839. *An Electrometric Method for Measuring the Thickness of the Air-formed Oxide Film on Pure Iron and Mild Steel.*

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A method has been developed of estimating the thickness of the air-formed oxide film on pure iron and mild steel. The film was cathodically reduced in deaerated 0·2N-potassium chloride and the thickness of the film calculated from the quantity of electricity consumed. Sources of error were examined, and the method was confirmed gravimetrically. The air-formed film on pure iron and mild steel was between 26 Å and 40 Å thick, depending upon the surface condition.

The thickness of the air-formed oxide film on iron was first obtained electrometrically by Miley and Evans,[1] who determined the number of coulombs required to reduce the film when immersed in ammonium chloride solution in an open beaker, as between 170 and 210 Å. However, more recent measurements by other methods [2] yielded much lower values, *i.e.*, 20—40 Å. (Thicknesses were expressed in Å/apparent cm.^{2}.)

We have now reassessed the electrometric method. It was felt that an improved technique might yield results closer to those from other methods, and be useful for investigating inhibition (following paper).

Campbell and Thomas,[3] investigating oxide and sulphide films on copper, greatly improved the cathodic reduction method by deaerating their electrolyte, potassium chloride, and using very small current densities, which permitted accurate measurements of the time of reduction. Kubanov and Leikis [4] cathodically reduced the air-formed film on iron in 2N-sodium hydroxide, in absence of air, but the potential–time curve had no arrest corresponding to the reduction of the oxide film.

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[1] Miley and Evans, *J.*, 1937, 1295.

[2] Gulbransen, *Trans. Electrochem. Soc.*, 1942, **82**, 375; Winterbottom, *J. Iron Steel Inst.*, 1950, **165**, 9; Sloman, Eighth Report on the Heterogeneity of Steel Ingots, Iron and Steel Inst., Special Report No. 25, 1939, p. 60.

[3] Campbell and Thomas, *Trans. Electrochem. Soc.*, 1939, **76**, 303.

[4] Kubanov and Leikis, *Acta Physicochim., U.R.S.S.*, 1946, **21**, 769.

The electrometric method is open to three sources of error: (1) If deaeration of the electrolyte is insufficient, oxygen will be reduced with the oxide; (2) the electrolyte may attack the film before or during the measurement; (3) all the oxide may not be reduced; this may occur if the film contains magnetite (magnetite produced on iron at 250° cannot be reduced [5]).

We examined the cathodic reduction of the air-formed film on iron and mild steel in 0·2N- and 0·1N-ammonium chloride, 0·1N-sodium hydroxide, and 0·2N-potassium chloride, with two methods of deaeration. Both ammonium chloride solutions rapidly removed the film and attacked the metal, irrespective of the method of deaeration; when the deaeration was very efficient the film was removed by sodium hydroxide and potassium chloride attacked the film very slowly. However, attack by potassium chloride was negligible provided that the current was applied as soon as the iron specimen touched the solution. The effect of the surface condition of the specimens and the chemistry of the reduction process were examined and the fact that all the film substance was reduced confirmed by means of a microbalance. The thicknesses of the air-formed films on pickled iron, hydrogen-reduced iron, and pickled mild steel were estimated.

EXPERIMENTAL

Materials.—Iron contained C, 0·0036; Si, 0·001; Mn, 0·005; S, 0·0057; Al, 0·001; O_2, 0·0024; N_2, 0·0016%, and was in sheets 0·018 in. thick. Mild steel contained C, 0·06; S, 0·021; P, 0·015; Mn, 0·36; Ni, 0·048; Cu, 0·04; Sn, 0·008 wt. %; Si, trace only, and was in sheets 0·016 in. thick.

Specimens.—Pickled. The specimens, 2 × 1 cm., degreased by swabbing in benzene, then acetone, were pickled in dilute hydrochloric acid (1 : 4 acid : water) at 20° for 20 sec., washed in six portions of absolute alcohol, dried quickly on filter paper, and stored in a desiccator ($CaCl_2$) for 48 hr.

