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A ^{57}Fe Mössbauer study of rust converters

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Abstract

Rust converters are substances used to prepare corroded surfaces in structures, with the purpose to transform the rust oxides or hydroxides to more stable products, thus constraining their participation in further corrosion processes and allowing the application of paint schemes. In this work, results obtained from two different experimental works, which evaluated different converter formulations and type of corroded surface are presented and compared. Some of the experimental conditions were similar in both works, i. e., AISI SAE 1008 carbon steels were used, and the samples were pretreated to obtain a certain degree of oxidation using the same standard method by immersion-drying conditions. However, in the first work, the formulations used different concentration in tanic and phosphoric acids as the independent variable and pure isopropilic alcohol, pure terbutilic alcohol and a mixture of them were used as solvents; whereas in the second work, phosphoric acid content was maintained constant and variations in tannic acid and as solvents mixtures of isopropilic and terbutilic alcohol were used. Converters were applied over the samples, some of these previously grinded (the superficial rust layer thus eliminated) and others without grinding, before painting and exposed to tests in accelerated corrosion chambers. The transformation of the rust was monitored by Mössbauer ^{57}Fe spectroscopy, both at room temperature and at 77 K. It was found that each content in tannic acid has a mixture of alcohols that improved the rust conversion.

--------- *Key words:* rust converters, atmospheric corrosion, Mōssbauer spectroscopy, steel.

Estudio de convertidores de herrumbres mediante espectroscopia Mössbauer ^{57}Fe

Resumen

Los convertidores de herrumbre son sustancias químicas que se utilizan para la preparación de superficies de estructuras que se encuentran corroídas, y buscan la transformación de los óxidos e hidróxidos presentes en la capa de herrumbre en una capa más estable, que tenga carácter pasivante, para evitar

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su participación en los procesos de corrosión posteriores y para permitir la aplicación de un sistema de pintura. En este trabajo, se presentan los resultados obtenidos en la evaluación de algunos convertidores de óxido formulados en dos trabajos diferentes. Algunos aspectos experimentales fueron similares en ambos trabajos, como: en los dos casos se usó un acero de bajo carbono AISI SAE 1008 y las muestras fueron preherrumbradas según un ensayo acelerado de corrosión por inmersión emersión. De otro lado, hubo diferencias en la formulación de los convertidores; en el primer trabajo, se utilizaron diferentes contenidos de ácidos tánico y fosfórico, y como solventes se usaron alcoholes isopropílico y terbutílico puros, así como una mezcla de ambos, mientras que en el segundo trabajo se dejó constante el contenido de ácido fosfórico en 35% y se varió el contenido de ácido tánico, así como la relación de alcoholes usados como solventes. Los convertidores fueron aplicados en muestras cepilladas y no cepilladas, antes de ser pintadas y expuestas a las cámaras de corrosión acelerada. Las transformaciones de la herrumbre fueron seguidas por espectroscopia Mössbauer ^{57}Fe, tanto a temperatura ambiente como a 77 K. Se encontró que para cada cantidad de ácido tánico se tiene una relación de alcoholes que permiten mayor grado de conversión de la herrumbre.

---------- *Palabras clave:* convertidores de herrumbre, corrosión atmosférica, espectroscopia Mössbauer, aceros.

Introduction

Converters, i.e. substances that can convert rust on a corroded surface to a passivated form of oxide, have been studied since some years ago. Converters are formed by an organic and/or inorganic acid and an organic solvent. However, it is not yet possible to find in the market a really satisfactory product, since reported results on the efficient protection are highly controversial [1, 2, 3]. In fact, the difficulty lies in finding the appropriate components, their optimal concentrations, the proper time of the reaction, and the appropriate conditions for their most effective application, i.e., the nature of the rust to be converted (e.g. thickness, age of formation, composition), the most suitable painting system and the best atmospheric conditions for their application. In relation to the composition, it is well known that the most common rust converters are based on tannic and phosphoric acids. However, the results reported with respect to the anticorrosive properties and mechanisms of reaction are questionable. Since 1997 our research group have been performing several experiments to get good formulations of rust converters [4, 5].

