Mössbauer Investigations of Some Chemical Treatments of Iron Surfaces

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The nature of corrosion- and abrasion-resistant surface phases formed by the chemical treatment of iron-containing solids has been investigated by conversion electron and conventional transmission mode Mössbauer spectroscopy. Corrosion-resistant films produced by oxidising alkaline solutions contain iron(III) oxyhydroxides and their formation appears to resemble the actual process of corrosion. Nitriding processes which harden the surface by reaction of the metal with cyanide ions give superficial phases which include the iron nitrides Fe_2N and Fe_4N. Sulphiding processes produce abrasion resistant surfaces by reaction of the metal with thiocyanate ions and give a surface phase containing the iron sulphide ' Greigite.' No evidence was found for the presence of iron carbides in materials treated by cyanate or thiocyanate.

THE normal environments of metals often constitute thermodynamically unstable conditions and have the tendency to convert the metal to a more stable species by the formation of oxides or hydroxides. Hence corrosion is a natural process which is usually unwanted, frequently difficult to control, and gives rise to surface films which may be firmly and integrally bonded to the metal and profoundly influence the technical application of the metal itself.

Studies of the nature of such films have led to the development of artificial coatings to protect the metal from corrosion. Consequently several chemical surface treatments based on the production of phosphate or chromate coatings have been developed. For similar reasons other processes such as nitriding or sulphiding, which influence the mechanical properties of the metallic surface, have been formulated to protect the metal from superficial abrasion. Despite the commercial importance of these processes the chemical composition of many of the surface phases and the nature of their interaction with the metal substrate has not been established.

One technique which has potentially important application in the investigation of such matters is conversion electron Mössbauer spectroscopy (c.e.m.s.). Unlike many spectroscopic methods c.e.m.s. is able to examine surface layers of less than 300 nm depth. The principles of the technique are well documented [1] and its use in the study of corrosion has recently been reviewed.[2] The potential value of c.e.m.s. in investigating the nature of protective films has recently been illustrated by a study of the phosphating of metallic iron [3] and an investigation [4] of the implantation of nitrogen into iron foils. It is of further importance to note that when used in conjunction with conventional transmission mode Mössbauer spectroscopy c.e.m.s. provides a powerful method of comparing the nature of materials when formed as either bulk or surface phases.[1,2,5]

We report here the investigation of three established metallurgical processes: blackening, nitriding, and sulphiding. These treatments are commonly used in the formation of corrosion- and abrasion-resistant surface films [6] and although the actual details of the separate treatments are subject to minor variation according to commercial requirements the principles of each individual process are essentially similar.

EXPERIMENTAL

The investigations reported here involved the examination of metallic iron plates (0.25 mm thick), foils (0.025 mm thick), and iron powder (90 mesh) treated by the following processes.

Blackening, Method (1).—The metal was immersed in a solution of sodium hydroxide (15 g), sodium nitrate (25 g), and sodium nitrite (0.5 g) in water (50 g) at 130 °C for 30 min. Drying in a desiccator gave a dark grey surface to the metal.

Blackening, Method (2).—The metal was subjected to a two-stage process involving initial immersion in the above solution followed by further treatment at 160 °C for 30 min. The brown metal was dried in a desiccator.

Blackening, Method (3).—The metal was treated by a three-stage process involving initial immersion in a solution of sodium hydroxide (7.5 g), disodium phosphate (1.6 g), and sodium nitrite (0.5 g) in water (6.4 g) at 125 °C for 15 min. The brown metal was subsequently treated with a solution of sodium hydroxide (3 g) and sodium nitrite (2 g) in water (4 g) at 135 °C for 15 min to give a dark grey surface and finally immersed in a solution of sodium hydroxide (6 g), disodium phosphate (1 g), trisodium phosphate (1.5 g), and sodium nitrite (0.3 g) in water (6 g) at 160 °C for 15 min. The brown metal was dried in a desiccator.

Nitriding.—The metal was treated in a bath containing potassium cyanate (3 g) and manganese dioxide (0.15 g) at 600 °C for 10 min to give a black surface coating.

Sulphiding.—The metal was subjected to a bath containing sodium hydroxide (1 g) and sodium thiocyanate (10 g) at 180 °C for 10 min to give a black flaky surface.

