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Mössbauer spectroscopy has been used to analyze the internal and external rust layers of a weathering steel exposed for ten months to an urban-industrial atmosphere. Superparamagnetic α-FeOOH and γ-FeOOH were found in both layers. The external one also contained small sized δ-FeOOH and/or amorphous iron oxyhydroxide. These compounds were not present in the internal layer at this stage of the patina formation.

INTRODUCTION

In the last ten years several studies have been carried out to determine the nature of the oxide products formed on low alloy steels called weathering steels. It has been established that small additions of alloying elements such as copper, chromium and phosphorus considerably improve the resistance of iron to atmospheric corrosion, particularly in industrial environments, but the operating mechanism is not yet fully understood.

Okada et al.[1], using reflected polarized light, observed that the rust on carbon steels and low alloy steels consisted of optically active and optically isotropic layers. In the first stages of rust formation on both steels, they

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[+] To whom all correspondance should be addressed found that the optically active and the optically isotropic layers were partially mixed. This morphology was observed for carbon steels even after 5 years exposure. On the other hand, Okada et al. found that on low alloy steels exposed to the atmosphere for periods longer than a year there was a separation between the two layers: the optically isotropic layer covered the metal surface and it was in turn covered by the optically active layer. Using X-ray diffraction they concluded that the rust on carbon steel and on weathering steels was composed of α-FeOOH and γ-FeOOH. But the rust on carbon steel contained small amounts of Fe_3O_4 while in the rust on weathering steels there was almost no Fe_3O_4.

Miranda[2] also analyzed the composition of the corrosion products formed on weathering steels during accelerated corrosion tests (the CEBELCOR inmersion-emersion tests). Using electron and X-ray diffraction he found only γ-FeOOH in the external rust layer, while employing infra-red spectroscopy he observed that the whole rust was formed by α-FeOOH and γ-FeOOH. Miranda also reported that using X-ray microdiffraction α-FeOOH could be identified in the inner isotropic layer.

Misawa et al. analyzed the rusts formed on mild and low alloy steels by means of infra-red and far infra-red spectrophotometries and X-ray diffraction[3,4]. The main products of atmospheric rusting after 2.5 years exposure, were for both steels α-FeOOH, γ-FeOOH and a fine particle sized δ-FeOOH[3] or an amorphous FeOOH[4]. Their results didn't show a significant difference in the amount or distribution of the rust products on mild and low alloy steels. They reported also that the relative amount of γ-FeOOH is larger in the low alloy steel rust than on mild steel, and also larger in the inner layers of rusts on both steels than in the outers; both α-FeOOH and amorphous ferric oxihydroxide are abundant in outer layers[4].

In the present work we employed Mössbauer spectroscopy to analyze the composition of the external and internal rust layers of a weathering steel. Mössbauer spectroscopy is proving to be a useful technique for investigating oxidation and corrosion phenomena on iron and its alloys[5,6], specially when ultrafine particles are present or for poorly crystalline materials where other techniques give poor information. There are three important parameters derived from an experimental spectrum which are very sensitive to the oxidation state of the iron nucleus and to the type, number and distortion of the ligands. Different iron compounds give characteristic spectra used to identify the presence of each of them in an unknown sample.

EXPERIMENTAL

Tests were carried out on a low-alloy steel belonging to the so called "weathering steels". The steel composition is shown in Table 1. Plates 30 cm long, 10 cm wide and 0.2 cm thick, were exposed for 10 months in an urban-industrial atmosphere, facing north at an 30° angle. After this exposure time, samples of the outer layer of rust were taken by slightly scraping part of the surface with a razor. In another areas of the sheet the external rust was eliminated by adhering the rust surface to an aluminium plate with an epoxi resin[7]. Once the resin dried, the plates were knocked apart, remaining the main volume of the rust adhered to the resin. Then, samples of the rust immediately adjacent to the surface were scraped with a razor.

Mössbauer spectra were measured in a transmission geometry with an ELRON Mössbauer spectrometer in a constant acceleration mode with an

TABLE 1

Steel composition

Element	C	Mn	Si	S	P	Cr	Ni	Mo	Sn	Cu	Fe
% weight	0.11	0.37	0.22	0.023	0.085	0.69	0.11	0.10	0.06	0.38	diff.