Hydrogen-reduced. Specimens, swabbed with benzene and acetone and allowed to dry, were placed in the apparatus shown in Fig. 1. The furnace was evacuated to 10^{-5} mm. Hg by a three-stage mercury-diffusion pump; the temperature was raised to 380° and hydrogen, at just below atmospheric pressure, admitted and left in contact with the specimens for $\frac{1}{2}$ hr. The furnace was again evacuated, the temperature raised to 460°, and hydrogen re-admitted and kept with the specimens for 1 hr. The furnace was cooled to room temperature and again evacuated. Air was admitted slowly and the specimens were removed and stored in a desiccator ($CaCl_2$) for 48 hr.

Apparatus.—In preliminary experiments difficulty was experienced in maintaining good electrical contact between the specimen and the platinum hook (*F* in Fig. 3). This was overcome by suspending the specimen as shown in Fig. 2 *B*(ii), which was superior to the system shown in Fig. 2 *B*(i) since the specimen made contact at two points. The glass bead was used to weight the specimen and immediately before an experiment the iron wire was scraped at the point where it made contact with the platinum.

Two methods of deaerating the electrolyte were examined. The first consisted of alternately freezing and thawing the solution under vacuum,[6] and the second was similar to that used by Mills and Willis.[7] The apparatus is shown in Fig. 3. The solution was contained in flask *A* and the specimen was suspended from the platinum hook *F*. Vessels *A* and *B* were evacuated through *C* until the solution boiled, tap *D* was then opened for a few minutes to evacuate directly the reaction vessel *B*. Taps *C* and *D* were closed and oxygen-free hydrogen was admitted through *E* into *B* and bubbled into *A* through the solution. This cycle was repeated seven times, after which the solution was blown into *B* to the desired level by admitting hydrogen into *A* by tap *G*, the flow being stopped by opening *D* to equalise the pressures in *A* and *B*. After the reaction vessel was charged with electrolyte a pressure of 1 atm. of hydrogen was maintained in the apparatus to minimise air leakage into the cell, and to prevent appreciable change of the partial pressure of hydrogen above the iron specimen during reaction.

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[5] Davies, Evans, and Agar, *Proc. Roy. Soc.*, 1954, *A*, **225**, 443; Buob, Beck, and Cohen, *J. Electrochem. Soc.*, 1958, **105**, 74.

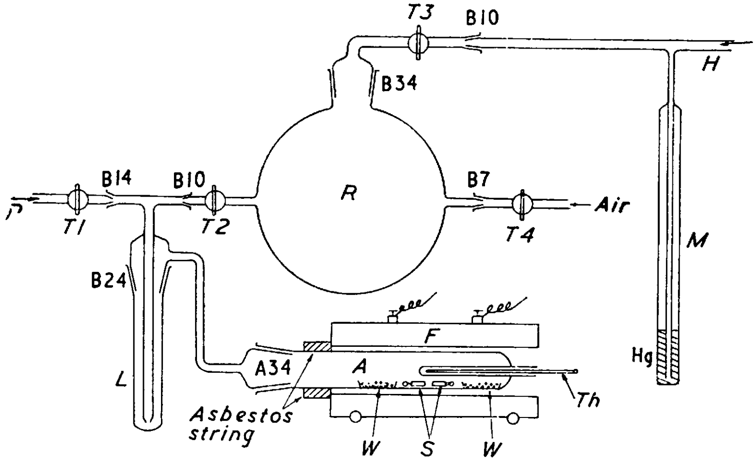
[6] Mayne and Menter, *J.*, 1954, 100.

[7] Mills and Willis, *J. Electrochem. Soc.*, 1953, **100**, 452.

The caps H and H_1 were of soda-glass with standard ground-glass joints; sealed through the top of each was a platinum hook. One of these was used as an anode to supply constant current to the iron specimen, a standard Ag/AgCl electrode being suspended from the other.

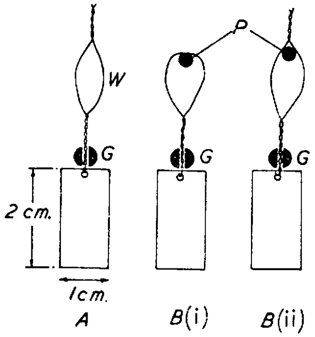
Whilst the electrolyte was being deaerated the specimen was held in the position shown in Fig. 3 by an external magnet. After the reaction chamber was filled, the specimen was dropped into the solution and the cathodic reduction begun immediately. The effect of the electrolyte on the film was thus minimised. The potential of the specimen was measured against the Ag/AgCl electrode on a " Cambridge " valve potentiometer, readings being taken every 15 sec.

