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THE INFLUENCE OF PHOSPHORIC ACID ON STEEL AND ON ITS CORROSION PRODUCTS: A MÖSSBAUER SPECTROSCOPIC APPROACH*

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INTRODUCTION

PHASE transformations such as chemical reactions of steel surfaces with phosphoric acid are of interest from several points of view. For example, industrial steel coating requires in many cases a pretreatment of the surface with phosphoric acid. Although this procedure is preceded by a rigorous cleaning of the surface, residual or subsequently formed oxides and corrosion products can never be excluded completely. Therefore, attention must be paid not only to the effect of phosphoric acid on the metal surface, but also to its reaction with oxides and further corrosion products.

Phase transformations are also the goal in employing what are described as rust transformers. Most of these commercial products consist mainly of concentrated phosphoric acid. It was shown in a Mössbauer spectroscopic study that they fail to form a protective oxide layer on the steel surface.[1] To understand their effect, a detailed knowledge of the influence of phosphoric acid on the rust components is necessary. This holds also for applications of phosphoric acid in nuclear power plants where phosphoric acid is used in the careful removal of radioactive corrosion products from the internal surface of vessels and tubes.

Related problems of interest in this context are the interaction of phosphates as adhesives on metallic iron, the behaviour of phosphates used as corrosion inhibitors in systems carrying water, and the interaction of soil components (e.g. goethite, α-FeOOH) with fertilizers containing phosphates.

EXPERIMENTAL METHOD

Steel plates (German standard steel St37, 50 × 100 × 1 mm) were cleaned mechanically and with acetone and exposed at room temperature in an atmosphere whose corrosivity was controlled by the equilibrium with 0.5 N HCl. Afterwards the samples were impregnated with an excess of concentrated phosphoric acid (15 mol l^{-1}) and, in some cases, several commercial rust transformers containing phosphoric acid (1.4–4.6 mol l^{-1}) and dried at room temperature for several days.

The phase analysis of the samples was performed by Mössbauer spectroscopy using a commercial spectrometer for transmission and scattering experiments with ^{57}Co/Rh γ-ray sources of 10 and 150 mCi, respectively.[2] For gamma scattering experiments at low temperature, a special styrofoam cryostat cooled by liquid nitrogen was used.

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*Dedicated to Professor U. Gonser on the occasion of his 60th birthday.

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The transmission technique is well applicable to studies of powdered materials, e.g. loose rust, and thin foils, but the thickness of samples is limited to about 15 mg cm^{-2} of iron. The Mössbauer scattering technique is a non-destructive method applicable to studies of surface compounds on thick substrates. It provides a preferential sensitivity with respect to surface layers and allows studies of underlayer corrosion, bnt it takes much more time than transmission measurements do.

EXPERIMENTAL RESULTS

Mössbauer spectra of a rusty steel plate, untreated and treated with a rust transformer, respectively, are shown in Fig. 1. Before all treatments, the loose rust was removed carefully from the surface. Figure 1(a) shows the gamma scattering Mössbauer spectrum of the sample before the treatment with a rust transformer, measured at 80 K. Figure 1(b) is the same spectrum, but the sextet resulting from the metallic substrate is subtracted. Figure 1(c) shows the gamma scattering spectrum of the same sample after treatment with a commercial rust transformer; again the

