

Formation of Surface Phosphate Phases on Metallic Iron

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Summary Conversion electron Mössbauer spectroscopy shows that iron(II) phosphate octahydrate is formed as a surface phase when metallic iron is treated by two different phosphating processes; modest heating in air dehydrates this surface species to iron(II) phosphate tetrahydrate whereas the bulk octahydrate is converted under similar conditions into an iron(III) species.

TABLE. Iron-57 CEMS parameters of surface phases on metallic iron.

Treatment	Drying conditions	δ (± 0.15) /mm s ⁻¹	Δ (± 0.30) /mm s ⁻¹
Footner process	<i>Vacuo</i>	1.47	2.43
		1.60	3.00
	107 °C, 17 h	1.19	2.81
Zinc phosphate	<i>Vacuo</i>	1.50	2.68
		1.70	3.09
	107 °C 17 h	1.17	2.71
Sulphuric acid	<i>Vacuo</i>	1.01	2.01

THE treatment of steel surfaces with dilute phosphoric acid solutions of iron, manganese, and zinc has been used for many years in processes designed to produce corrosion-resistant finishes. Iron-57 conversion electron Mössbauer spectroscopy (CEMS) has been shown to be a useful method of investigating solid surfaces¹ since 95% of the 7.3 keV internally converted electrons resulting from the decay of excited ⁵⁷Fe nuclei to the ground state originate from within 300 nm of the surface² and 66% have been found³ to emanate from within 54 nm.

The iron foils investigated here were treated by (a) the 'Footner process' involving initial immersion into 12% sulphuric acid (60 °C; 2 min), washing with water (65 °C), and immersion in 2% phosphoric acid (85 °C; 7 min) and by (b) a solution of zinc dust (0.1 g) in 44% phosphoric acid (20 ml; 60 °C; 5 min). Both samples were finally washed with water (45 °C) and dried *in vacuo* before being heated in air at 107 °C for 17 h. The samples were investigated by CEMS using a resonance counter of similar construction to an earlier design.⁴

All the conversion electron Mössbauer spectra showed the superimposition of quadrupole-split absorptions representing the surface phase (see Table) on a magnetic hyperfine pattern characteristic of bulk metallic iron.

The surface species formed on iron foils when treated by the two phosphating processes give similar Mössbauer spectra characterised by two quadrupole split peaks. The ⁵⁷Fe Mössbauer parameters resemble those recorded by conventional transmission Mössbauer spectroscopy of Fe₃(PO₄)₂·8H₂O (δ 1.33, Δ 2.50; δ 1.41, Δ 2.85 mm s⁻¹) which agree with values reported elsewhere⁵⁻⁷ and are consistent with the occupation by octahedrally co-ordinated iron of two different structural sites.⁸ The treatment of iron foil with sulphuric acid produces a surface material which gives a different Mössbauer spectrum composed of one doublet with parameters characteristic of a high-spin iron(II) species. It seems that the initial treatment of iron foil with sulphuric acid in the 'Footner process' has little effect on the ultimate surface product.

Heating of the phosphated iron foils converts the surface iron(II) phosphate octahydrate into a species which gives a single quadrupole-split Mössbauer spectrum with parameters similar to those reported⁶ by transmission Mössbauer studies of Fe₃(PO₄)₂·4H₂O (δ 1.18; Δ 2.41 mm s⁻¹). This may be somewhat surprising since the heating of bulk iron(II) phosphate octahydrate under similar conditions

gives a material with transmission Mössbauer parameters $(\delta 0.39, \Delta 0.92 \text{ mm s}^{-1})$ characteristic of a high-spin iron(III) species and similar to those reported during investigations of iron(III) phosphate.⁹ F.J.B. acknowledges the award of a fellowship by the S.R.C.

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