A Conversion Electron Mössbauer Investigation of the Phosphating of Iron Surfaces

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Conversion electron Mössbauer spectroscopy has been used to establish the formation of iron(II) phosphate octahydrate on the surface of metallic iron following treatment by various phosphating processes. Heating in air dehydrates the surface phase, whereas bulk samples of the powdered iron(II) phosphate octahydrate are readily converted to an iron(III) species even under anaerobic conditions. Phosphating processes which produce heavier surface coatings lead to the inclusion of hydrolysed iron(III) species in the iron(II) phosphate surface phase. Exposure of the surface phases to water vapour gives partial oxidation of the iron(II) phosphate to an iron(III) hydrate.

CONVERSION electron Mössbauer spectroscopy (CEMS) has been shown to be a sensitive technique for the study of solid surfaces.[1] The decay of excited ^{57}Fe nuclei to the ground state by the re-emission of resonantly absorbed γ-radiation occurs with only 10% probability, whereas the transition to the ground state by the ejection of a back-scattered 7.3 keV internally converted electron occurs with 90% probability. Previous CEMS studies have indicated that 95% of the conversion electrons which are detected in the resonance counter emanate from within 300 nm of the surface [2] and 66% from [3] within 54 nm.

The phosphating of steel has been used for many years in conjunction with other treatments to produce corrosion-resistant finishes. The processes have generally involved immersion of the metal into liquids based on dilute phosphoric acid solutions of iron, manganese, and zinc, and have been envisaged [4] as involving the reaction of free phosphoric acid with the iron to produce an insoluble phosphate on the surface.

Initial CEMS investigations [5] of the phosphating of iron by zinc phosphate and the ' Footner Process ' have been followed by further studies of the treatment of iron with other phosphating solutions and are reported here. The effects of modest heating of the phosphated materials have been monitored by CEMS and are compared with the effects recorded by conventional transmission Mössbauer spectroscopy when bulk samples of the surface species are subjected to the same thermal treatments. The detection by the CEMS technique of the changes in the surface composition when the phosphated iron foils are exposed to water vapour is also described.

EXPERIMENTAL

Iron foil (0.25 mm thick) was immersed in an 80% phosphoric acid solution (20 g l^{-1}, 5 min, 70 °C) which had been conditioned to iron phosphate by the addition of steel wool until the evolution of hydrogen had ceased. The foil was rinsed in water and dried by air blasting before heating (5 min, 60 °C).

Another iron foil was treated in a peroxide-accelerated zinc phosphate bath with a 0.25% zinc content at 30 °C.

Iron-57 Mössbauer spectra were recorded with a conventional constant-acceleration spectrometer and a ^{57}Co–Rh source. The internally converted electrons were detected with a 95% helium–5% methane gas mixture in a resonance counter similar to that described earlier.[6] The drive velocity was calibrated with iron foil.

RESULTS AND DISCUSSION

All phosphating treatments gave grey deposits on the metallic iron foil.

The Mössbauer parameters of those portions of the CEM spectra which were not attributable to the bulk magnetic metallic iron substrate and which therefore represent the surface phase are recorded in Table 1. Data recorded from materials investigated by transmission Mössbauer spectroscopy are given in Table 2. Mössbauer parameters reported in the literature, which were used for characterising the surface species, are recorded in Table 3. The treatment of iron foil with an iron phosphate solution gave a heavier surface coating (*ca.* 1.4 g m^{-2}) than previous treatments.[5] The CEM spectra

TABLE 1

Iron-57 conversion electron Mössbauer parameters

Sample	Drying conditions	δ* $\pm$0.15	Δ $\pm$0.30
		mm s^{-1}	
Iron treated with iron phosphate solution	Air blasting	0.43	0.84
		1.26	2.50
		1.54	3.04
	60 °C, 5 min	0.43	0.78
		1.18	2.29
		1.55	3.02
Iron treated by ' heavy ' zinc phosphate process	Air blasting	0.54	0.75
		1.39	2.45
		1.70	3.07
Iron treated by ' Footner Process ' and exposed to water vapour	*In vacuo*	0.43	0.76
Iron treated with iron phosphate solution and exposed to water vapour	*In vacuo*	0.40	0.77
		1.34	3.22

* Relative to metallic iron.