Ar/CO_2 filled Reuter Stokes RSG-61-M2 proportional counter. Spectra were displayed in a multichannel analyzer operated in the time mode. The source used was ^{57}Co in Pd matrix. The samples, in the form of powder were weighed to give an iron content of approximately 8 mg cm^{-2} and were encapsulated between thin acrylic disks. Measurements were carried out with the source at room temperature and the absorber at room, liquid nitrogen and intermediate temperatures. For these temperatures an appropiate cryostate with automatic control was used.

Spectra were least squares fitted[8] employing a pure Lorentzian shape and constraining the corresponding peaks. The quality of the computer fit was checked by a χ^2 test and only those of lower value were accepted.

Counting statistics (N) at room temperature was about $3x10^6$ counts/channel and therefore the statistical error per channel was about 0.06%. At liquid nitrogen temperature this figures are 10^6 counts/channel and 0.1% respectively; the measurement time was smaller than in the first case in order to guarantee the stability of our equipment. Temperature stability at room temperature was better than 0.2°C and better than 2°C at liquid nitrogen temperature over the whole run.

RESULTS AND DISCUSSION

Mössbauer spectra at room temperature of the internal and external rust layers show similar characteristics: two pairs of peaks in the paramagnetic region and a slight indication of peaks in the magnetic region (Figs 1a and 1b). Lowering the temperature a hyperfine magnetic spectrum appears superimposed with the central doublets. At liquid nitrogen temperature the best fit for internal rust layer sample spectrum indicates the presence of two sextettes in the magnetic region and a doublet in the paramagnetic one, Fig. 2a, while the external sample shows the presence of the two sextettes and two doublets in the paramagnetic region, Fig. 2b.

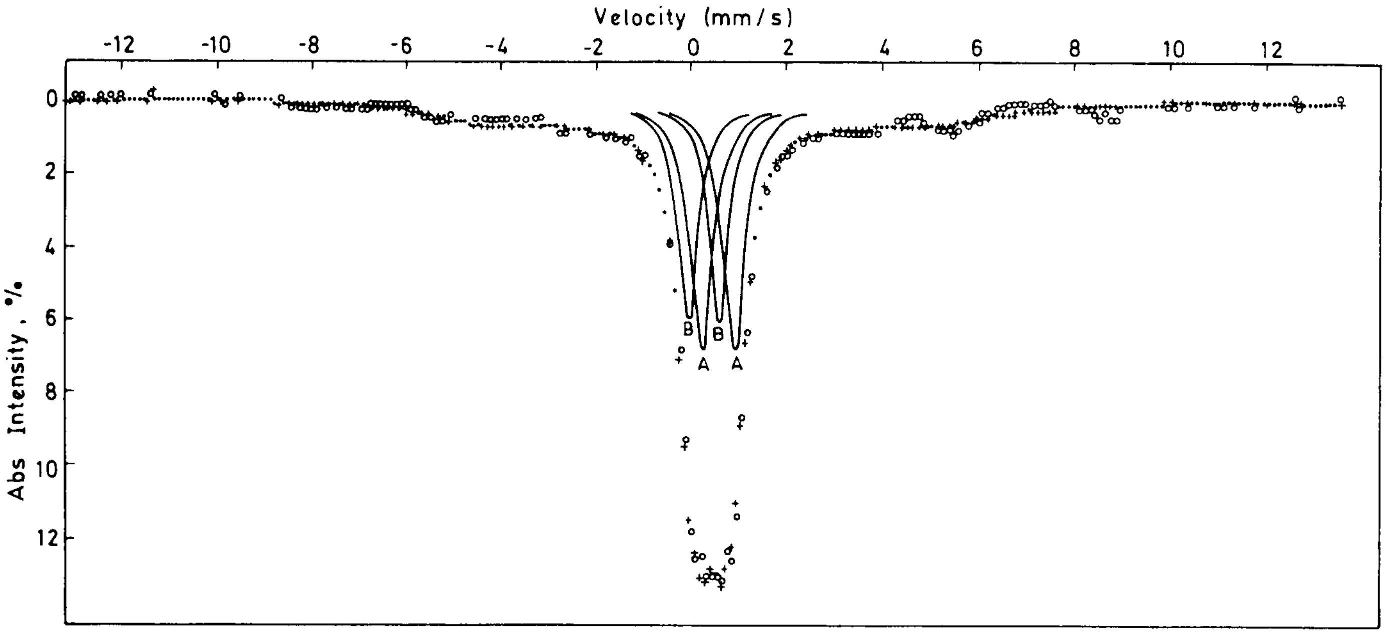

Fig. 1a. Mössbauer spectrum of internal rust sample at room temperature. (o) experimental points, (+) fitted points, full circles, both coincide