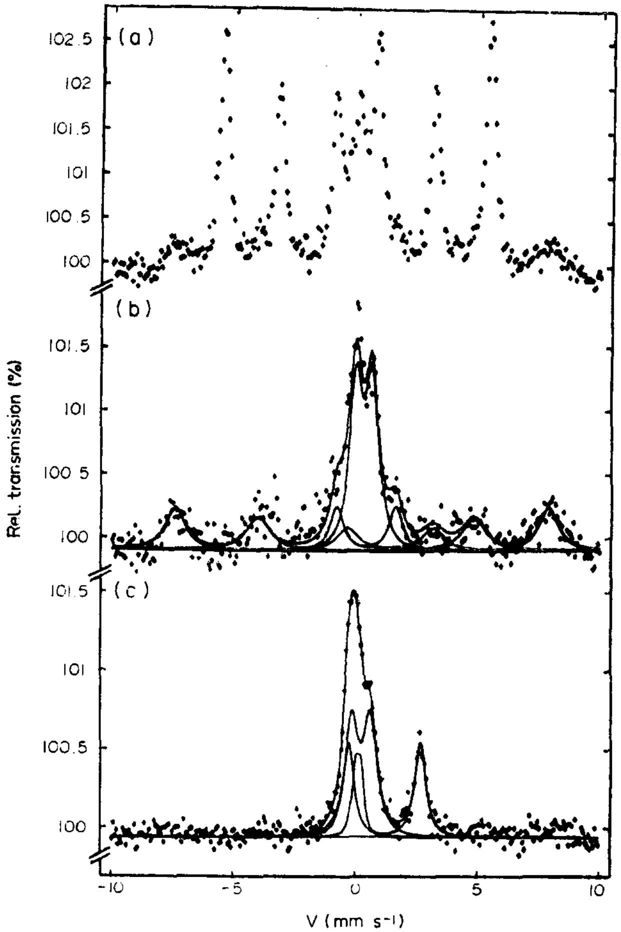

FIG. 1. Gamma scattering Mössbauer spectra of a rusty steel plate before treatment (a), after subtraction of the sextet belonging to the metal substrate (b), and after treatment with a commercial rust transformer and subtraction of the metal sextet (c), measured at 80 K.

magnetic sextet of the metallic substrate has been subtracted. Measurements at 80 K allow a distinction to be made between β-FeOOH (indicated by the line sextet in Fig. 1b) and γ-FeOOH (the intense doublet in Fig. 1b).[4] The appearance of β-FeOOH is understandable, because it is known that atmospheric corrosion in the presence of chloride ions may lead to the formation of β-FeOOH besides other corrosion products.[3] There is an additional doublet with a large splitting indicating the presence of some ferrous species. Within the experimental error limits the relevant spectral parameters (see Table 1) correspond to those of $FeCl_2{\cdot}4H_2O$.[1,4] From Fig. 1(c) it can be seen that the treatment with the rust transformer causes the magnetic sextet and the doublet of Fig. 1(b) to disappear in favour of two different doublets and an additional broad single line (cf. Table 1).

TABLE 1. ISOMER SHIFT δ (RELATIVE TO METALLIC IRON) AND QUADRUPOLE SPLITTING Δ (FULL DISTANCE BETWEEN THE DOUBLET LINES), IN mm s^{-1}, DERIVED FROM THE MÖSSBAUER SPECTRA

Figure		Fe^{2+}-doublet	Fe^{3+}-doublet	Singlet
1(b)	δ	1.58 ± 0.26	0.40 ± 0.03	— —
	Δ	3.48 ± 0.47	0.66 ± 0.05	— —
1(c)	δ	1.28 ± 0.05	0.32 ± 0.05	0.22 ± 0.10
	Δ	2.94 ± 0.08	0.77 ± 0.10	
2(b) 300 K	δ			0.42 ± 0.03
80 K	δ			0.49 ± 0.03
3(c)	δ	1.32 ± 0.03	0.30 ± 0.03	—
	Δ	2.25 ± 0.04	0.62 ± 0.04	—
4(b)	δ	—	—	0.43 ± 0.03
5(b)	δ	—	—	0.42 ± 0.03

The parameters of the sextet lines of Figs. 1(b), 2(b), 4(b) and 5(b) are not included in this table.

