Deformation of Single Crystals of Tin in Solutions of Oleic Acid

THE work of Rehbinder and his co-workers on the effect of surface-active substances on the strength of crystalline solids has been followed with considerable interest in this laboratory. In a paper published with Lichtman and Maslennikov, Rehbinder[1] reports a 50 per cent decrease in the yield value of single crystals of tin and zinc when immersed in a 0·2 per cent solution of oleic acid in a non-polar paraffin oil. He also reports a five-fold increase in the electrical resistance of a single crystal of tin when elongated almost to fracture in the same solution, in comparison with the resistance of a specimen of the same orientation similarly extended in air. These effects are ascribed to the opening and extension of the micro-cracks in the crystal by the 'wedging action' of a film of liquid drawn into the micro-cracks by an adsorbed layer of oleic acid molecules. This principle of 'adsorption reduction of hardness' has been widely applied in various processes for the mechanical destruction of brittle bodies[2].

Crystal No.	Condition	Peak stress (gm./mm.^{2})	Elongation at peak (%)	Angle between specimen axis and slip plane χ_0	Angle between specimen axis and slip direction λ_0	Critical shear stress S (gm./mm.^{2})
4·10	As prepared (*a*)	123	2·6	43	46	58
	Clean (*b*)	132	2·4			63
	Clean in paraffin (*c*)	112	1·0			53
	Clean in solution of oleic acid (*d*)	125	4·1			59
3·5	As prepared (*a*)	124	1·3	48	49	61
	Clean (*b*)	119	1·9			58
	Clean in paraffin (*c*)	108	0·8			53
	Clean in solution of oleic acid (*d*)	111	1·1			54
3·7	As prepared (*a*)	136	0·8	30	30	59
	Clean (*b*)	124	1·8			54
	Clean in paraffin (*c*)	129	1·3			56
	Clean in solution of oleic acid (*d*)	134	0·5			58

This effect is obviously of considerable importance for the theory of metallic friction and boundary lubrication. It was therefore decided, as a prelude to further work on the effect of surface-active substances on metallic friction, to repeat Rehbinder's experiments, using so far as possible the technique described by him.

The specimens used were single crystals of tin (99·98 per cent pure) approximately 1 mm. in diameter and 13 cm. in length prepared by the Kapitza method[3]. Orientations were determined by X-ray rotation diagrams and in some cases checked by goniometer measurements of etch pits. Taking the slip system[4] as (110) [001], crystals were selected the orientations of which were near $\chi_0 = 45°$, since Rehbinder and Lichtman[5] report that the depression in yield value is a maximum at this orientation (χ_0 is the angle between specimen axis and the slip plane). Each crystal was then cut into six specimens, four for tensile tests, and two for electrical resistance measurements.

Tensile tests were carried out using a Polanyi-type apparatus[6], the four specimens of one crystal being tested under the following conditions: (*a*) in air, as prepared, with an oxidized surface; (*b*) in air, but cleaned for two minutes in *N* hydrochloric acid, washed in hot water, dipped in *N* ammonium hydroxide to neutralize any remaining acid, again dipped in very hot water and allowed to dry in air; (*c*) cleaned as in (*b*) and immersed in B.P. paraffin oil; (*d*) cleaned as in (*b*) and immersed in the same paraffin oil with 0·2 per cent oleic acid by weight added.

The absolute rate of extension was constant, and the rate of elongation of individual specimens, which depended on their initial length, varied from 0·2 to 0·35 per cent per minute.

The results of three typical tests are given in the accompanying table. All tensile curves showed a definite peak at approximately 2 per cent elongation. The critical shear stress in the (110) [001] slip system was calculated from this peak stress.

It will be seen that, under the conditions of these experiments, alteration of the surface condition produces no significant change in the critical shear stress.

Similar negative results were obtained with a series of crystals in which χ_0 varied from 30° to 60°, at rates of elongation of 0·2–4 per cent per minute.

In his paper, Rehbinder does not specify the particul r paraffin used. Since it seemed possible that the viscosity of the solution might have some effect on the magnitude of the 'wedging action', the experiments were repeated using hexadecane and kerosene as solvents to provide a wide range of viscosities. Again no effect was observed.

The two remaining samples of crystals used in the tensile tests w re then elongated almost to fracture (150–200 per cent elongation) in air and in the original oleic acid solution. For the same elongation, no significant difference in electrical resistance was observed.

In view of the very large effects reported by Rehbinder, and of their wide application, these negative results are put forward with some diffidence in the hope that workers in other fields may be able to offer some explanation. Further work is in progress with other metals and surface-active compounds.

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D. S. KEMSLEY

Tribophysics Division,
Council for Scientific and Industrial Research,
University of Melbourne, N.3.

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