously showed that a mercury film of thickness $\sim 1\ \mu$ causes embrittlement of zinc ([2]). In the present work it has been established that if, immediately after the experiment, the plate is subjected to bending, then the entire surface encompassed by the mercury spot becomes covered with a network of fine cracks. If, however, the specimen is bent not immediately after the experiment but after several hours, no such surface cracking is observed; this means that almost all the mercury that had been on the surface has time to diffuse into the bulk of the zinc.

It was to be expected that the lowering of the strength of zinc within the limits of the spreading spot would manifest itself much more clearly when thin specimens were tested. A corresponding series of experiments was carried out on high-purity zinc wire (99.99% Zn) of diameter 0.6 mm and length 10–15 cm. The specimens were placed vertically in the bath and kept in contact with mercury for a definite time. They were then removed from the bath and subjected to the simplest mechanical test: they were wound at constant speed onto a round rod of diameter 3 cm. At this radius of curvature the wire used by us bent readily in the absence of mercury, without revealing cracking. The specimen was wound onto the rod starting from the upper end, which had not been touched by mercury. At a definite distance from the lower end (as a rule, precisely at the point to which the visible mercury front had managed to reach) the specimen broke. The experiments gave the following results:

Contact time of the specimen with mercury	1	5	20	60	min
Length of the section that became brittle	7	15	25	41	mm

The data given reveal, on the whole, the same dependence of the height of mercury rise on time as in the case described above (cf. Fig. 1). Some numerical discrepancies are evidently connected with differences in the purity of the specimens, the quality of their surface, and the grain size.

It should be noted that the spreading of mercury over the surface of zinc could be observed only when the experiments were carried out in a medium preventing the formation of an oxide film. The optimal conditions for spot growth were obtained using a 10–20% ammonia solution. When the ammonia concentration was reduced to 2.5–5%, some slowing of the process was observed. Use, as a medium preventing oxidation of zinc, of a 5% hydrochloric acid solution and a 5% sodium hydroxide solution showed practically the same results as in the case of a 10% ammonia solution.

Moscow State University
named after M. V. Lomonosov

Received
4 XII 1960

CITED LITERATURE

1. P. A. Rebinder, V. I. Likhtman, L. A. Kochanova, DAN, **111**, 1284 (1956).

2. E. D. Shchukin, N. V. Pertsov, Yu. V. Goryunov, Kristallografiya, **4**, 887 (1959).

3. B. D. Summ, Yu. V. Goryunov, N. V. Pertsov, E. D. Shchukin, P. A. Rebinder, DAN, **136**, No. 6 (1961).

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