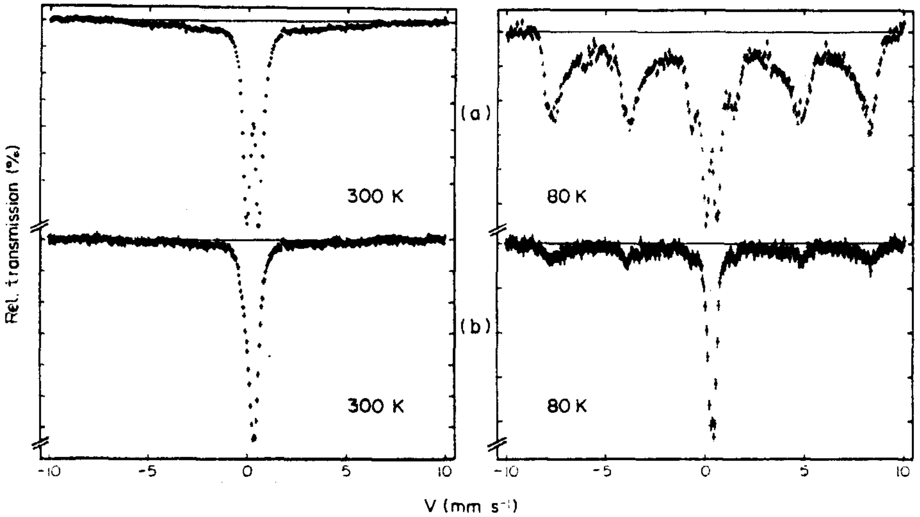

FIG. 2. Mössbauer transmission spectra of loose rust, the upper spectra (a) recorded before, the lower spectra (b) recorded after treatment with phosphoric acid, measured at 300 and 80 K as indicated.

It is reasonable to assume that the phase transformation of the rust components is mainly due to the influence of the high phosphoric acid content in the rust transformer (4.3 mol l^{-1} in Fig. 1). For comparison, an example of the effect of phosphoric acid on loose rust is shown in Fig. 2. The upper spectra (Fig. 2a) show that the rust sample used consisted of β-FeOOH (the sextet at 80 K) and γ-FeOOH (the doublet at 80 K) with a small contribution from magnetically ordered oxides (the deformed background at 300 K). The lower spectra (Fig. 2b) were recorded after treatment of the rust with phosphoric acid. It is evident that nearly all rust components are transformed to a product which shows both at room and liquid nitrogen temperature a broadened single line in the Mössbauer spectrum. This result is discussed later.

Investigations of the kind described here demonstrate that a detailed study is necessary of the influence of phosphoric acid on those oxides which are the most important corrosion products of steel, i.e. α-, β-, γ-FeOOH, α-, γ-Fe_2O_3, Fe_3O_4, and

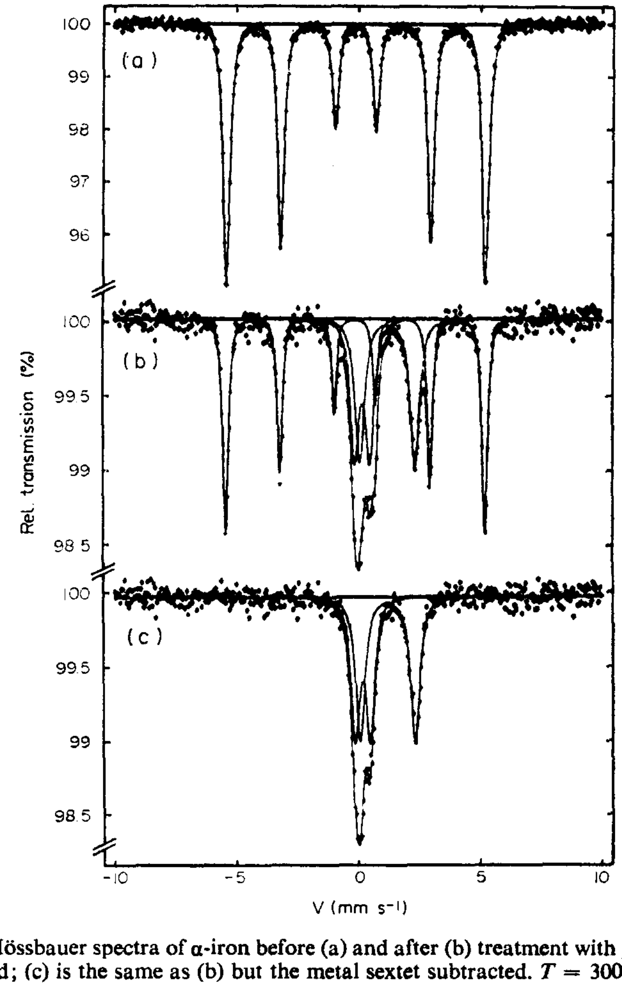

FIG. 3. Mössbauer spectra of α-iron before (a) and after (b) treatment with phosphoric acid; (c) is the same as (b) but the metal sextet subtracted. $T = 300$ K.

