Oxidation of Barium : a Confirmation of Mott's Theory of Oxidation

MEASUREMENTS of the rate of taking up of oxygen by barium films¹ have been continued in an attempt to discover the mechanism of the growth of the oxide layer. The results obtained support the ionic theory of oxidation of metals developed by Mott². In this theory it is supposed that positive metal ions and electrons diffuse from the metal through the oxide, the metal ions moving via interstitial positions in the oxide lattice. At the free surface of the oxide, these ions combine with adsorbed oxygen. In this way the thickness of the oxide layer is increased. In oxide films less than about 50 Å. thick, the movement of ions is influenced principally by the strong electric field which is set up across the oxide because of the contact potential difference between the metal and the adsorbed oxygen. In thicker films the movement of ions, and hence the rate of growth of the oxide, is influenced chiefly by temperature. From the theory it is further predicted that, whatever the thickness of oxide, the movement of ions becomes controlled by temperature when this is raised above a critical value. Therefore, above the critical tem-perature the oxide layer should continue to grow until all the metal has been oxidized. Below the critical temperature, it is predicted that the growth of oxide stops at a limiting thickness. Further, the limiting thickness itself should vary with temperature when this is less than the critical value.

In the present work measurements have been made, at different temperatures, of the amounts of oxygen gas taken up by barium films. These amounts are proportional to the thickness of oxide layer formed. The critical temperature has been found to be 35° C. The thickness of the protective oxide layer formed at ambient temperature (20° C.) was found to be about 25 monolayers, that is, about 50 A. The thickness of the protective oxide layer decreased with temperature below 35° C., as foretold by Mott's theory. At temperatures above 35° C., the thickness of oxide depended only upon that of the barium film, for the metal oxidized right through, becoming translucent. The rate of growth of the oxide layer has been found to vary with temperature in different manners above and below the critical temperature, again in agreement with Mott's theory.

The speed of pumping of oxygen per unit area of barium film (litres sec.-1 cm.-2) increased with temperature only above 35° C., but the actual speeds of pumping were merely about 1/25 of what they would have been if every oxygen molecule striking the oxide surface had stuck. Interpreting these two results with the aid of Mott's theory, it is concluded that the speed of pumping of oxygen by barium is limited by the superficial density of interstitial barium in the oxide. This conclusion has been confirmed by experiments in which the speed of pumping per unit area has been increased, up to five-fold, by depositing the barium upon a particular substrate material (a mixture of barium and strontium oxides, formed from the carbonates as in oxide-coated thermionic cathodes) selected to cause lattice imperfections³.

The formation of the first monolayer or two of oxide is outside the scope of Mott's theory, which concerns the laws of further thickening of an oxide layer. It has been found that the speed of pumping at first increased in proportion with the square root of the time for which the barium was exposed to oxygen. Also, the rate of rise of speed was independent of the temperature of the barium film. The amount of oxygen taken up while the speed was increasing according to the parabolic law was found to be that to give a single monolayer. These results are explained by the idea that oxidation starts at nucleation centres in the barium surface, followed by a spreading across the surface to form a complete monolaver. Thereafter the speed remains constant, and the oxidation proceeds in the manner described by Mott's theory.

It is hoped to publish this work more fully elsewhere.

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¹ Bloomer, R. N., Nature, **178**, 1000 (1956).
² Mott, N. F., Trans. Farad. Soc., **43**, 429 (1947).
³ Wright, D. A., J. Electronics, **1**, 521 (1956).

A New Type of Zinc Sulphide Crystals

By sublimation of zinc sulphide in an atmosphere of hydrogen, I have obtained a new kind of zinc sulphide crystals. Fig. 1 shows two different views of a beautiful sample of these crystals.

While some similarity is apparent with the spiroidal zinc sulphide crystals prepared by W. W. Piper and described by W. L. Roth¹, the newly observed crystals are peculiar for being definitely non-planar, for the intriguing changes in the direction of growth, and for developing from a common point in two different directions after completing a few loops. For the sample illustrated in Fig. 1 this happens twice, after approximately five loops and on the end loop.



Fig. 1. $(\times 7\frac{1}{2})$