The variables studied in both works have been the nature of the rust, appropriate components of converters and the atmospheric conditions for their applications.

In the first work [4], the reaction mechanisms as well as the protection efficiency were studied to 18 formulations of rust converters, with the objective of find a good rust converter, with appropriate anticorrosive properties. The concentrations of both tannic and phosphoric acids, as well as the kind of solvent used were the main variables considered. The effect of washing the converter previously to the application of the paint was also investigated. In this work the non-adherent rust was not removed for application of the converter.

A similar investigation on additional 15 formulations of rust converters was performed in the second work [5]. However, the concentration of tannic acid and solvents were the variables considered. The effect of the scraping off the non-adherent rust before the converter application was also considered.

The aim of the present study is to use the best results of former two works in order to get a deeper comprehension of the reaction mechanisms of converters, using as a main tool the Mössbauer spectroscopy.

Experimental

In the table 1 are presented the main experimental data from the two works reported.

Room temperature (RT) and 77 K Mössbauer spectra were obtained in transmission mode using a constant acceleration drive and triangular reference signal. A ^{57}Co/ Rh source with initial activity of 25 mCi was used. The spectra were adjusted using a program called MOSF [6].

Results and discussion

First work

Mössbauer spectra for the non-converted sample was acceptably adjusted using two sextets and one doublet. The two sextets exhibited parameters, which are typical of magnetite. The deviation of the ideal 1,8 value for the ratios of A and B sites suggest that magnetite is either not stoichiometric, that exhibits poor cristalinity or that a substitution of iron for an alloying element has happened. On other hand, the hyperfine parameters of the doublet recommend either the presence of one iron oxyhydroxide of poor crystallinity or a mixture of some of them. These compounds were found to be goethite of poor crystalinity and lepidocrocite. Additionally, the area values show that magnetite is the most abundant among the iron phases present in the rust.

On the other hand, the spectra of the samples with converter were also adequately fitted with

Table 1 Main experimental aspects involved in the previous related works

	First work [4]	***Second work [5]***
Samples	AISI-SAE 1008 steel	AISI-SAE 1008 steel
Corrosion essay	Samples corroded to degree C in 3,5% NaCl solution (055900 SIS standard).	Samples corroded to degree C in 3,5% NaCl solution (055900 SIS standard).
Scrapping off	No	Non-adherent rust eliminated with a manual brush of steel bristle.
Composition of the rust on the steel surface	Magnetite: 70%; Lepidocrocite and Goethite: 30%	Magnetite: 31%; Magnetic goethite: 35%; Superparagmanetic goethite, Akaganeite, and Lepidocrocite: 34%
Used formulae	3, 5 and 10% tannic acid. 30 and 35% phosphoric acid. 50% of terbutyl and 50% of isopropyl alcohol.	3, 5 and 10% tannic acid. 35% phosphoric acid. Five mixtures isopropyl and terbutyl alcohol.
Converter application	Brush	Gun

two sextets and two doublets (figure 1). The two sextets were again attributed to magnetite, which also exhibits a deviation of the ideal 1,8 in the A_B/A_A area ratio. It has been determined amount of ^{57}Fe in magnetite transformed by the action of the converter in relation to the amount of ^{57}Fe in magnetite present in the rust sample. If it is assumed that the Mössbauer factors are similar to all the iron phases present, then it is found that only between 7 and 24% of the ^{57}Fe in magnetite has been transformed by the action of the rust converters. These results indicates that an important fraction of the magnetite remains without conversion, supporting the idea that the converters can not fully penetrate the rust layer.

The first doublet in the spectra of the sample with converter is attributed to overlapping contributions coming from goethite of poor crytallinity, ferric tannate and ferric phosphate. The second doublet suggests the presence of ferrous phosphate.

