

## LETTERS TO THE EDITORS

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## The Reh binder Effect

REHBINDER and his colleagues have recorded in a series of papers<sup>1</sup> that surface-active liquids, brought into contact with the surface of metals, in particular of single crystals, markedly diminish the mechanical strength. In *Nature* recently<sup>2</sup>, D. S. Kemsley, trying to obtain the effect, described experiments on single crystals of tin which gave negative results throughout. When noted research workers obtain completely different results, it seems likely that certain differences in conditions must be responsible.

In this laboratory, we have long been familiar<sup>3</sup> with the effect of surface contaminations, in particular oxides, in raising the critical shear stress and, in general, mechanical resistance under like conditions of strain in single crystals. It seemed possible that the attack of the surface-active substance on a strengthening oxide layer might be responsible for the Reh binder effect. Accordingly, the effect of a 0.2 per cent solution of oleic acid in non-polar paraffin, which Reh binder found to be particularly effective, was tried, with cadmium single crystals, on (1) crystals in which the surface had been rigorously cleaned by thermal evaporation *in vacuo*; (2) a crystal in which the surface had been deliberately oxidized by heating in air; (3) a crystal of which the surface had been deliberately oxidized and then washed successively with decinormal hydrochloric acid, distilled water, decinormal sodium hydroxide and distilled water; (4) a crystal of which the surface had been contaminated by being left in the open in the laboratory for several months. The method of experiment was to subject the crystal to stress which produced a very small rate of flow, and then, after some minutes, to pour the liquid around the crystal. With (1) no effect was obtained, the crystal continuing to flow at an unchanged rate; with (2) there was, after an hour or so, a marked increase in rate; with (3) there was a similar effect, with the increase in rate occurring slightly earlier; with (4) there was, after 45 minutes, an increase in rate which soon led to a rate twelve times the original.

These experiments seem to indicate that the Reh binder effect is due to a disintegrating action of the agent on the oxide film, which in its original condition strengthens the crystal, and not to any penetration of the liquid deep into the crystalline microcracks, as supposed by Reh binder. This action takes some tens of minutes to establish an effect. The slowly formed oxide layer at atmospheric temperature appears to be more effective than that deliberately and quickly produced, which is easily understandable. Mr. M. J. Makin and the senior signatory are at present looking into the effect with lead single crystals, and trying to obtain an electrical effect of the kind recorded by Reh binder.

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Reh binder and Logghinov, *Dok. Acad. Sci. U.S.S.R.*, **30**, 491 (1941).  
Reh binder, Lichtman and Maslennikov, *ibid.*, **32**, 125 (1941).  
Lichtman and Reh binder, *ibid.*, **32**, 130 (1941). Reh binder and Wenström, *Bull. Acad. Sci. U.S.S.R.*, Ser. Phys., No. 4/5, 531 (1937).  
<sup>2</sup> Kemsley, D. S., *Nature*, **163**, 404 (1949).  
<sup>3</sup> Roscoe, E., *Phil. Mag.*, **21**, 399 (1936). Andrade, E. N. da C., *Nature*, **164**, 536 (1949). Andrade, E. N. da C., and Randall, R. F. Y., *Nature*, **162**, 890 (1948).

## Rate of Self-Diffusion in Tin Crystals

IN non-cubic crystals the rate of self-diffusion can be expected to depend on the crystallographic direction parallel to which the diffusion is measured. Although the determination of this anisotropy is of interest for the theory of diffusion, experiments have so far only been carried out on bismuth<sup>1</sup> and zinc<sup>2</sup> crystals. The measurements made on zinc are not of high accuracy and their evaluation is open to doubt. The relation between the diffusion coefficient measured in a direction at an angle  $\theta$  to the principal axis and the diffusion coefficients parallel ( $D_c$ ) and at right angles ( $D_a$ ) to this axis is

$$D = D_c \cos^2 \theta + D_a \sin^2 \theta.$$

We have measured the rate of diffusion in single crystals of white (metallic) tin which has a body-centred tetragonal structure. A thin layer of the radioactive isotope tin-113 was plated on to a flat face of a single crystal of known orientation. The plated specimen was heated for a measured period (1-2 days) at a constant temperature in the range 180-225° C. The surface of the crystal parallel to the diffusion direction was then removed to eliminate surface diffusion effects. Thin layers parallel to the diffusion interface were cut off with a microtome and their activity measured by means of a Geiger counter. The diffusion coefficient for each specimen was obtained by plotting the logarithm of concentration against the square of the depth of the layer, which method follows from the solution of the diffusion equation for the boundary conditions applicable.

Table 1  
Diffusion-rate (in  $\text{cm}^2 \text{sec}^{-1}$ )

Temperature	$D_a$	$D_c$
180.5° C.	$5.5 \pm 0.2 \times 10^{-11}$	$9.9 \pm 0.3 \times 10^{-11}$
223.1° C.	$9.6 \pm 0.3 \times 10^{-11}$	$26.8 \pm 0.9 \times 10^{-11}$

From a number of values of  $D$  at constant temperature on crystals of different orientations,  $D_a$  and  $D_c$  were obtained using the above relation. Some of these values are given in Table 1. These values show the diffusion-rate to be an anisotropic property, the ratio  $D_c/D_a$  being about 2 at 180° C. and about 3 at 223° C. In the range of temperatures investigated,  $\log D_c$  and  $\log D_a$  are linear functions of  $1/T$ . If extrapolation to lower temperatures is allowed,  $D_a$  and  $D_c$  become equal at approximately 125° C., and below this temperature diffusion parallel to the tetragonal axis becomes slower than at right angles to it.

It is usual to interpret the slope of the straight line in the  $\log D$  v.  $1/T$  plot as the activation energy for diffusion  $Q$  divided by the gas constant  $R$ , and the intercept with the ordinate axis as a temperature-independent constant  $A$ . The values shown in Table 2 were obtained for  $A$  and  $Q$ . It should be noted that the larger  $A$  value accompanies the larger  $Q$  value, as is also the case for bismuth.

Table 2

Constant	$\alpha$ -axis	Parallel to $c$ -axis
$A$ ( $\text{cm}^2 \text{sec}^{-1}$ )	$3.7 \pm 1.5 \times 10^{-8}$	$8.4 \pm 3.0 \times 10^{-4}$
$Q$ (cal./gm. atom)	$5.9 \pm 0.4 \times 10^3$	$10.5 \pm 0.5 \times 10^3$

An explanation of the anisotropy in terms of the mechanism of diffusion does not yet seem possible. The ratio  $A_c/A_a \sim 10^4$  certainly cannot be explained by the different jump distances in the  $c$ - and  $a$ -directions, but a qualitative consideration similar to that given by Huntington<sup>3</sup>, for the case of zinc, may also be justified in our case. A consideration of the