

A MÖSSBAUER STUDY OF THE CRYSTALLINE STRUCTURE OF THE PASSIVE FILM FORMED ON IRON IN AQUEOUS SULFATE SOLUTION CONTAINING SULFITE IN LOW CONCENTRATION*

Cs. VÉRTES,† M. L. VARSÁNYI,† A. VÉRTES,†† W. MEISEL§ and P. GÜTLICH§

†Department of Physical Chemistry and of Nuclear Chemistry, Eötvös University, H-1518 Budapest, Hungary

‡Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg-University, D-6500 Mainz, Germany

(Received 14 December 1992; in revised form 14 April 1993)

Abstract—Electrochemically induced passivation of evaporated, enriched ^{57}Fe in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ aqueous solution (pH 6.5) was followed by conversion electron Mössbauer spectroscopy. The transformation of amorphous iron oxide or hydroxide into crystalline $\gamma\text{-FeOOH}$ could be observed with the increase of the polarization time. The comparison of the original quantity of evaporated, enriched ^{57}Fe layer on the surface of the samples with the dissolved iron, measured in the solutions after the polarization, proved the existence of pitting corrosion at this pH.

Key words: conversion electron Mössbauer spectroscopy, enriched ^{57}Fe , acid rain, pitting corrosion, sulfite ion.

INTRODUCTION

The passivation of low carbon steel, as the result of electrochemical polarization was studied in aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ at $3.5 \leq \text{pH} \leq 8.5$ [1–4]. The sulfite was used to model the effects of acid rain. These measurements showed that the main component of the passive film was $\gamma\text{-FeOOH}$ [1–4]. The aim of this paper is to collect more detailed information about the chemical and crystalline structure of the passive film by using a thin, evaporated, enriched ^{57}Fe layer on the surface of the studied anode.

EXPERIMENTAL

The evaporation of enriched (86%) ^{57}Fe was carried out in a Balzers 350 evaporation equipment at a pressure of $1.3 \times 10^{-3} \text{ Pa}$. The thickness of the enriched ^{57}Fe layer was $15 \pm 3 \text{ nm}$ and its geometric surface was 2.5 cm^2 . Carefully polished disks of low carbon steel were used as supports.

The electrochemical treatments were done in aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ at pH 6.5, while the electrolyte was stirred continuously and Ar gas was bubbled through it to reach an inert atmosphere and a deaerated solution. Potentials mentioned in this paper are referred to the standard hydrogen electrode (*she*) while a saturated $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode was used in the measurements.

The conversion electron Mössbauer spectra were recorded at room temperature using a flow proportional counter filled with 96% He + 4% CH_4 . The spectra were fitted by a least squares procedure using approximate Voigt functions. All isomer shifts mentioned are related to α -iron.

RESULTS AND DISCUSSION

The Mössbauer spectra are shown in Fig. 1 and their parameters are tabulated in Table 1. All spectra consist of a magnetically split sextet from the α -iron substrate and a quadrupole doublet representing the surface layer formed as a result of polarization. The minor components can be attributed to iron nitrides and carbides formed during the evaporation due to residual gases present in the vacuum chamber[5].

The evaporated, enriched ^{57}Fe layer magnifies the Mössbauer lines of the outer passive layer comparing to those of the substrate. The area percentage of the Mössbauer lines belonging to the passive layer after 30 min passivation is 6.9% in the case of natural iron anode and this value is 39.6% in the case of an enriched ^{57}Fe anode. Thus, very accurate Mössbauer parameters of the electrochemically formed surface layer can be determined even after a short polarization time (30 min) if enriched ^{57}Fe is used on the surface.

The half width at the half of the maximum of the central doublet lines is 0.32 mm s^{-1} and the quadrupole splitting is 0.81 mm s^{-1} after a polarization time of 30 min. These relatively high values are evidence that the passive layer consists of amorphous or small particles ($\leq 100 \text{ \AA}$) of iron oxide or hydroxide[6]. As the time of the polarization increases, these values

*Dedicated to Prof. Uli Gonser on the occasion of his 70th birthday.

†Author to whom correspondence should be addressed.