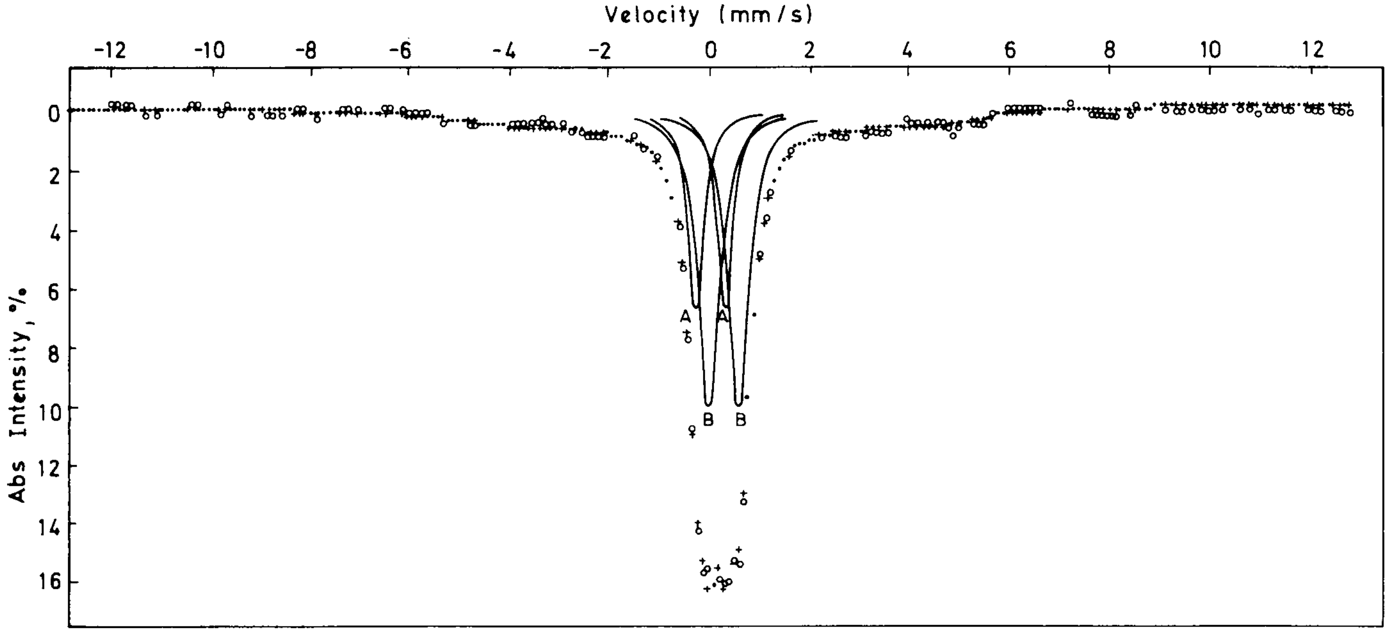

Fig. 1b. Mössbauer spectrum of external rust sample at room temperature. See the legend of Fig. 1a