FeO. Such studies, including the behaviour of metallic iron, have been performed, and some examples and the results are presented.

The effect of phosphoric acid on granulated metallic iron is demonstrated in Fig. 3. Figure 3(a) shows the spectrum of the untreated sample, Fig. 3(b) that of the treated sample. Figure 3(c) shows the spectrum of the reaction products, i.e. the spectrum of Fig. 3(b) with the magnetic sextet of the metallic iron subtracted. The two doublets of Fig. 3(c) can be ascribed to $Fe_3(PO_4)_2 \cdot 8H_2O$ and $FePO_4 \cdot 4H_2O$.[4-9] The same compounds are found to be formed after a treatment of magnetite (Fe_3O_4) and wüstite (FeO) with phosphoric acid.

The other oxides and oxyhydroxides mentioned above show quite a different behaviour; an example is demonstrated in Fig. 4. The reaction of phosphoric acid with haematite (α-Fe_2O_3) leads to the appearance of a single broad line in the Mössbauer spectrum. The same line appears, if phosphoric acid reacts with maghemite (γ-Fe_2O_3), goethite (α-FeOOH), akaganeite (β-FeOOH), or lepidocrocite (γ-FeOOH). In all these cases, the neutral ferrous and ferric phosphates did not appear, as demonstrated by the absence of the corresponding doublets in the Mössbauer spectra. We ascribe the single line to the formation of the acid ferric phosphate $FeH_3(PO_4)_2 \cdot 2.5H_2O$.

The appearance of the broad single line spectrum was unexpected, because the large variety of iron phosphate spectra reported in the literature does not include such a singlet. In a separate study we found that a synthesized sample of $FeH_3(PO_4)_2 \cdot 2.5H_2O$ ferric phosphate showed essentially the same singlet spectrum, although X-ray powder spectra of this material do not indicate a cubic structure. The formation of this species from corrosion products has not been reported before.

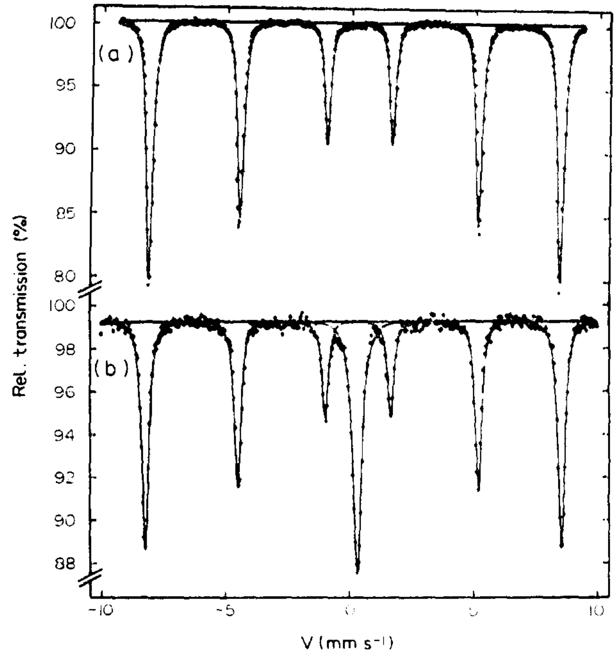

FIG. 4. Mössbauer spectra of α-Fe_2O_3 before (a) and after (b) treatment with phosphoric acid. $T = 300$ K.