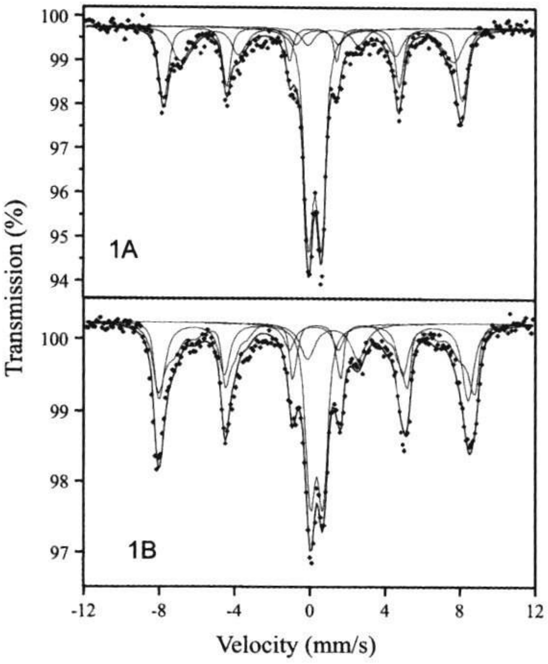

Figure 1 Mössbauer spectra for converted rust at (a) RT and (b) 77 K

Second work

The spectrum of the non-converted sample was acceptably adjusted using three sextets and one doublet (figure 2a). In this spectrum, the two sextets exhibited parameters which are typical of magnetite (table 2). The strong deviation of the ideal 1,8 value for the ratios of A and B sites,

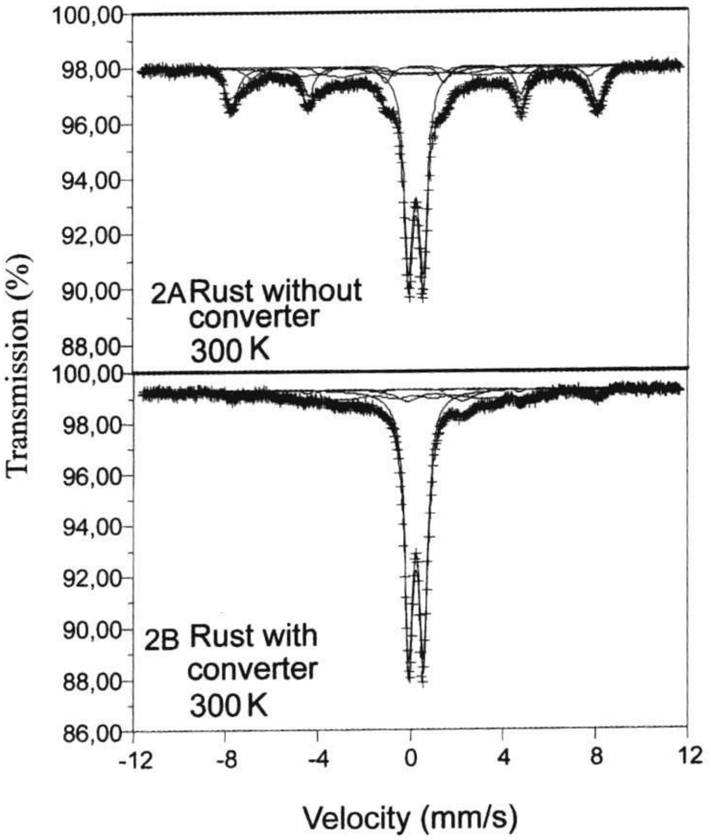

Figure 2 RT Mössbauer spectra of: (a) rust without converter, and (b) rust with converter

Table 2 Mössbauer parameters for the sextet components obtained at RT and 77 K for some selected samples

