Letters

On the determination of oxide overlayer thicknesses by ^{57}Fe conversion electron Mössbauer spectroscopy

Recently, a number of groups have reported [1–3] on the usefulness of ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS) in the *in situ* study of the early stages of the oxidation of iron and iron alloys. In particular, Sette Camera and Keune [1] have reported on the relative areas of the hyperfine patterns attributable to the oxide overlayers and iron substrates in CEM spectra of iron foils which had been oxidized in air for various times at 500° C. Using Swanson and Spijkerman's [4] early data on the attenuation of internal conversion electrons in thin iron films as calibration points, Sette Camera and Keune estimated the oxide thicknesses and arrived at a parabolic rate coefficient of $6(\pm 3) \times 10^{-12}$ cm^2 sec^{-1} for the oxidation process. This procedure made good use of the data accessible to Sette Camera and Keune. It was nevertheless an approximation and it relies on a large interpolation between the two calibration points obtained by Swanson and Spijkerman. Moreover, Swanson and Spijkerman's data relate to the attenuation of conversion electrons emanating from stainless steel in iron overlayers rather than iron oxide overlayers on iron. We have made a fuller analysis of the attenuation of conversion electrons in iron and iron oxides containing natural abundances of ^{57}Fe, and from these experimental data it was possible to obtain parameters for the curve relating the attenuation of conversion electrons emanating from an iron substrate to the oxide overlayer thickness [2]. Using this curve (Fig. 1) we have re-estimated the oxide thicknesses from the spectral area data of [1] (see Table I) and replotted the new thicknesses against the square root of oxidation time (Fig. 2)*. The straight line is almost parallel to that of Sette Camera and Keune but passes closer to the origin. The parabolic rate constant is $5(\pm 2) \times 10^{-12}$ cm^2 sec^{-1}, close to the comparative values of 4.4×10^{-12} cm^2 sec^{-1} and 3.5×10^{-12} cm^2 sec^{-1} derived from more conventional studies [5]. It should be further noted that using Fig. 1 the oxide thickness is estimated to be 270 nm after 180 sec oxidation compared to the value of 200 nm given in [1]. This new value is in excellent agreement with the oxide thicknesses tabulated by Hussey and Cohen [5] who give oxides thicknesses of 280 nm and 250 nm at 10^{-3} and 10 Torr O$_2$ pressure, respectively, for 180 sec

TABLE I Relative area (%) of oxide layer (Fe_3O_4 + α–Fe_2O_3) as a function of oxidation time obtained by ^{57}Fe CEMS studies of oxidized iron foils. Data taken [1].

Oxidation time, *t* (sec)	Relative area of oxide layer (%)
0	0
45	59.6
90	78.1
180	88.5

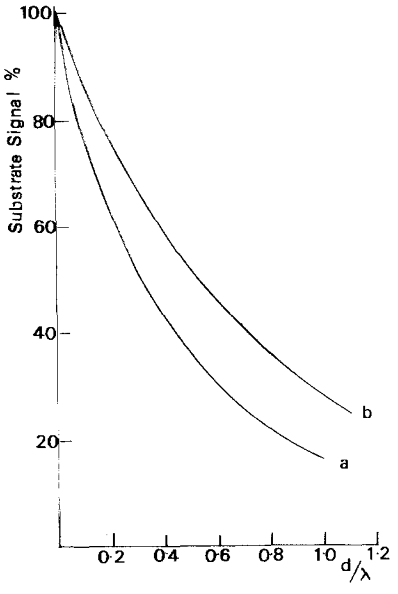

Figure 1 Graph showing the calculated fraction of the substrate signal as a function of d/λ (d = overlayer thickness, λ = electron linear attenuation coefficient. λ_{Fe} = 107 nm, λ_{oxide} = 162 nm for (a) iron on stainless steel and (b) iron oxides on iron. These data may be used to estimate the thickness of an iron oxide overlayer on an iron substrate by measurement of the relative areas of the signal arising from the substrate and overlayer in a ^{57}Fe CEM spectrum obtained using a He/CH$_4$ proportional counter.