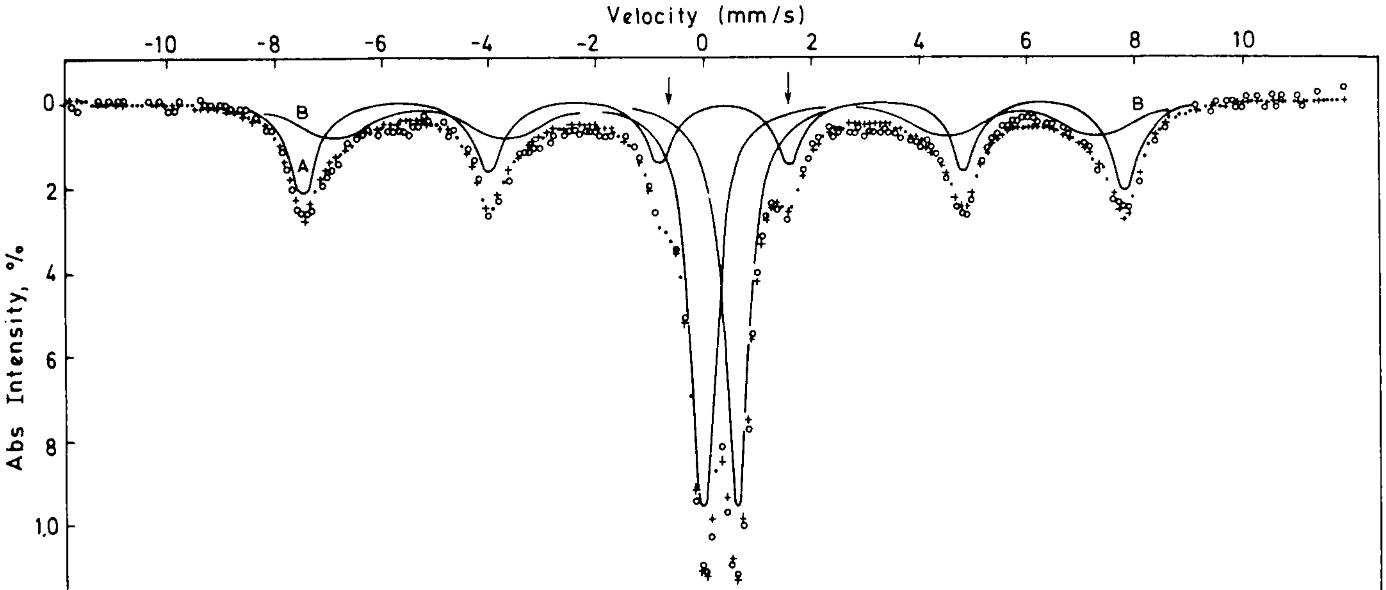

Fig. 2a. Mössbauer spectrum of internal rust sample at liquid nitrogen temperature. Arrows indicate peaks 3 and 4 of spectrum B. See the legend of Fig. 1a

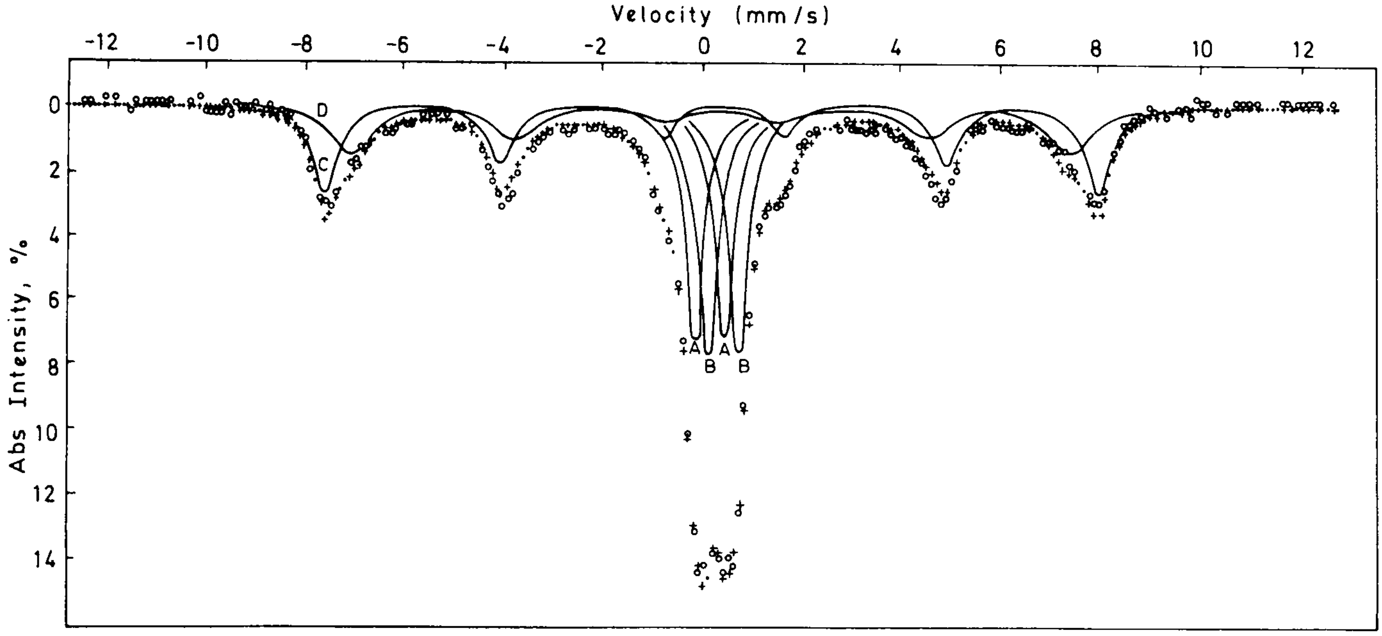

Fig. 2b. Mössbauer spectrum of external rust sample at liquid nitrogen temperature. See the legend of Fig. 1a

