

## Mössbauer Effect and Iron Corrosion Kinetics

THE formation and maintenance of a protective film on the surfaces of mild steel equipment used to generate steam are important for safe and economical operation. Knowledge of the kinetics of the film's growth may lead to an understanding of the mechanisms of the process, and various properties have been measured: weight increase, detachment by chemical action and chemical analysis of the film, the movement of radioactive and other markers<sup>1</sup>, and measurements of the rate of effusion through the walls of the vessel of hydrogen produced in the reaction<sup>2</sup>. Most of these methods involve assumptions about the nature and composition of the materials encountered, or else require a series of measurements on a number of different samples of identical nature. The use of the Mössbauer effect in iron-57, though well known<sup>3</sup>, has so far been little used for corrosion studies. This method has several advantages: for example, different iron oxides and other likely corrosion products can usually be identified<sup>4</sup> from a few milligrams.

We used thin natural iron foils (Johnson Matthey 99.99 per cent pure X-ray filters, 0.02 mm thick) electroplated on one side with 1 mg/cm<sup>2</sup> pure electromagnetically separated iron-57. These were heated in deoxygenated Analar water in a 'Teflon' liner which was placed in an autoclave and heated at temperatures between 180° C and 290° C for various lengths of time. The foils were fixed to the top of the liner, which made a tight seal and prevented chemical or electrochemical contact with the water outside. The liner was removed and opened under nitrogen at 25° C so that transmission Mössbauer spectra could be obtained without exposure to the atmosphere. Several measurements could thus be made on the same foil after different periods of heating. The use of a layer of pure iron-57 greatly increased the sensitivity of the experiment (natural abundance is 2.17 per cent).

A typical spectrum is shown in Fig. 1. The peaks from ferrous and ferric ions in the tetrahedral A and octahedral B sites<sup>5</sup> in the surface layer of magnetite are superimposed on the six-line pattern from the underlying iron. The parameters of the magnetite agree well with those found for the natural material<sup>6</sup>, and in no case was any absorption observed from other possible corrosion products such as ferrous hydroxide or 'hydrated magnetite' (unpublished results of A. M. P. with B. T. Mould). Satisfactory least-squares computer fits were made in all cases, assuming Lorentzian line shapes.

The area associated with a Mössbauer absorption peak can be expressed by the relation  $A_i = \frac{1}{2} \pi f_s \Gamma_i L(t_i)$ , where  $L(t_i)$  is a saturation function depending on the effective

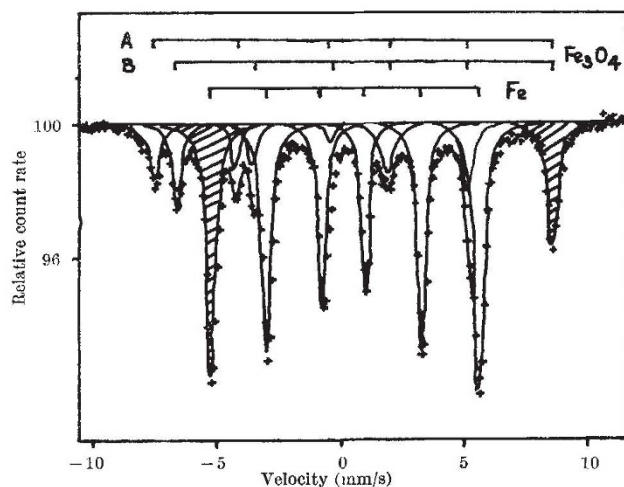


Fig. 1. Mössbauer spectrum of magnetite film on iron foil (the shaded lines at negative and positive velocities are used as measures of the iron and magnetite respectively).

