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1963

SovietRxiv

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PHYSICS

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Self-Diffusion on the Surface of Polycrystalline Silver

(Presented by Academician P. A. Rebinder on 2 XI 1962)

1. Diffusion of atoms on the surface of a solid has been little studied. Knowledge of the kinetics of this process is of considerable interest not only for the development of general concepts concerning kinetic phenomena in solids, but also in connection with its role in many practically important phenomena. As an example, we may point to the effect of surface-active media on the mechanical properties of solids (the Rebinder effect). The mobility of adsorbed impurities along the surfaces of inhomogeneities in a solid substantially determines the effectiveness of the influence of the impurity on the properties of the solid.

Only a few quantitative studies of the process of surface diffusion are known in the literature, in particular of self-diffusion on metallic surfaces, where the features of the process can be traced in the purest form; moreover, a considerable portion of these studies ($^{1-3}$) is devoted to the study of self-diffusion on the surface of silver. These works, however, lead to substantially different results, probably because of imperfections in the experimental methods of investigation that were used.

In view of the importance of the problem, it seemed expedient to us to investigate the surface self-diffusion of silver, making use of the "layered specimen" method (^{4}), which makes it possible, in determining the value of the surface diffusion coefficient D_s, first, to take into account the "drain" of the diffusing component from the surface of the specimen into the bulk and, second, to estimate the thickness of the near-surface layer δ_s in which the process under study takes place.

2. The "layered specimen" method consists of the following. From sheets of foil of the metal whose surface diffusion is being studied, a small stack is assembled, in which the individual foil sheets touch only at a few points of natural surface irregularities. The flat gaps between the individual sheets turn out to be $\simeq 1\mu$. A radioactive isotope is applied to the surface of a section perpendicular to the plane of the foil sheets; it diffuses into the stack along the free surfaces of the sheets and partly leaves the surfaces for the interior of the sheets. After isothermal diffusion annealing, on the basis of a layer-by-layer analysis of the stack, the dependence of the concentration (activity) of the diffused isotope on

Fig. 1. Typical curve of the dependence $\ln \overline{C} = (\varphi x^{4/3})$. Temperature 310°C; $t = 4.3 \cdot 10^5$ sec.

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the distance x from the initial plane is constructed, $\ln \bar{C} = \varphi(x^{4/3})$. This curve is the source of information on D_s and δ_s, which are determined with the aid of the relations*

$$\delta_s D_s = 0.324\,\frac{D_v^{1/2}}{t^{1/2}}\left[\frac{d}{d(x^{4/3})}\ln \bar{C}\right]_{x=0}^{-3/2}; \tag{1}$$

$$D_s = \left[8t\,\frac{d}{d(x^2)}\,\Delta \ln \bar{C}\right]^{-1}. \tag{2}$$

* Strictly speaking, the derivative $d \ln \bar{C}/dx^{4/3}$ should be taken not at $x = 0$, but near zero. Estimates show that if the measurements of $\bar{C}$ are made with an accuracy of $\simeq$ 10%, then up to values $x \simeq 2 \cdot 10^{-1}\,\frac{t}{\delta_s}\,(D_{sD} v)^{1/2}$ the curve in the coordinates $\ln \bar{C}$–$x^{4/3}$ practically does not differ from a straight line, and thus the tangent considered coincides with the direction of this straight line.

Here D_v is the volume-diffusion coefficient; t is the diffusion-annealing time; $\Delta \ln \overline{C}$ is the difference between the value of $\ln \overline{C}$ and the ordinate of the corresponding point on the tangent drawn at the origin to the curve $\overline{C} = \varphi(x^{4/3})$. For the annealing times and the counting technique used by us, with activity measured by means of a scintillation counter (CsJ (Tl) crystal), the relative error in determining the activity (and, accordingly, $\overline{C}$) did not exceed 2%. In the experiments, 99.97% pure silver was used in the form of sheets 20–25 μ thick. To increase the sensitivity of the method, the packets consisted of 20 sheets. The isotope of silver Ag^{110} was used as the diffusing material. Before assembling the packet, the sheets were annealed in an atmosphere of flowing dry hydrogen; diffusion anneals were carried out in the temperature interval 270–695°C in the same atmosphere. The stabilized grain size in the silver sheets was 300–500 μ.