Iron-57 Mössbauer spectra were recorded with a conventional constant acceleration spectrometer and a 10 mCi † $^{57}Co/Rh$ source. The internally converted electrons were detected with a helium–methane (95 : 5) gas mixture in a resonance counter similar to that described earlier.[7] The drive velocity was calibrated by iron foil. The spectra were computer-fitted by standard procedures.[8]

The surface products formed on the metal plates by some

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† Throughout this paper: $1\ Ci = 3.7 \times 10^{10}\ s^{-1}$; $1\ Oe = 79.578\ A\ m^{-1}$.

of the chemical treatments did not give satisfactory c.e.m. spectra. In these cases the immediate surface materials were removed either by scraping or by ' peeling ' with adhesive tape. The foils were examined by both c.e.m.s. and transmission mode Mössbauer spectroscopy, the plates by c.e.m.s., whilst the powders and removed surface products were investigated in the transmission mode.

RESULTS AND DISCUSSION

All the spectra gave values for χ^2 of less than 500 except where indicated in the text. The c.e.m. spectra from both plates and foils showed the superposition of non-magnetic patterns on signals characteristic of the underlying magnetic iron substrate. The ^{57}Fe c.e.m.s. parameters which were not attributable to the bulk magnetic iron substrate and which therefore represent the surface phase are recorded in Table 1. Data recorded from materials investigated by transmission mode Mössbauer spectroscopy are given in Table 2.

TABLE 1

Iron-57 conversion electron Mössbauer parameters (mm s^{-1})

	Iron plate			Iron foil		
Treatment	$\delta^{a}(\pm 0.02)$	$\Delta(\pm 0.04)$	$\Gamma(\pm 0.03)$	$\delta^{a}(\pm 0.02)$	$\Delta(\pm 0.04)$	$\Gamma(\pm 0.03)$
Blackening						
Method (1)	0.19^{b}	0.77	1.20			
Method (2)	0.32	0.85	0.52	0.32	0.72	0.75
Method (3)	0.32	0.82	0.55	0.42	1.10	0.83
Nitriding	0.39^{b}	0.28	0.33			
Sulphiding	0.39^{b}	0.89	0.46	0.31	0.76	0.66

[a] δ is relative to magnetic iron. [b] After peeling.

TABLE 2

Iron-57 transmission Mössbauer parameters

Treatment	Iron powder			Iron foil		Peelings[a]		
	$\delta^{b}(\pm 0.02)$/ mm s^{-1}	$\Delta(\pm 0.04)$/ mm s^{-1}	$\Gamma(\pm 0.03)$/ mm s^{-1}	$H_{int.}(\pm 3)$/ kOe	$\Gamma(\pm 0.04)$/ mm s^{-1}	$\delta^{b}(\pm 0.02)$/ mm s^{-1}	$\Delta(\pm 0.04)$/ mm s^{-1}	$H_{int.}$/ kOe
Blackening								
Method (1)	0.34	1.06	0.48					
Method (2)	0.46^{c}	0.87	0.54	330	0.70			
Method (3)	0.46^{c}	0.87	0.56	330	0.70			
Nitriding				224	0.90			
Sulphiding				330	0.41	(1) 0.8		290
						(2) 0.4		280
						(3) 0.3	0.7	

[a] Estimated parameters. [b] δ is relative to magnetic iron. [c] Spectra recorded at 77 K.

Blackening.—The peeled iron plate subjected to Blackening Method (1) gave a c.e.m. spectrum showing the superposition of a doublet on a magnetic hyperfine pattern characteristic of metallic iron. Plates and foils subjected to Methods (2) and (3) gave similar c.e.m. spectra (Figure 1) consisting of a quadrupole-split absorption, characteristic of the surface phase superimposed on a low intensity six-line hyperfine pattern arising from the underlying metallic iron substrate. The detection of signals from the substrate suggests that the surface film is less than the maximum probing depth of the technique of 300 nm (ref. 1) or, alternatively, that this phase does not form a continuous film over the iron surface. The sensitivity of the c.e.m. technique to the surface phase is illustrated by the transmission mode Mössbauer examination of the iron foils subjected to the blackening process which gave only magnetically split spectra characteristic of metallic iron but with broader linewidths than expected.

