Reports of the Academy of Sciences of the USSR

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1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962. Volume 146, No. 3

PHYSICAL CHEMISTRY

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THE INFLUENCE OF MICRORELIEF ON THE LAWS GOVERNING THE SPREADING OF A LIQUID METAL OVER A SOLID METALLIC SURFACE

(Presented by Academician P. A. Rehbinder, 23 V 1962)

The study of the laws governing the spreading of liquids over the surface of solids and, in particular, the spreading of adsorption-active metallic melts over the surface of solid metals has recently acquired great scientific and practical importance in connection with the study of the adsorption effect of lowering the strength of solids. In considering the spreading of a liquid metal over a solid metallic surface in the absence of external forces, including gravity, it is necessary to emphasize that up to now essentially only one form of such a process has been studied, namely surface diffusion, i.e., the migration of monolayers of liquid molecules (atoms) from the contour of a drop deposited on a solid surface and having a definite contact angle (see, for example, ([1–4])). Meanwhile, many phenomena associated with the adsorption effect—for example, the formation of long macroscopic cracks in the presence of a locally deposited drop of a surface-active melt ([5])—are accompanied by a qualitatively different form of spreading of the liquid drop: spreading-out. By "spreading-out" we mean the viscous flow of a gradually thinning phase layer of liquid, connected directly not with the action of gravity, but with a decrease in the free surface energy of the system. In other words, the condition for spreading-out is the condition of complete wetting of the surface.

In analyzing the problem of wetting, most authors confine themselves to a formal consideration of the relation between the quantities σ_{12}, σ_{32}, and σ_{31} (respectively, the specific free surface energies of the liquid and the solid at the boundary with the medium in which the experiment is carried out, and at the boundary between the solid and the liquid), assuming that complete wetting is possible if

$$\sigma_{32} > \sigma_{12} + \sigma_{31}; \quad (1)$$

Fig. 1. Profilograms of the microrelief of zinc plates with different surface quality: a—smooth surface (9th class of finish); b—rough surface (6th class of finish), obtained by preliminary etching in nitric acid

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in the opposite case, i.e., when

$$\sigma_{32} < \sigma_{32} + \sigma_{31}, \tag{2}$$

a drop with a finite contact angle is formed. It should be emphasized, however, that in the latter case spreading of the liquid is also possible (by surface diffusion); over a sufficiently long time this may lead to complete disappearance of the deposited drop. However, inequalities (1) and (2) can be used to determine the character of liquid spreading only for an ideally smooth surface of a solid body ([6–8]). Since under real conditions every solid surface possesses a certain microrelief characteristic of it, for a correct description of liquid spreading it is necessary, along with the physical properties of the system, also to take into account the geometrical features of the surface. P. A. Rehbinder ([6]) considers an additional frictional force acting along the contour, whose magnitude is related to the degree of surface roughness. This force retards the advance of the front of the spreading drop and leads—

leads to the fact that the advancing contact angle is larger than the receding angle of a drop (wetting hysteresis). B. V. Deryagin ([7]), theoretically studying the dependence of the contact angle on microrelief, came to the conclusion that, under the condition $K \cos\vartheta \geqslant 1$, spreading of a liquid over a rough surface along microdepressions and grooves may occur (K is the roughness coefficient, i.e., the ratio of the true surface to the apparent one; ϑ is the contact angle on an ideally smooth surface).

In studying the spreading of mercury over a polycrystalline zinc surface free of an oxide film* we were able for the first time to observe, on one and the same liquid-solid pair, depending on the microrelief of the surface** (Fig. 1), both possible forms of liquid propagation—spreading and surface diffusion. On a smooth surface (Fig. 1a), mercury forms a drop with a contact angle ϑ of about 7°; from the contour of this drop a round matte spot slowly spreads, whose radius grows in accordance with the dependence characteristic of diffusion processes, $r \sim t^{0.5}$ (Fig. 2, a), and the mass of the drop m does not affect the rate of displacement of the spot front. The spreading of mercury over the surface of long, narrow zinc plates immersed at one end in a beaker with a sufficiently large amount of mercury proceeds analogously (Fig. 3, a); it is characteristic that the rate of propagation of mercury over a smooth surface does not depend on the angle of inclination of the plates to the horizontal.