TABLE 2

Mössbauer parameters of the fitted spectra

At room temperature

	Central region			
	Q.S. (mm/s)	I.S.$^{+}$ (mm/s)	Q.S. (mm/s)	I.S.$^{+}$ (mm/s)
Int. layer	0.63(4)	0.23(6)	0.63(6)	0.04(8)
Ext. layer	0.59(4)	0.12(6)	0.60(6)	0.30(8)

At liquid nitrogen temperature

	Central region			
	Q.S. (mm/s)	I.S.$^{+}$ (mm/s)	Q.S. (mm/s)	I.S.$^{+}$ (mm/s)
Int. layer	0.62(4)	0.30(6)	--	--
Ext. layer	0.62(4)	0.40(6)	0.61(5)	0.15(6)

Superimposed hyperfine scpectra

	H (Koe)	*Q.S. (mm/s)	I.S.$^{+}$ (mm/s)	γ (mm/s)
Int. layer	468(2)	-0.11(3)	0.30(3)	0.4
	445(8)	-0.11(8)	0.31(8)	1.1
Ext. layer	484(2)	-0.11(3)	0.30(3)	0.4
	453(7)	-0.11(8)	0.28(8)	0.9

(+) Referred to Pd matrix at room temperature

*Q.S. = $\frac{e^{2}qQ}{8}(1-3\cos^{2}O)$

In the graphs are shown the experimental spectra, the individual calculated spectra labelled with capital letters and their sum. The Mössbauer parameters appear in Table 2, in which we have indicated only the paramagnetic region at room temperature. In Table 3 is shown the relative contribution of each oxihydroxide obtained from the corresponding area ratios.

TABLE 3

Relative concentration of oxihydroxides

	T	Sextett	γ-FeOOH doublet	Other doublet
Int. layer	R	25%	43%	32%
	L.N.	55%	45%	--
Ext. layer	R	21%	27%	52%
	L.N.	45%	29%	26%

Internal sample Mössbauer parameters indicate the presence of γ-FeOOH[9] with a relative contribution of 43%. At liquid nitrogen temperature, instead of the second doublet, a magnetic spectrum appears showing the presence of superparamagnetic α-FeOOH. This magnetic spectrum asymmetrically broadened is fitted by 2 sextettes pointing out the existence of ultrafine α-FeOOH($\leq$ 80 A) with an excess of water[10,11].

External sample Mössbauer parameters indicate also the presence of γ-FeOOH, but now its contribution is about 28% of the total. Lowering the temperature, the other doublet present decreases its relative intensity from 52 to 26% and a superimposed spectrum appears, whose parameters correspond to a ultrafine α-FeOOH. The parameters of the just mentioned doublet would indicate the presence of small sized δ-FeOOH ($\leq$ 100 A) or an amorphous oxihydroxide (gel)[12]. If a paramagnetic fraction of ultrafine α-FeOOH were present at liquid nitrogen temperature these particles would be smaller than those in the internal layer. But since the values of

H and of the line widths show the presence of larger particles (10), the contribution of ultrafine α-FeOOH to this doublet is discarded.

Mössbauer spectroscopy shows that: the internal layer α-FeOOH particles are smaller than those contained in the external one: the relative amount of γ-FeOOH is larger in the internal layer; only in the external layer there is evidence of the presence of amorphous oxihydroxide and/or ultrafine δ-FeOOH. We have observed no trace of either Green Rust I and II or Fe_3O_4 in both layers.

Misawa et al.[4] support the hypotesis that the low corrosion rate of weathering steels is due to the formation of a compact, crack-free protective layer of amorphous ferric oxihydroxide on the steel surface. Okada[1] considers also that an inner layer of an amorphous spinel-type iron oxide is the responsible of the significant corrosion resistance of weathering steels in the atmosphere. On the other hand, Miranda[2] favours the hypotesis of a protective inner layer rich in α-FeOOH.

Our results are not in agreement with those obtained by Miranda. They are coincident with most of Misawa's observations but differ in the fact that in our case neither δ-FeOOH nor amorphous compounds are observed in the internal rust layer. It is worth noting that, at least in the beginning of the rust formation, there is no amorphous iron oxihydroxide in the rust layer adjacent to the steel surface. Instead we do find an ultrafine α-FeOOH. However, the data presented correspond to a rust film 10 months old, that is, a nonstabilized patina. It would be necessary to analyze a consolidated rust film to confirm our results.

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