All three blackening methods produced surface layers which gave similar Mössbauer spectra, indicative of surface phases of comparable composition. The Mössbauer parameters resemble those reported[9] for hydrolysed iron(III) species (δ *ca.* 0.35 mm s^{-1}, Δ *ca.* 0.72 mm s^{-1}), iron(III) hydroxides,[10] and thin layers[11] of γ-FeO(OH) (Δ *ca.* 0.73 mm s^{-1}), and thereby indicate that the blackening process carried out in highly alkaline conditions is mainly associated with the formation of thick surface-protective phases containing iron(III) hydroxides or oxyhydroxides. Indeed, this process may be envisaged as giving rise to the initial formation of a soluble iron(II) hydroxide, which in the presence of oxygen could be converted to the stable iron(III) oxyhydrate (FeOOH) and/or the practically insoluble iron(III) hydroxide. In this respect it is interesting that some blackening processes[6] involve the use of oxidising agents such as dichromates, permanganates, and peroxides which by becoming incorporated in the initial coating could facilitate the oxidation of iron(II) to iron(III). The suggestion[6] that the process involves the formation of a protective coating consisting of a least stable crystalline iron(II) oxide (FeO, wustite) phase at the metal surface covered by a loose and porous film of iron(II)–iron(III) oxide (Fe_3O_4, magnetite) which supports an adherent dense film of iron(III) oxide (Fe_2O_3, haematite) is not supported by the data reported here. The c.e.m. spectra showed no patterns characteristic of magnetically ordered oxides such as haematite or magnetite in the surface phase, neither did the spectra provide any evidence for the presence of iron(II). It seems therefore that the conditions under which the blackening process is conducted emulate the formation of natural protective coatings during corrosion which also consist of iron oxides, hydroxides, or oxyhydroxides and presumably involve oxygen as the main reacting element.

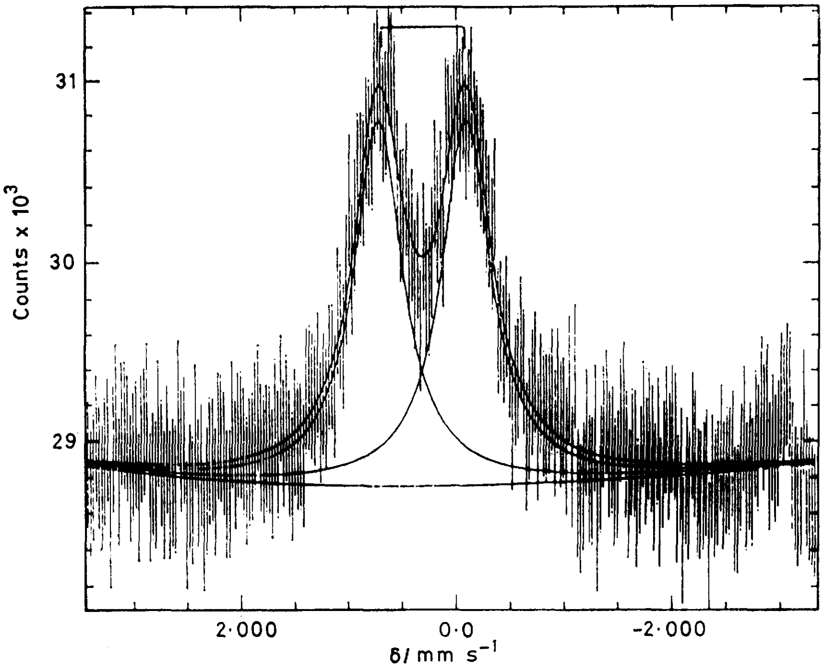

FIGURE 1 Conversion electron Mössbauer spectrum of iron plate treated by Blackening Method (3)

The transmission Mössbauer spectra of the iron powders treated by the blackening processes were very similar to those recorded by c.e.m. from the iron plates and foils. The blackening processes which produce better corrosion resistance and thicker coatings [Methods (2) and (3)] gave c.e.m. and transmission mode spectra with broader linewidths ($\Gamma > 0.51$ mm s^{-1}) than those normally recorded from crystalline iron compounds. Although the line-broadening may be attributed to increasing thickness of the surface phase it is also possible that the surface films produced by Methods (2) and (3) contain poorly crystalline iron(III) hydroxides and oxyhydroxides in which iron occupies a range of slightly different sites and gives a somewhat amorphous surface coating. Moreover, it is reasonable to expect that the surface phase should contain a number of similar species which give comparable Mössbauer parameters with signals from the less dominant species being concealed under the intense doublet. Indeed, the similarity between Mössbauer parameters for hydrolysed iron(III) species, iron(III) hydroxides and oxyhydroxides, makes it difficult to distinguish between species which differ only in the relative number of hydroxide and oxide ions present. Furthermore the possibility of establishing the identity of these different species by low-temperature Mössbauer experiments is not applicable in these cases since materials such as γ-FeO(OH)[11] and natural iron gels[9] are paramagnetic at 77 K and do not give spectra showing magnetic hyperfine interactions. However, the transmission Mössbauer spectra of the iron powders did show some weak absorptions indicative of the presence of magnetically ordered species and, although not amenable to resolution even at low temperatures, suggest that iron is capable of producing a complex mixture of species when treated by the blackening process.