thickness of the absorber  $t_i$  for the  $i$ th line<sup>6</sup>, which in turn is given by  $t_i = \frac{1}{2} \pi \Gamma_i \sigma_0 b_i f_a n$ ,  $\Gamma_i$  and  $\sigma_0$  being respectively the natural width of the peak and the nuclear cross-section for recoilless scattering,  $f_a$  and  $f_s$  the recoilless fractions of absorber and source respectively,  $n$  the number of iron-57 nuclei per unit area of the absorber perpendicular to the incident radiation, and  $b_i$  a factor which allows for the hyperfine splitting of the total cross-section  $\sigma_0$  and a larger than natural linewidth  $\Gamma_i$ . The areas shaded in Fig. 1 were used as measures of the amount of iron and magnetite present, that on the left hand side for iron, and that on the right hand side for magnetite. As a first approximation we supposed that the effective thicknesses were proportional to the observed areas. From the total amount of iron present the values of  $t_i$  were recalculated from published values<sup>6</sup> of  $L(t_i)$ . Assuming  $f_a = 0.7$  for magnetite as well as for iron<sup>7</sup>, the thickness of the film,  $y$ , was obtained as a function of time. We assumed that all the magnetite absorption came from the enriched film, and that no material was lost from the foil; the very small amount of deposit on the walls of the line suggested that this was a reasonable approximation.

We assumed that the rate of film growth was described by a law of the form  $dy/dt = K y^n$ . Logarithmic plots at different temperatures gave  $n = 3.0 \pm 0.2$ , and an Arrhenius activation energy of  $15.6 \pm 0.5$  kcalories. The value of  $n$  is in good agreement with the work of Douglas and Zyzyes<sup>8</sup>, and can be explained in terms of a diffusion-controlled reaction supported by a potential gradient such as might exist between the metal surface and a chemisorbed water molecule at the film-water interface. The activation energy is less than that observed in 13 per cent NaOH by Potter and Mann<sup>9</sup> (30 kcalories), and much less than that for diffusion in the absence of any potential gradient in Fe<sub>3</sub>O<sub>4</sub> and FeO (55 and 3 kcalories respectively)<sup>10</sup>. It is, however, comparable with that for the decomposition of ferrous hydroxide (30 kcalories when pure, but decreasing to 10.2 kcalories in the presence of other ions such as Ni<sup>2+</sup>) (ref. 11). We therefore suggest that our value of 15.6 kcalories represents the activation energy for decomposition of the ferrous hydroxide formed at the surface of the film. Diffusion through the film would be augmented by the potential gradient set up by chemisorbed water molecules which react to form ferrous hydroxide with the ferrous ions diffusing to the surface, thus destroying the potential gradient. We think that the higher value of Potter and Mann<sup>9</sup> can be accounted for by the known inhibiting effect of hydroxide ion on the decomposition of ferrous hydroxide<sup>11</sup>. Although a value of 17 kcalories has been found for the self-diffusion of oxygen in magnetite<sup>12</sup>, the details of preparation of the magnetite suggest that it probably had different properties from those of the bulk material (unpublished results of A. M. P. with B. T. Mould).

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- Douglas, D. L., and Zyzyes, F. C., *Corrosion*, **13**, 433f (1957).
- Fraser, W. A., and Bloom, M. C., *Corrosion*, **18**, 163f (1962).
- Gol'danskii, V. I., and Herber, R. H., *Chemical Applications of Mössbauer Spectroscopy* (New York, 1968).
- Terrell, J. H., and Spilkerman, J. J., *App. Phys. Lett.*, **13**, 11 (1968).
- Bauminger, R., Cohen, S. G., Marinov, A., Ofer, S., and Segal, E., *Phys. Rev.*, **122**, 1447 (1961).
- Lang, G., *Nucl. Instrum. Meth.*, **24**, 425 (1963).
- Debrunner, P., and Morrison, R. J., *Rev. Mod. Phys.*, **36**, 463 (1964).
- Douglas, D. L., and Zyzyes, F. C., *Corrosion*, **13**, 361f (1957).
- Potter, E. C., and Mann, G. M. W., *Proc. Second Intern. Cong. Metall. Corros.*, New York (1963).
- Himmel, L., Mehl, R. F., and Birchenall, C. E., *J. Metals*, NY, **5**, 827 (1953).
- Shipko, F. J., and Douglas, D. L., *J. Phys. Chem.*, **60**, 1519 (1956).
- Castle, J. E., and Surman, P. L., *J. Phys. Chem.*, **71**, 4255 (1967).