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*No attempt has been made to plot points when the substrate signal is obscured by the signal from the overlayer. For this case only a lower limit of ~ 500 nm may be put on the oxide thickness.

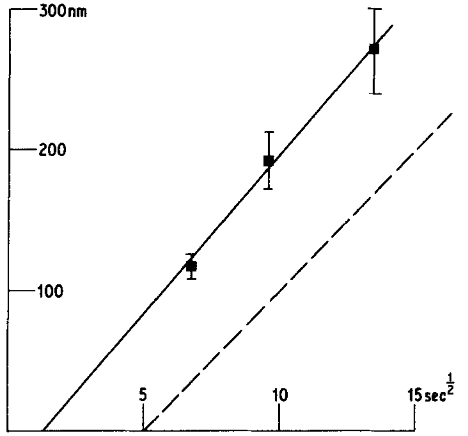

Figure 2 Oxide thickness plotted against the square root of time. The full line is constructed using oxide thicknesses derived from Fig. 1 and the dashed line is taken from [1]. Note that the re-estimated oxide thicknesses obtained from Fig. 1 are considerably larger.

oxidation at 500° C. These thicknesses may be compared because the oxidation rate is fairly independent of O_2 pressure at these initial stages.

These underestimation of oxide thicknesses [1] occurred because the calibration points used relate to the attenuation of electrons, emanating from stainless steel substrates, in iron overlayers rather than iron oxide overlayers on iron. For electrons with energy of ~5 keV the linear attenuation coefficients can be taken to be inversely proportional to the density of the matrix and it is, therefore, to be expected that a thicker oxides thicknesses of 280 nm and 250 nm at 10^{-3} and 10 Torr O_2 pressure, respectively, for 180 sec iron overlayer [6]. This is clearly seen by reference to the figures.

References

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*Received 28 June
and accepted 6 September 1978.*

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Application of the Mössbauer effect to the characterization of the mixed valence compound α-Rb_xFeF_3

The magnetic properties of a number of complex fluorides of transition metals have been studied previously by means of the Mössbauer effect. Here, the application of the Mössbauer effect to the characterization of a mixed valence compound, α-Rb_xFeF_3 ($0.18 < x < 0.29$) [1, 2] is reported. The structure [1] of this insulating material is very similar to that of $Rb_2Fe_5F_{17}$, both closely resembling that of the tungsten bronze, α-M_xWO_3 [3] (M = K, Rb, Cs). The X-ray powder patterns have identical *d*-values and similar intensities except for a few of the weaker lines [4]. Thus it is very difficult to distinguish between α-Rb_xFeF_3 and $Rb_2Fe_5F_{17}$ by the X-ray powder method. According to the formula α-Rb_xFeF_3 ($0.18 < x < 0.29$), iron is present as both Fe^{2+} and Fe^{3+}. Mössbauer measurements were made on a single crystal grown by the flux method [5]. ^{57}Fe Mössbauer spectra were recorded with a conventional constant acceleration spectrometer, using ^{57}Co (Rh) source. The spectra were computer fitted by means of a modified program [6].

A room temperature Mössbauer spectrum of Rb_xFeF_3 is shown in Fig. 1. It consists of two quarupole doublets as indicated in the figure. The longer doublet is due to high spin Fe^{3+} on the basis of its isomer shift, 0.56 mm sec^{-1}; and the quadrupole splitting, 0.58 mm sec^{-1} [7] (relative to metallic iron). The isomer shift and the quadrupole splitting of the second doublet is less well determined because one of its absorption peaks is hidden, but possible values of the isomer shift and the quadrupole splitting are 1.43 and 2.77 mm sec^{-1}, respectively, which are typical values for high spin Fe^{2+} [7]. The broadness of the Fe^{2+} lines presumably arises from inhomogeneous quad-