Nitriding.—The iron plate subjected to a bath containing potassium cyanate and manganese dioxide gave, after peeling, a c.e.m. spectrum [Figure 2(*a*)] showing a doublet similar to that reported[12] for paramagnetic ε-Fe_2N (δ 0.40 mm s^{-1}, Δ 0.26 mm s^{-1}). The transmission mode Mössbauer spectrum for the foil when subjected to similar treatment showed the presence of a magnetically ordered species (δ 0.28 mm s^{-1}, $H_{int.}$ 224 kOe) [Figure 2(*b*)], which resembles that reported[4,13-17] for the iron nitride Fe_4N. The departure of the peak intensity ratios from their expected distribution may reflect the presence of other phases, including magnetically ordered Fe_3N[4,16-18] and Fe_3C.[19,20] Attempts to account for the enhanced absorption at *ca*. 0 mm s^{-1} by introducing a contribution corresponding to that for ε-Fe_2N were unsuccessful. The poor physical quality of the nitrided foil precluded the examination of the material by c.e.m.s. Hence the absence of a doublet characteristic of ε-Fe_2N in the transmission mode Mössbauer spectrum of the foil suggests that this species is characteristic of the most superficial regions of the surface phase and illustrates the high surface sensitivity of the c.e.m.s. technique. The failure of this transmission mode spectrum to show a