TABLE 2

Iron-57 transmission Mössbauer parameters

Sample	Treatment	δ* $\pm$0.07	Δ $\pm$0.14
		mm s^{-1}	
$Fe_3[PO_4]_2 \cdot 8H_2O$	107 °C, air, 17 h	0.39	0.92
	107 °C, N_2, 17 h	0.39	0.92
	25 °C, *in vacuo*, 3 h	1.36	2.43
		0.28	0.97
	25 °C, *in vacuo*, 17 h	1.31	2.37
		0.28	0.92
$Fe[PO_4] \cdot 4H_2O$		0.40	0.64

* Relative to iron metal.

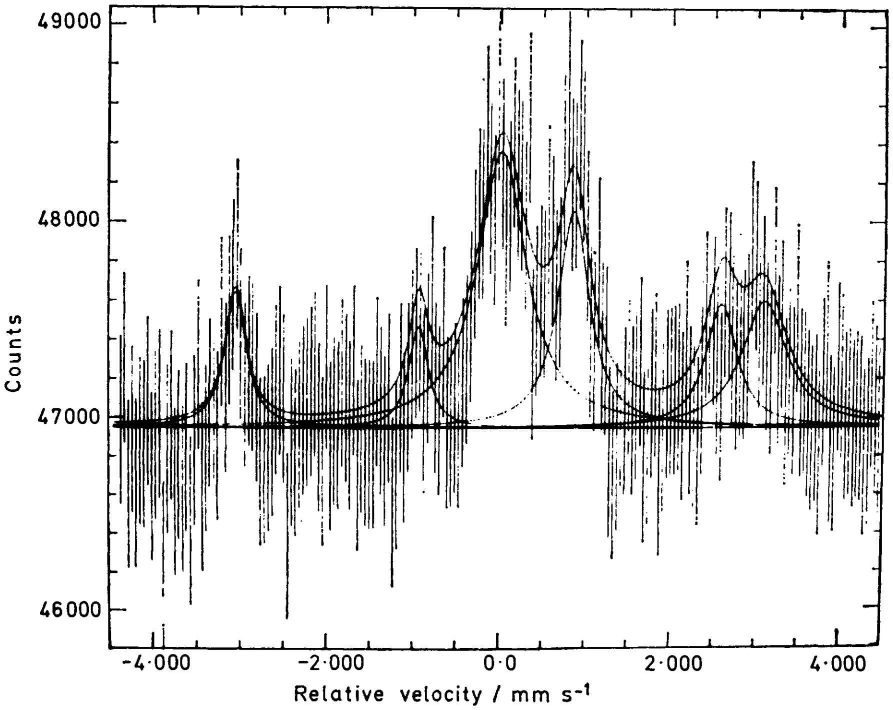
TABLE 3

Iron-57 Mössbauer parameters used for characterising the surface species

Mössbauer mode	Sample	Drying conditions	δ	Δ	Ref.
			mm s^{-1}		
CEMS	Iron foil treated by Footner process	*In vacuo*	1.47	2.43	5
			1.60	3.00	
		107 °C, 17 h	1.19	2.81	5
CEMS	Iron foil treated by zinc phosphate	*In vacuo*	1.50	2.68	5
			1.70	3.09	
		107 °C, 17 h	1.17	2.71	5
Transmission	$Fe_3[PO_4]_2 \cdot 8H_2O$		1.33	2.50	5
			1.41	2.85	
			1.21	2.50	8
			1.23	2.98	
			1.15	2.51	9
			1.20	2.97	
Transmission	$Fe_3[PO_4]_2 \cdot 4H_2O$		1.18	2.41	9
Transmission	$Fe[PO_4]$		0.43	0.68	13
Transmission	Iron(III) species in a mixed iron(II)–iron(III) phosphate		0.36	0.75	13
Transmission	$Fe[OH]_3 \cdot 0.9H_2O$		0.50	0.72	11
CEMS	γ-FeOOH			0.73—0.94	12