3. A typical experimentally found curve

$$\ln \overline{C} = \varphi(x^{4/3})$$

is shown in Fig. 1. The possible cause giving rise to the first descending branch of this curve is diffusion along grain boundaries. The second branch of the curve is due to surface diffusion.

Fig. 1. Typical curve of the dependence $\ln \overline{C} = (\varphi x^{4/3})$. Temperature 310°C; $t = 4.3 \cdot 10^5$ sec.

Fig. 2. Temperature dependence of D_s and D^*.

Figure 2: Fig. 2. Temperature dependence of D_s and D^*.

From the course of the first branch, the quantities D^* and δ^* were found, and from the course of the second branch, D_s and δ_s. The temperature dependences of D_s and D^* are described by the formulas

$$D_s = 0.3 \exp(-11800/RT), \qquad D^* = 8.1 \cdot 10^{-2} \exp(-17800/RT),$$

and are shown in Fig. 2. The quantities δ_s and δ^* were determined with an accuracy insufficient for detecting their temperature dependence; the mean values of these quantities turned out to be, respectively,

$$\delta_s \simeq 8 \cdot 10^{-7} \text{ cm} \quad \text{and} \quad \delta^* \simeq 6 \cdot 10^{-6} \text{ cm}.$$

For comparison, Fig. 2 includes data obtained in works ($^{1-3}$). It is noteworthy that the values of D_s obtained in our experiments are very close to the known data of the work of Nickerson and Parker (^{1}), in which the distribution of the diffusing component as a function of distance from the middle of the radioactive mark was measured by means of a sensitive counting-rate measurement technique. This circumstance, taking into account that in work (^{1}) anneals were carried out in the range of comparatively low temperatures (225-350°C) for a short time (1-2 hours), argues in favor of the fact that Nickerson and Parker investigated proper surface diffusion and, correspondingly, the second branch on the curve

$$\ln \overline{C} = \varphi(x^{4/3})$$

(Fig. 1) is due to diffusion along the surface. The activation energy of the process, according to (^{1}), is 10,300 cal/mol, which is close to the value found by us, 11,800 cal/mol.

According to the estimate made of the value of δ_s, "surface" diffusion takes place in a layer whose thickness is of the order of 10-20 interatomic distances.

Without discussing the origin of the structural features of this layer and of the elementary diffusion act in it, let us only note that the activation energy found is close to the activation energy of the self-diffusion process in liquid silver (8150 ± 1130 cal/mol) (^{5}).

An unambiguous interpretation of the meaning of the quantity D^* is difficult. Undoubtedly, the first descending branch of the curve is to a known extent due to diffusion along grain boundaries.

Fig. 2. Temperature dependence of D_s and D^*.
a—data of the present report; **b**—data of work (^{1}); **c**—data of work (^{2}) for polycrystalline silver; **d**—data of work (^{3})

It is necessary, however, to draw attention to the fact that the values of the surface self-diffusion coefficients of silver found in the works of Winegard and

Chalmers (2) and Winegard (3), who experimented with single crystals, are close to the values of D^* (see Fig. 2). In works (2, 3) the distribution of the diffusing component was determined by the autoradiography method, which has insufficient sensitivity to detect the diffusion described by us by the coefficient D_s. Let us also note that the values of D found in (2, 3) proved to be smaller than D_s, but considerably larger than the coefficient of volume diffusion.

From a comparison of the facts described, two assumptions naturally follow: either the single crystals investigated in (2, 3) were very mosaic, and then the effect observed autoradiographically was due to diffusion along block boundaries; or in (2, 3) "near-surface" diffusion in a thick layer was observed. This process could to some extent have influenced the course of the first branch in the curve of Fig. 1. Verification of the assumptions put forward can be carried out in experiments performed by the "layered specimen"method with packets composed of single-crystal plates.

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Received
29 X 1962

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