

Anodic Behaviour of Mild Steel in Strongly Alkaline Solutions

IN connexion with the well-known intercrystalline failure of mild steel in concentrated solutions of sodium hydroxide, it would appear that a study of the anodic behaviour of iron in such solutions might lead to results of considerable interest. A search of the literature soon reveals, however, that but little attention has been devoted to this matter. The work of Grube and Gmelin¹, who carried out a careful and extensive investigation in this field, is therefore of special importance. These workers obtained evidence that anodic dissolution takes place in two distinct potential stages: at low current densities electrolysis proceeds at a potential of about -0.85 V. (hydrogen), whereas at higher values it changes suddenly to $+0.65$ V., when oxygen evolution commences. The critical current density was found to increase rapidly with temperature. Evidence is adduced by Grube and Gmelin that the lower (more negative) potential stage is associated with the formation of ferrous ion, and the higher with oxidation to the hexavalent ion Fe^{6+} ; anionic complexes being formed having the probable compositions $(\text{FeO}_2)^-$ and $(\text{FeO}_4)^-$ respectively.

I have carried out a few exploratory experiments on similar lines, with special reference to the influence of the molality of the solution. I used unstirred solutions, with a vertical electrode, though the degree of agitation and the position of the electrode appear to have little influence in this case. Some results are represented in the accompanying figure. These refer to a dead soft mild steel (0.05 per cent carbon) and were obtained at 80°C . The curves of potential against the saturated calomel electrode are plotted to a base of apparent current density.

A certain amount of instability of the lower potential stage was observed near the critical current density, especially at the lower molalities. Further work indicated that this effect was attributable to the influence of time, in that the electrode tended to become passive at a current density considerably

below the supposed critical value, provided sufficient time were allowed; for example, in a 12.9 molar solution, in which the apparent critical current density was about 0.003 amp./cm.², the electrode became passive after 40 minutes at 0.001 amp./cm.², and after 10–12 minutes at 0.002 amp./cm.².

A simple and plausible explanation of the existence and quasi-stability of the lower potential stage seems possible on the following lines. As is customary in such work, and like Grube and Gmelin, I subjected the anode to a previous cathodic polarization in order to remove the air-formed oxide film on the metal. Now experiments in a somewhat different connexion have shown that hydrogen is occluded by iron when the latter is cathodized in strongly alkaline solutions in quantities which increase rapidly with the strength of the solution. It seems probable, therefore, that during the initial stages of anodic polarization this occluded hydrogen will effectively prevent the formation of an adherent oxide film and consequent onset of passivity².

It is hoped to supplement these initial results and to publish a fuller account of this work later.

CHAS. D. WEIR

James Watt Engineering Laboratories,

University, Glasgow, W.2.

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¹ Grube and Gmelin, *Z. Elektrochem.*, **26**, 459 (1920).

² Cf. Carius, "Korrosion metallischer Werkstoffe" (ed. Bauer-Kröhnke-Masing, Leipzig, 1936), **1**, 135.

X-Ray Diffraction Studies of Yielding in Mild Steel

SIMILAR results to those described by J. M. Cowley and M. S. Paterson in their communication in *Nature*¹ concerning the examination of 'Hartmann's lines' (also known as 'Lüders' lines) in steel using X-ray diffraction methods were reported by me in 1927², and again in 1937³ in consequence of a fuller investigation of steel and 'duralumin'. That was the first time the result of X-ray diffraction studies of 'Hartmann's lines' was published, so far as I am aware. Researches on the subject of 'Hartmann's lines' in steel, including a study of their properties, and of which my first memoir was a part, were carried out in the Department of Metallurgy of the University of Birmingham by Mr. T. Henry Turner, Dr. J. D. Jevons and myself, being under the supervision of the first-named.

A noteworthy disclosure in Messrs. Cowley and Paterson's communication is the presence of a considerable proportion of diffuse spots (indicating distorted crystals) with respect to the metal near a 'Hartmann's line' near the centre of a region of 'Hartmann's lines' but not actually forming any part of a 'Hartmann's line' (see their Fig. 1 and Fig. 2*d*), whereas almost all the spots are diffuse if the part under examination is all part of a 'Hartmann's line'. Further X-ray diffraction studies of such distortion near 'Hartmann's lines' would be of much interest.

E. W. FELL

120 Witherford Way,

Selly Oak,

Birmingham.

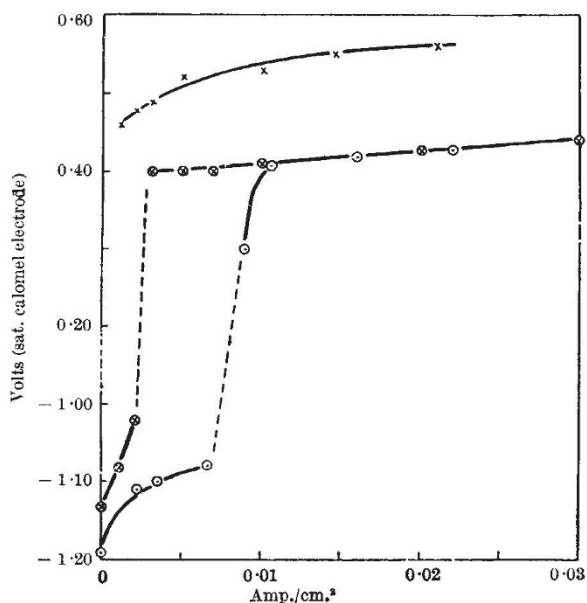
June 27.

¹ *Nature*, **159**, 846 (1947).

² Fell, E. W., Carnegie Scholarship Memoirs (Iron and Steel Institute), **16**, 126 and Fig. 17, Pl. xiii (1927).

³ Fell, E. W., Carnegie Scholarship Memoirs (Iron and Steel Institute), **26**, 135 and Figs. 19–30. Pls. xiii–xviii (1937).

⁴ Fell, E. W., *J. Iron and Steel Inst.*, **132**, 75 (1935).



ANODIC ELECTROLYSIS OF MILD STEEL IN AQUEOUS SODIUM HYDROXIDE: ×, 1.5 M; ⊕, 6.2 M; ○, 12.9 M