Fig. 2. Dependence of the radius of a mercury spot r (mm) on time t (sec) for different masses of mercury m: 1—1 mg, 2—5 mg, 3—10 mg; a—for a smooth surface, b—for a rough surface

Figure 2: Fig. 2. Dependence of the radius of a mercury spot r (mm) on time t (sec) for different masses of mercury m: 1—1 mg, 2—5 mg, 3—10 mg; a—for a smooth surface, b—for a rough surface

Figure 3 diagram

Figure 3: Figure 3 diagram

Fig. 1. Profilograms of the microrelief of zinc plates with different surface quality: *a*—smooth surface (9th class of finish); *b*—rough surface (6th class of finish), obtained by preliminary etching in nitric acid.

The spreading of mercury over a rough surface obtained after preliminary 10-minute etching of zinc plates in 12% nitric acid (Fig. 1b) has a qualitatively different character: the radius of the spot formed when a drop of mercury is applied to the zinc surface grows in this case according to the law $r \sim t^{0.3}$, and the rate of displacement of the spot front is appreciably greater than in surface diffusion and increases with increasing mass of mercury (Fig. 2, b). The following circumstances convincingly show that the process observed in this case is precisely spreading, and not two-dimensional diffusion of mercury.

Fig. 2. Dependence of the radius of a mercury spot r (mm) on time t (sec) for different masses of mercury m: 1—1 mg, 2—5 mg, 3—10 mg; *a*—for a smooth surface, *b*—for a rough surface.

1. When mercury is applied to a rough surface, a drop with a finite contact angle is not formed; observation of the spreading process under a microscope confirms that growth of the spot is accompanied by motion of the phase layer of mercury.

2. The rate of rise of mercury along narrow plates with a rough surface increases as the angle of inclination of the plates to the horizontal decreases

* The medium dissolving the oxide film was a 10% ammonia solution.
** Profilograms of the surface of the zinc plates were obtained in the surface-quality laboratory of the Scientific Research Institute of the Bearing Industry.

(Fig. 3, b); obviously, the effect of gravity can manifest itself only in the spreading of a phase layer of sufficient thickness.

3. It can be shown that the circular spreading of a drop under the action of surface-tension forces should occur according to the law $r \sim t^{1/4}$ (9), which agrees satisfactorily with the experimentally observed dependence $r \sim t^{0.3}$. Indeed, let us assume, as a first approximation, that the mercury layer at each given instant of time t has a constant thickness

Fig. 3. Dependence of the distance h (mm) to which mercury spread over a zinc plate on the time t (sec.) at different angles of inclination of the specimen to the horizontal β: 1 -90°, 2 -22°, 3 -10°; a —for a smooth surface, b —for a rough surface

$z(t) = m/\pi r^2 \delta$, where m is the mass of the applied drop, $r = r(t)$ is the radius of the spot, and δ is the density of mercury. Then the volume of mercury bounded by a cylinder of radius ρ ($\rho < r$) is $V(\rho, t) = (m/\delta)\rho^2/r^2$, and the mean flow velocity through the lateral surface of this cylinder is $v(\rho, t) = -(1/2\pi\rho z)\partial V/\partial t = (\rho/r)\, dr/dt$, i.e., it increases linearly from the center of the circle to the periphery. In the case of quasi-stationary viscous Newtonian flow with a velocity gradient constant over the layer thickness, the force of viscous resistance in an elementary ring of width $d\rho$ is: $dF = \eta[v(\rho, t)/(z/2)]2\pi\rho\, d\rho = \eta(\rho/r)\, dr/dt\, 2(\pi\rho^2\delta/m)\, 2\pi\rho\, d\rho$ (η is the viscosity of mercury); integrating the latter relation, we find the total force impeding the flow: $F = (4\pi^2/3)(\eta\delta/m)r^4\, dr/dt$. Equating the force of viscous resistance F to the spreading force $2\pi r(\sigma_{32} - \sigma_{12} - \sigma_{31}) = 2\pi r\Delta\sigma$, acting on the contour of the mercury film, we obtain the equation of motion of the mercury front: $(1/m)r^3 dr = (3/2\pi)(\Delta\sigma/\eta\delta)\, dt$. After integration we have

$$r = \left(\frac{6}{\pi} m \frac{|\Delta\sigma|}{\eta\delta}\right)^{1/4} t^{1/4} = At^{1/4}. \tag{3}$$