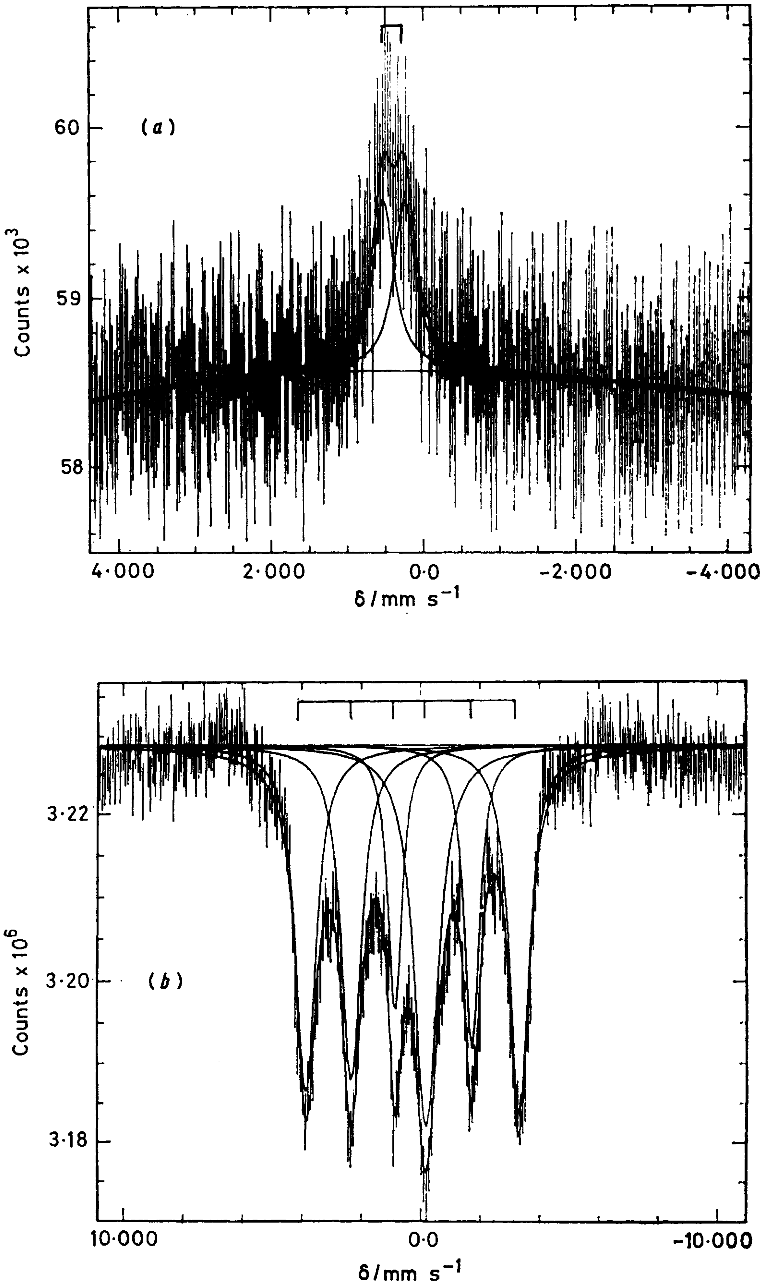

FIGURE 2 (a) Conversion electron Mössbauer spectrum of nitrided iron plate following 'peeling'; (b) transmission mode Mössbauer spectrum of nitrided iron foil

magnetically split hyperfine pattern typical of metallic iron indicates that the nitriding reaction has occurred throughout the bulk of the thin iron foil.

The coatings formed on the surfaces of steels by the nitriding process have been described [6,21] as containing iron nitride and are considered to enhance the hardness, fatigue resistance, and abrasion resistance of the surface as well as to offer some protection to corrosion from water. It has also been suggested [6,21-23] that the nitride phase is formed by active nitrogen and attains a depth depending on how far the nitrogen is able to diffuse during the nitriding process. The treatment in a cyanate bath is reported [6] to give a layer with a thickness less than 10 μm which would therefore be within the probing depth of c.e.m.s. The intensity in the c.e.m. spectrum of the contribution from the surface Fe_2N species suggests that a lack of impedence gives rise to the preferential formation of this phase. The low-intensity magnetic hyperfine pattern in the c.e.m. spectrum, although possibly originating from the metallic iron substrate, could not be resolved with certainty.