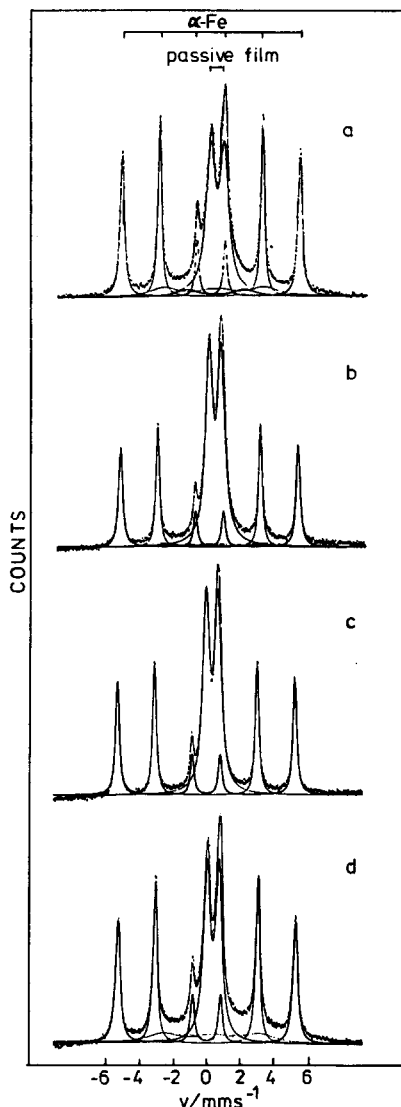


Fig. 1. Mössbauer spectra of the evaporated, enriched ^{57}Fe layer after the polarization at +1100 mV for 30 min (a), 3 h (b), 6 h (c), and 12 h (d).

decrease, demonstrating the process of crystallization. The Mössbauer parameters of the central doublet finally reach those of the crystalline $\gamma\text{-FeOOH}$. (See Table 1.)

During the polarization we followed the quantity of the dissolved iron by spectrophotometric measurements of the solutions, as well. After 12 h of polarization the quantity of iron obtained was equal to a ~ 30 nm thick surface layer and this thickness is more than that of the total evaporated ^{57}Fe on the surface of the substrate. On the other hand the area percentage of the doublet after 12 h of polarization was 35% while this value was only 15.9% in the case of natural iron (see Fig. 2)[3]. These experimental results prove that some enriched ^{57}Fe remained on the surface of the anode even after 12 h of polarization time. If we compare these experimental findings with the above mentioned quantity of the dissolved iron, we have to conclude that also some natural iron (being under the ^{57}Fe layer) should be dissolved

through the holes (pittings) of the passive film. The current density, measured during the polarization, started to increase rapidly after the third hour of passivation and this is an other evidence of the pitting corrosion.

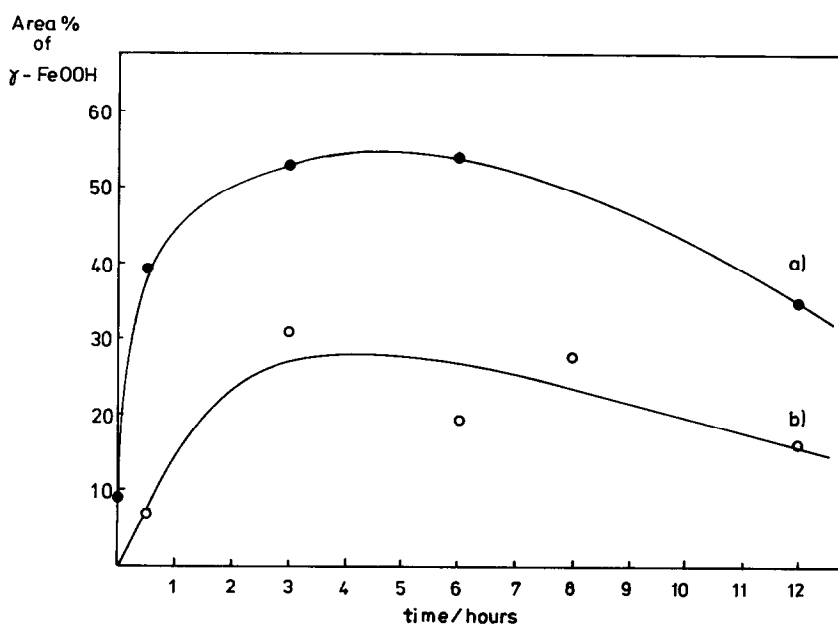
The pitting attack of HSO_3^- ions on low carbon steel samples under the same conditions was already proved by other measurements, as well[2, 3, 4]

CONCLUSIONS

The described measurements gave evidence that an amorphous layer, a precursor of $\gamma\text{-FeOOH}$, forms on the surface of an iron anode in aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ at pH 6.5 during the first short period (30 min) of polarization. This layer transforms into crystalline $\gamma\text{-FeOOH}$ after a longer time of polarization (6 h).