FIG. 1.



A, Reaction vessel; *F*, movable furnace; *H*, inlet for deoxygenated hydrogen; *L*, liquid-air trap; *M*, manometer; *P*, connection to pumps and McLeod gauge, *via* liquid-air trap; *R*, 7 litre hydrogen reservoir; *S*, specimens; *Th*, thermometer; *W*, platinised asbestos wad.

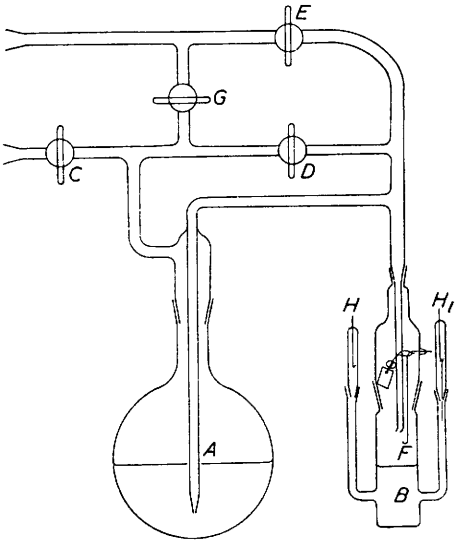
FIG. 2.



A *B*(i) *B*(ii)

G, Glass bead.
P, end section of platinum wire hook.
W, pure iron wire.

FIG. 3.



Development of Method.—Pickled iron specimens were cathodically polarized in 0·2N and 0·1N-ammonium chloride deaerated by both methods, at 10—40 μA/cm.². The potential always fell as soon as the current was applied and after 0·1—0·2 mc had passed became constant. A large pickled specimen, 10 × 1 cm., was left in contact with 0·1N-ammonium chloride, which had been deaerated by seven cycles of freezing and thawing, for 15 min. The specimen was then removed from the solution magnetically and the vacuum broken; the iron content of the solution, estimated colorimetrically with thioglycollic acid, was 100 μg. If the air-formed film is taken to be 40 Å thick and assumed to consist of γ-Fe_2O_3, then the total film on 20 cm.^{2} would contain only 28 μg. of iron. Deaerated ammonium chloride must both rapidly dissolve the air-formed film and attack the iron.

When 0·1N-sodium hydroxide was used the cathodic potential–time curves showed definite arrests, irrespective of the method of deaeration. In some experiments with 0·1N-sodium hydroxide, deaerated by 7 cycles of freezing and thawing, the specimens behaved as if they carried no oxide film and this conclusion was confirmed by the shape of the anodic polarization curves, which showed three arrests and were similar to those obtained with iron [6] from which the air-formed film had been removed by treatment with acid. Attempts to detect the calculated amount of iron in solution were unsuccessful, but it was concluded that sodium hydroxide may attack the oxide film provided that the solution is highly deaerated.

0·2N-Potassium chloride yielded potential–time curves with definite arrests, which corresponded very well with those obtained in most experiments with 0·1N-sodium hydroxide. Both methods of deaeration were satisfactory. No evidence was obtained that the film was severely attacked; unfortunately, the estimations of iron were near the limit of sensitivity of the method, but the results suggested that when the specimen was kept with deaerated 0·2N-potassium chloride for 30 min. as much as 20% of the film might be dissolved. This was why the current was applied immediately the specimen touched the solution.

The general conclusions were that both methods of deaeration were satisfactory for potassium chloride, and also for sodium hydroxide provided that deaeration by freezing and thawing was not carried too far. However since Mills and Willis's method [7] was quicker it was adopted as standard procedure. Furthermore, it was concluded that ammonium chloride was an unsuitable electrolyte, since it removed the oxide film; and that either 0·2N-potassium chloride or 0·1N-sodium hydroxide could be used, but that potassium chloride was preferable, since the Ag/AgCl electrode is more reproducible than the Ag/Ag_2O electrode.