CONCLUSIONS

The experiments demonstrate that two kinds of processes have to be considered: (i) The influence of concentrated phosphoric acid on metallic iron, Fe_3O_4, and FeO results in the formation of a mixture of $FePO_4.4H_2O$ and $Fe_3(PO_4)_2{\cdot}8H_2O$. (ii) The influence of concentrated phosphoric acid on α-, γ-Fe_2O_3, α-, β- or γ-FeOOH results in the acid ferric phosphate $FeH_3(PO_4)_2{\cdot}2.5H_2O$. This product exhibits a relatively high stability and is currently the subject of further studies,[10] because no detailed studies of this species are known yet.

The following rule may be suggested: acid ferric phosphate is produced if the substrate contains only Fe^{3+} ions; the presence of Fe^{n+} ions with $n < 3$, in addition to Fe^{3+} ions, leads to the formation of both the normal ferric and ferrous phosphates, and the acid salt will not be found. FeO seems to violate this rule in that it can form the normal as well as the acid phosphate simultaneously. This may be due to the well-known instability of FeO at room temperature, which may cause different oxides to be formed immediately before the treatment with phosphoric acid.

It is known that, among the iron oxides, only wüstite, magnetite, and maghemite are able to form a closed protective layer inhibiting further corrosion.[11] In the experiments described above it was found that in no case had either the pure phosphoric acid or any of the applied commercial rust transformers converted rust or some rust components into these species. This explains why the rust transformers have always been found to fail in fulfilling their claims.

There is another aspect, which is of interest for analytical work by Mössbauer spectroscopy. Sometimes oxidic samples contain superparamagnetic particles which contribute to a central doublet and/or to a "triangular" broad background in the Mössbauer spectrum. It is not possible to determine the nature of these small particles without cooling the sample. However, the existence of magnetite in the original

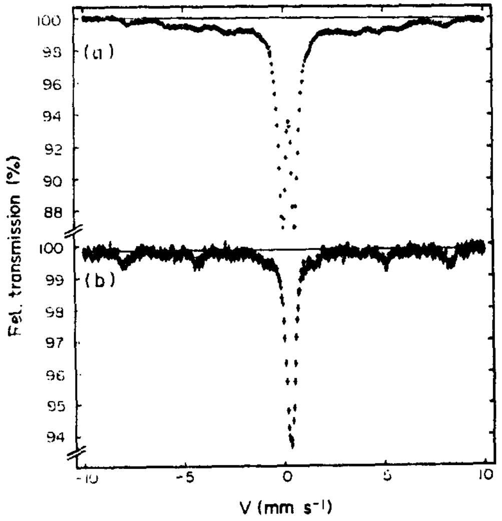

FIG. 5. Room temperature Mössbauer spectra of a rust sample containing α-, β-, γ-FeOOH and α-Fe_2O_3 before (a) and after (b) treatment with phosphoric acid.

sample is demonstrated, if after application of phosphoric acid the broad background is transformed into the two doublets of ferric and ferrous phosphate.

Although the experiments described here gave clear qualitative results, they give no detailed information on the kinetics of the phosphatization. The rate of the reaction with phosphoric acid is expected to be different for the different kinds of corrosion products. This can be seen in Fig. 5. The Mössbauer spectra of this rust sample showed the presence of a mixture of α-, β-, and γ-FeOOH, and α-Fe_2O_3. After treatment with phosphoric acid, all these rust components except for part of the α-Fe_2O_3 have been transformed to the acid ferric phosphate. This can be seen in Fig. 5(b), where the sextet corresponds to the remaining fraction of α-Fe_2O_3 of Fig. 5(a). The inner sextet lines (α-FeOOH) and the doublet (β-, γ-FeOOH) in Fig. 5(a) have disappeared in Fig. 5(b), i.e. α-Fe_2O_3 is more stable against phosphatization than the other corrosion products are. An open question is, whether a metallic substrate influences the phosphatization process of the corrosion products. This is of practical interest and subject of further investigations. From Fig. 1(c), the participation of the steel substrate in this process cannot be definitely concluded. Detailed intensity studies are necessary.

Besides the transformation of corrosion products, the treatment of corroded samples with phosphoric acid or some rust transformers may also result in the formation of a protective phosphate layer on the substrate metal. If this layer is very thin as compared with the covering layer, it cannot be detected by the Mössbauer technique without a removal of the covering products.

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