Table 1. Results of the computer evaluation of the Mössbauer spectra recorded *ex situ* after the passivation of the evaporated, enriched ^{57}Fe layer in the aqueous solution of $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ at the pH 6.5

Characterization of sample	Isomer shift, δ^* mm s^{-1}	Quadrupole splitting, $\Delta\ddagger$ mm s^{-1}	Magnetic field, $H\ddagger$ T	Half width, $\text{HW}\S$ mm s^{-1}	Area fraction, $A\parallel$ %
Polarized + 1100 mV for -30 min	0.00	—	33.0	0.14	45.5
				0.12	
				0.12	
—3 hours	0.00	0.11	18.5	1.00	15.0
				0.80	
				0.70	
—6 hours	0.35	0.81	—	0.32	39.5
				0.14	
				0.12	
—3 hours	0.00	—	33.0	0.12	37.7
				0.12	
				1.00	
—6 hours	0.33	0.10	20.8	0.80	9.3
				0.70	
				0.26	
—12 hours	0.36	0.72	—	0.24	53.0
				0.13	
				0.12	
—6 hours	0.00	—	33.0	0.12	46.1
				0.12	
				0.24	
—12 hours	0.36	0.70	—	0.16	44.1
				0.14	
				0.14	
—3 hours	0.36	0.10	17.8	1.20	20.9
				1.00	
				0.90	
—6 hours	0.36	0.72	—	0.23	35.0
				0.16	
				0.14	

* Isomer shifts are relative to α -iron.† Error of δ and Δ is $\pm 0.03 \text{ mm s}^{-1}$.‡ Error of H is: $\pm 1 \text{ T}$.§ Error of HW is: $\pm 0.01 \text{ mm s}^{-1}$.|| Error at $A\%$ is: $\pm 3 \text{ rel}\%$.Fig. 2. Area percentages of the Mössbauer lines of the passive layer for the evaporated, enriched ^{57}Fe layer (a), and for the low-alloy steel (b) in $0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ NaHSO}_3$ aqueous solution at pH 6.5. (The full lines are a guide for the eyes only.)

The comparison of the residual enriched ^{57}Fe on the surface with the dissolved iron measured in the solution leads to the conclusion that pitting corrosion takes place at this pH and contributes significantly to the iron dissolution. This behaviour is similar to the addition of Cl^- ions to the solutions, which initiates pitting corrosion after some incubation time, as found in [7].

REFERENCES

1. M. L. Varsányi, Cs. Vértés, W. Meisel, P. Griesbach, A. Vértés, P. Gütlich and L. Kiss, *J. electrochem. Soc.* **139**, 1301 (1992).
2. Cs. Vértés, M. L. Varsányi, W. Meisel, A. Vértés, E. Kuzmann and P. Gütlich, *Hyperfine Interactions* **69**, 731 (1991).
3. Cs. Vértés, M. L. Varsányi, W. Meisel, A. Vértés, P. Gütlich and L. Kiss, *Electrochim. Acta*, **38**, 253 (1993).
4. Cs. Vértés, M. L. Varsányi, W. Meisel, A. Vértés and P. Gütlich, *Nucl. Instr. and Meth.* **876**, 20 (1993).
5. Zs. Kajcsos, W. Meisel, E. Kuzmann, C. Tosello, M. L. Gratton, A. Vértés, P. Gütlich and D. L. Nagy, *Hyperfine Interactions* **57**, 1883 (1990).
6. M. E. Brett, K. M. Parkin and M. J. Graham, *J. electrochem. Soc.* **133**, 2031 (1986).
7. J. F. Marco, J. R. Gancedo, W. Meisel, P. Griesbach and P. Gütlich, *Corrosion* **47**, 498 (1991).