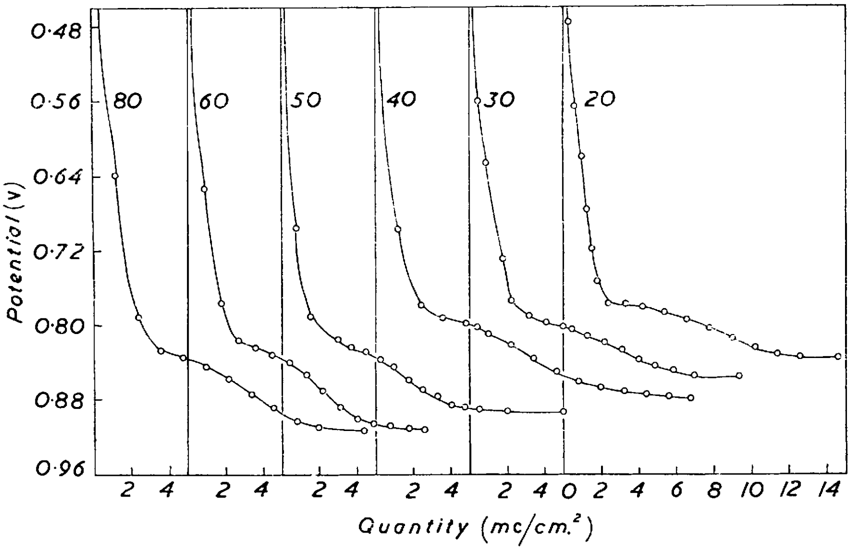
The effect of the surface condition of the iron specimen was examined in both 0·2N-potassium chloride and 0·1N-sodium hydroxide. Reproducible end-points were obtained with specimens reduced in hydrogen, and also with specimens pickled with standardized times and temperatures. Specimens prepared in either manner yielded concordant results when reduced in both electrolytes. Specimens electropolished in acetic anhydride–perchloric acid gave very irreproducible results, probably owing to variables in the technique of electropolishing; this was not investigated further. Cathodic reduction curves obtained with abraded specimens had no arrests, possibly because the oxide is shattered and may contain magnetite owing to the high surface temperature produced during abrasion.

The chemistry of the reduction was next examined. A large specimen, 40 cm.^{2}, was cathodically polarized in deaerated 0·2N-potassium chloride for 20 min. at 40 μA/cm.^{2}. The specimen was removed and the iron in solution determined. In two experiments the solution contained 7·5 μg. of iron, but in a third no iron was detected. It was found subsequently that the air-formed film on pickled iron required about 7 mc for reduction. On the assumption that the film consisted of γ-Fe_2O_3 and was reduced only to the ferrous condition, then 160 μg. of iron would have passed into solution. Consequently it was concluded that the oxide was converted during reduction into metallic iron.

To ensure that all the film was reduced, the results obtained by cathodic reduction were checked with an " Oertling " microbalance, sensitive to ±3 μg. For each experiment eight small specimens were prepared for cathodic reduction and three large specimens 7·5 cm. × 4 cm. for weighing. After degreasing the large specimens were adjusted in weight to within 200 μg. by filing, again degreased, pickled, dried on filter paper, stored overnight in a desiccator, and adjusted to within 20 μg. The heaviest specimen was kept as a standard; the other two were used in the experiment.

The two large specimens and the eight small specimens were heated in an oven at 70° to remove adsorbed gas. After cooling in a desiccator, the large specimens were weighed against the standard and four small specimens were cathodically reduced. The two large specimens and the four remaining small specimens were then heated to a given temperature between 120° and 200°, then cooled in a desiccator. The large specimens were reweighed, the small specimens cathodically reduced, and the increase in weight obtained with the large specimens compared with the difference in weight calculated from the cathodic reduction curves. Four experiments, in which the final heating temperatures were 130°, 160°, 170°, and 200°, gave measured and calculated values in good agreement. Averaging the errors, we found that the increase in weight due to oxygen as calculated from the cathodic reduction curves was 3·5% greater than the increase as measured by the microbalance, so the whole film was reduced during cathodic treatment.