The resulting relation not only correctly establishes the character of the dependence of r on t, but also makes it possible to explain the influence of the mass of mercury on the rate of the process (Fig. 2, b): the experimental dependence of the coefficient A on m ($A \sim m^{0.26}$) practically coincides with the theoretical relation $A \sim m^{1/4}$.

4. The difference between spreading and surface diffusion is very clearly manifested when studying the influence of temperature on the course of spreading (Fig. 4). The spreading rate is practically independent of temperature (Fig. 4, b); this is explained by the fact that the quantities determining the value of the coefficient A (see equation (3)) change only slightly in the temperature interval investigated. On the contrary, the rate of surface diffusion increases sharply with increasing temperature (Fig. 4, a), in accordance with the temperature dependence of the surface-diffusion coefficient: $D_{\mathrm{p}} \sim \exp(-U/kT)$ (U is the activation energy)*.

5. Let there be a groove on the surface of a solid body with a transverse section in the form of an isosceles triangle with included angle α; then a liquid which forms a drop on a smooth surface with contact angle ϑ (in our case, about 7°) will spread along this groove if $\vartheta < (180^{\circ} - \alpha)/2$. Indeed, analysis of profilograms of surfaces with different degrees of roughness shows that two-dimensional diffusion is estab—

* Along with the spreading of mercury over the surface, its "absorption" into the

Fig. 4. Dependence of the radius of a mercury spot r (mm) on time t (sec.) at different temperatures: 1—0°, 2—20°, 3—40°C; a—for a smooth surface, b—for a rough surface; drop mass $m = 5$ mg

Figure 4: Fig. 4. Dependence of the radius of a mercury spot r (mm) on time t (sec.) at different temperatures: 1—0°, 2—20°, 3—40°C; a—for a smooth surface, b—for a rough surface; drop mass $m = 5$ mg

specimen simultaneously occurs owing to bulk diffusion; therefore the final value of the spot radius depends on the mass of the charge m (1). With increasing temperature the role of bulk diffusion increases; this leads to a decrease in the final dimensions of the spots (Fig. 4).

spreading takes place when the average value of the reentrant angle of the depressions on the surface proves to be approximately equal to 160°.

Thus, it is necessary clearly to distinguish two qualitatively different processes of propagation of a liquid metal over the surface of a solid metal free of oxide film: surface diffusion and spreading. Surface diffusion is observed at large contact angles; spreading occurs at comparatively small contact angles and with a sufficient degree of roughness of the solid surface. Both of these processes, observed by us as a function of the microrelief of the solid surface on one and the same object (mercury—zinc), differ not only in their quantitative regularities, but are also governed by fundamentally different mechanisms.

In connection with the foregoing, one may also put forward a more general supposition: it is not excluded that the spreading of a thin layer of liquid under the action of surface-tension forces alone over an ideally smooth surface generally cannot be observed, since the surface migration of liquid atoms leads to a decrease in the surface energy of the solid in the region ahead of the front of the liquid phase.

Fig. 4. Dependence of the radius of a mercury spot r (mm) on time t (sec.) at different temperatures: 1—0°, 2—20°, 3—40°C; a—for a smooth surface, b—for a rough surface; drop mass $m = 5$ mg.

In other words, complete wetting in the usual sense of this term may prove unattainable in the absence of the corresponding microrelief of the surface. The same phenomena may also account for the hysteresis of wetting: during advancing, the liquid moves over a solid surface covered with monolayers of this liquid, whereas during receding the liquid moves already over a comparatively thick phase layer; as a result, the contact angles during advancing and receding must differ. Similar considerations may also prove useful in analyzing the propagation of a liquid over a liquid surface.

The authors express their deep gratitude to Academician P. A. Rebinder for valuable advice in discussing the results of this work, and to N. N. Gerasimova.

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Received
15 V 1962

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