Given that the treatment involves the use of potassium

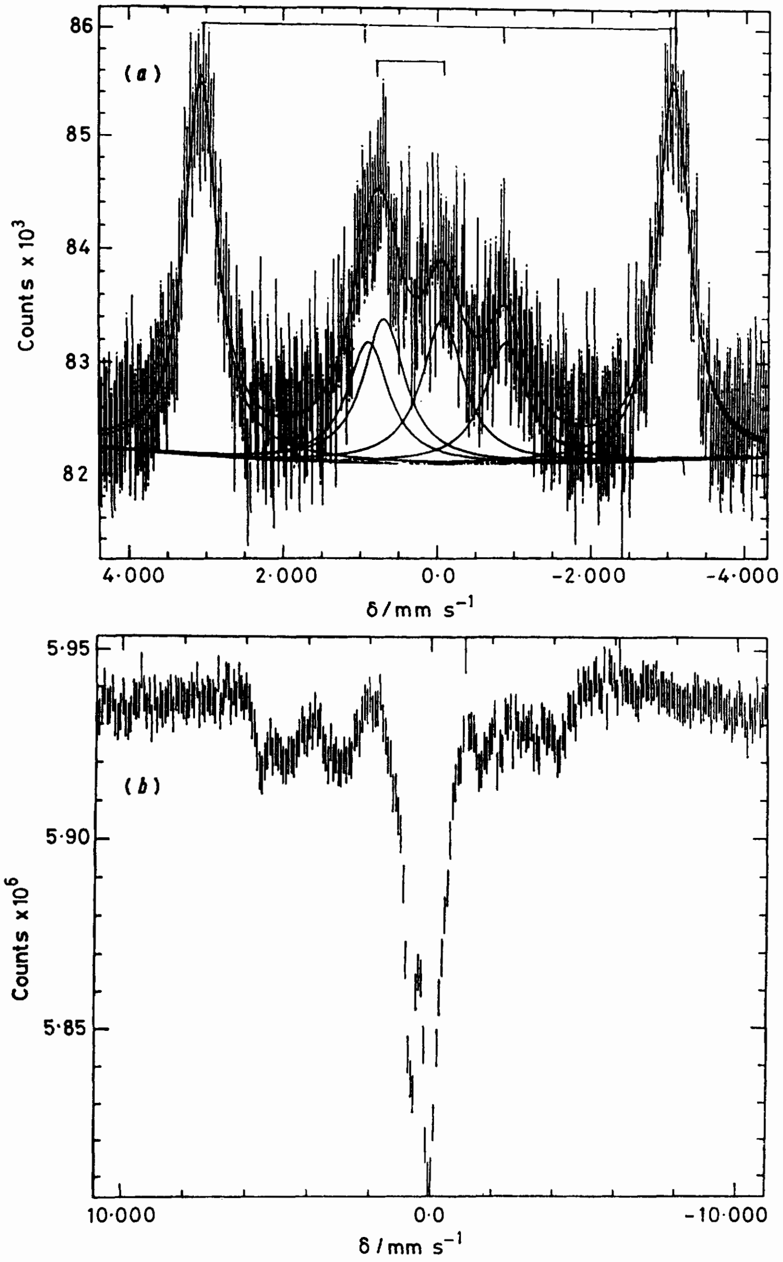

FIGURE 3 (*a*) Conversion electron Mössbauer spectrum of iron foil treated by the sulphiding process; (*b*) transmission mode Mössbauer spectrum of peeling from sulphided plate

cyanate and manganese dioxide it would be reasonable to expect the additional formation of iron carbides during these processes. Although the spectra gave no firm evidence for the formation of magnetically ordered iron carbides, it is not impossible that the broad doublet could conceal a signal from the paramagnetic austenite phase [24] which could arise from the coagulation of carbon near the surface of iron nitride.[25] Indeed, the presence of manganese dioxide in the bath might readily result in the formation of carbon monoxide which by reaction with the iron substrate could give an iron carbide. Such a scheme might be related to the increased nitriding potential when an oxidant is used in the process.

Sulphiding.—The treatment of the iron plate by the sulphiding process gave a flaky surface reaction product. Removal of this material produced a surface which gave a c.e.m. spectrum similar to that obtained from an iron foil subjected to similar treatment [Figure 3(*a*)] and which was characterised by the superposition of a doublet on a magnetic hyperfine pattern typical of metallic iron. The transmission mode Mössbauer spectrum of the iron plate ' peelings ' [Figure 3(*b*)] showed a doublet superimposed on a magnetically split pattern. Although repeated attempts to computer-fit the data were unsuccessful, a visual analysis suggested the presence of at least three contributions which included two magnetically split components (Table 2). The Mössbauer spectra [26-29] of the iron sulphide 'Greigite' of composition Fe_3S_4 have been interpreted in different ways, but parameters from spectra recorded at *ca.* 298 K have been reported and are reproduced in Table **3**.

TABLE 3

Iron-57 transmission Mössbauer parameters of 'Greigite'

Pattern	δ*/ mm s^{-1}	Δ/ mm s^{-1}	*H*/ kOe	Reference
1	0.39		297	26
2	0.28	0.48		26
3	0.31	0.55		26
1	0.36		308	29
2	0.45		291	29
3	0.37	0.64		29

* Converted relative to magnetic iron.

Although a comparison of the spectra suggests that the principal contribution to the iron plate 'peelings' is Greigite, indeed the most recent [29] analysis of the spectrum from synthetic Greigite reported the presence of two magnetically split components at 296 K, we would emphasise that the presence of additional species cannot be ignored. Hence the resistance of the data to computer-fitting is consistent with a complex spectrum arising from a heterogeneity of species which may include a contribution from magnetic iron.

The transmission mode Mössbauer spectrum of the sulphided iron foil showed a pattern characteristic of metallic iron. The χ^2 value (809) reflects the fitting of a transmission mode spectrum of the bulk when it is difficult to allow for the presence of the surface phase identified by c.e.m.s.

It has been suggested [22] that the low-temperature sulphiding process produces superficial iron sulphide integral with the metallic iron substrate and confers similar properties on the metal as are produced by the nitriding process. A range of stoicheiometries within the iron sulphides might reasonably be expected and given the use of sodium thiocyanate it would not be unreasonable to expect the additional formation of iron nitrides and carbides. Although the broad central doublet component of the spectrum precludes the unambiguous exclusion of these products, the spectra strongly indicate that the major phase is an iron sulphide.

In conclusion, it may be acknowledged that although the Mössbauer spectra of these phases formed during some metallurgical treatments are not unequivocal in their interpretation, they do indicate the nature of the major phase in each case and also illustrate the potential power of the techniques in investigations of this type.

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