FIG. 4. *Cathodic reduction of air-formed film on iron at the current densities (μA/cm.²) shown on the curves. The potential is given against the normal hydrogen electrode.*



Estimation of the Thickness of the Air-formed Film.—When pickled, or hydrogen-reduced, iron or mild steel was cathodically reduced in deaerated 0·2N-potassium chloride the potential first fell to that at which the entire oxide film was reduced to metal and then dropped to the potential of hydrogen evolution. The end-point in the curve was taken as the midpoint between the potential of the arrest and the potential of hydrogen evolution; this end-point invariably corresponded to the point of inflexion on the potential–time curve. The thickness of the oxide film was calculated from the number of coulombs required for reduction, the film being assumed to consist of γ-Fe_2O_3 of specific gravity 5 (see Table).

Current density (μA/cm.²)	Arrest potl. (mv)	Potl. of H_2 evoln. (mv)	Electricity to reduce film (mc/cm.²)	Thickness of film (Å/apparent cm.²)
		Pure iron, pickled		
20	−780	−836	7·5	41·5
30	−800	−856	7·5	41·5
40	−800	−880	7·5	41·5
50	−826	−896	6·8	38
60	−826	−914	7·2	40
80	−834	−914	7·5	41·5
Average	—	—	7·3	40
		Mild steel, pickled		
40	−790	−863	6·5	36
40	−790	−866	6·7	37
Average	−790	−865	6·6	36·5
		Pure iron, hydrogen-reduced		
40	−790	−890	4·2	23
40	−790	−880	4·4	24
40	−790	−878	4·8	27
40	−788	−890	5·3	29
40	−790	−880	4·8	27
Average	−790	−884	4·7	26

The results obtained when pickled iron was reduced at 20—80 μA/cm.² are shown in Fig. 4 and the Table. The higher the current density, the sharper the end-point, but if too high the time of reduction becomes inconveniently short. The optimum value was taken to be 40 μA/cm.², as used for the other materials.

DISCUSSION

Iron exposed to air becomes covered with an oxide film, first isolated by Evans.[8] Several workers have determined the composition by electron diffraction,[9] and have found that it consisted of an anhydrous cubic oxide, Fe_3O_4, γ-Fe_2O_3, or an intermediate compound. Davies, Evans, and Agar [5] could not cathodically reduce magnetite, produced by heating iron at 250° and above; furthermore, Evans and Davies [10] produced evidence supporting the view that the air-formed film contains at least 80% of γ-Fe_2O_3. Consequently, we calculated the thickness on the assumption that the film consisted of γ-Fe_2O_3.

The thickness of the air-formed film on pickled pure iron is independent of the current density used to reduce it. As the period of reduction varied from 4 to 16 min. we conclude that during this time the electrolyte had no appreciable action on it.

Good end-points were obtained in most experiments with 0·1N-sodium hydroxide, provided that the current was applied as soon as the specimen made contact with the solution; Kubanov and Leikis [4] did not obtain arrests when specimens carrying air-formed films were cathodically reduced; this may have been due to attack on the film due to delay, or to their use of 2N-sodium hydroxide.

The thickness of the air-formed film on pickled iron is 40 Å, on pickled mild steel 36·5 Å, and on hydrogen-reduced iron 26 Å. The last result is in good agreement with the value of 29 Å obtained by Gulbransen [2] when pure iron was reduced in hydrogen and the loss in weight determined by a microbalance; Winterbottom,[2] using an optical method, concluded that the thickness of the air-formed film on carbonyl iron was between 20 and 40 Å according to the surface condition; Sloman,[2] using the vacuum fusion method, measured the surface oxygen on cold-rolled but unabraded pure iron and obtained the value of 0·56 μg/cm.^{2}, which corresponds to a film thickness of 37 Å.

The electrometric method, with precautions, is thus useful for measuring the thickness of the air-formed film on iron and mild steel.

The authors thank Mr. C. A. J. Taylor for preparing diagrams for this and the following paper.

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[*Received, May 20th,* 1958.]

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[8] Evans, *J.*, 1927, 1020.
[9] Mayne and Pryor, *J.*, 1949, 1831.
[10] Evans and Davies, *J.*, 1956, 4373.