showed the superimposition of three quadrupole-split absorptions on a magnetic iron substrate pattern (Figure). One pair of doublets was similar to those observed in the Mössbauer spectra of metallic iron when treated by either phosphoric acid, the ' Footner Process ', or zinc phosphate solution.[5,7] The Mössbauer parameters of this portion of the CEM spectra correspond with those reported from transmission measurements of iron(II) phosphate octahydrate [5,8,9] and are consistent with the presence of octahedrally co-ordinated iron ions in two different structural sites.[10] However, in contrast to the materials investigated earlier,[5] the samples studied here with heavy surface coatings also showed the presence of an iron(III) derivative with ^{57}Fe Mössbauer parameters resembling those reported for hydrolysed iron(III) species [11] and similar to those observed during CEMS studies of surface layers of γ-FeOOH.[12] Very mild heating of the material treated by the iron phsophate solution gave a slightly green colour to the surface phase and comparison of the CEM spectrum with reported transmission spectra [9,11,12] suggested a surface mixture of iron(III) hydroxide and iron(II) phosphate, both octahydrate and tetrahydrate. Samples of metallic iron which had been treated by either the ' Footner Process ' or zinc phosphate solution gave, when heated at 107 °C for 17 h, a different surface phase which suggested dehydration to the iron(II) phosphate tetrahydrate.[5]

It was found, however, that treatment of powdered bulk grey iron(II) phosphate octahydrate by the same heating conditions gave conversion to an orange material



CEM spectrum of iron foil treated with iron phosphate solution with a transmission Mössbauer spectrum characteristic of a high-spin iron(III) species, the Mössbauer parameters of which (Table 2) resembled those recorded for iron(III) orthophosphate tetrahydrate and were similar to those found [13] for the iron(III) species in a phosphate containing both iron(III) and iron(II) ions. It was also found that heating the bulk iron(II) phosphate octahydrate in nitrogen gave an initial iron(II)–iron(III) mixture which was converted after 17 h at 107 °C to an orange material with a ^{57}Fe transmission Mössbauer spectrum identical to that observed when the octahydrate was heated in air (Table 2). Room-temperature treatment of the octahydrate *in vacuo* also gave partial oxidation to an iron(II)–iron(III) mixture (Table 2), although complete conversion to an iron(III) species was not observed.

It seems, therefore, that oxidation of bulk iron(II) phosphate octahydrate to an iron(III) species is as readily accomplished under anaerobic conditions as in the presence of air. Presumably the formation of iron(III) hydroxide in the surface layers is a direct consequence of the heavy phosphating process. It is interesting to note that the iron foil subjected to a heavy zinc phosphate treatment gave a less intense surface phosphate contribution to the spectrum, suggesting that the concentration of any iron-containing compounds in the superficial regions is extremely small. It is possible that the formation of a zinc phosphate (hopeite) phase on the iron substrate would account for the dominance of the magnetic iron contribution to the CEM spectra from such materials.

It appears that the phosphating of metallic iron gives the production of a surface iron(II) phosphate, which is stabilised as an iron(II) species and prevented from oxidation by the substrate. It also seems that superficial iron(III) compounds only occur in the form of hydroxide when medium or heavy phosphate coatings are produced.

Exposure of the iron foil treated by the ' Footner Process ' to water vapour gave a material for which the CEM spectrum (Table 1) showed the conversion of the iron(II) phosphate to a hydrolysed iron(III) species. The CEM spectrum of the iron foil supporting a heavier surface phosphate coating, following treatment by an iron phosphate solution, continued to show the presence of the iron(II) phosphate after exposure to water vapour (Table 1) although the intensity was reduced in favour of the iron(III) species. It seems, therefore, that a light iron(II) phosphate coating on metallic iron, as is produced by the ' Footner Process,' suffers oxidation and hydration when exposed to water vapour whereas the heavier coating produced by the iron phosphate solution is, as in the case of thermal treatments, protected from oxidation by the metallic iron substrate.

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