Sample	***Sextets***									
	$B_A(T)^a$ ± 0.1T	$\delta_A(mm/s)^b$ ± 0.01	$A_A(\%)^c$ ± 0.4	$B_B(T)^a$ ± 0.1T	$\delta_B(mm/s)^b$ ± 0.01	$A_B(\%)^c$ ± 0.4	$B_G(T)^a$ ± 0.1T	$\delta_G(mm/s)^b$ ± 0.01	$A_G(\%)^c$ ± 0.4	CF^d (%)
HSC	48,70	0,27	19,00	46,00	0,70	12,00	30,9	0,23	35,00	
HC15	49,20	0,30	3,00	45,90	0,70	1,00	313,00	0,23	25,0	90,00
HC15 (77 K)	517,00	0,33	1,30	475,00	0,34	57,91				

HSC: Non-converted rust.

HC15: Rust with converter.

a hyperfine field corresponding to sites A And B at magnetite, respectively.

b Isomeric shift respect to α-Fe.

c AA, A_B and $A_{G:}$ area occupied by sextets

d Fraction of ^{57}Fe in the magnetite converted under the action of acids, relative to the content of ^{57}Fe in the magnetite from the rusted sample.

which is more pronounced than in the previous work, suggests the presence of either strongly oxidized magnetite or a possible combination of the magnetite-maghemite. The later phase will be called the spinel phase.

The third sextet in this spectrum, which is not observed in the former work, suggests the presence of goethite with a certain degree of magnetic order. On the other hand, the doublet in the spectrum can be attributed to lepidocrocite, akaganeite and superparamagnetic goethite.

The spectrum obtained from the rust treated with the converters was well fitted with a model including three sextets and two doublets (figure 2b). Two of these sextets are ascribed to magnetite, and the third one was again attributed to goethite with a certain degree of magnetic order. The first doublet originates from the overlapping contributions coming from goethite, lepidocrocite, akaganeite and iron phosphates and tannates, while the second doublet was ascribed to ferrous phosphate.

The results show that 90% of the spinel phase was transformed due to the converter action, while only 29% of the magnetic goethite was affected. This means that an important fraction of the spinel phase was transformed. This result differs with the previous findings in which an important fraction of magnetite was not converted. Explanations to these results could be the followings: (a) maghemite and/or highly oxidized magnetite are easier to transform by the action of the converter than less oxidized or stoichiometric magnetite, (b) the formulations used in the second work have better capabilities for transforming the rust than formulations in the first work, (c) in the previous work, the magnetite layer is located in the inner layer, close to the steel surface, whereas in the second study the spinel phase is already in the outer layer, and (d) the application method could also affect the degree of penetration of the converter, and hence the degree of conversion of the iron phases (table 1). Of course more work is required to clearly resolve this issue.

Conclusions

We have reviewed two different works on the reaction mechanisms of some converters upon the rust using as a main tool Mössbauer spectroscopy. Our results suggest that the rust conversion factors can be affected by the following aspects: type and concentration of tannic and phosphoric acids, the type and concentration of alcohol, type and relative abundance of the iron phases, magnetite degree of stoichiometry (and/or mixture of magnetite/

Table 3 Mössbauer parameters for the doublets obtained at RT and 77 K for some selected

Sample	***Doublet***					
	Δ (mm/s)^a	***δ (mm/s)^b ± 0,01***	***A (%)^c ± 0,4***	***D(mm/s)^a***	***d (mm/s)^b ± 0,01***	***A(%)^c ± 0,4***
HSC	0,64	0,37	33,40			
HC15	0,61	0,36	64,30	2,37	1,18	7,60
HC15 (77 K)	0,56	0,33	32,69	3,00	1,10	8,16

HSC: Non-converted rust.

HC15: Rust with converter.

a Quadropole splitting.

b Isomeric shift respect to a-Fe at room temperature corresponding to sites A y B.

c A area occupied by the doublets.

maghemite), and the application method of the converter (brush or spray). The formulations used seems not to convert noticeably the magnetic goethite and akaganeite phases. It is demonstrated that Mössbauer spectroscopy is an important analytical tool in the study of the quantitative determination of the mechanism of reactions of the rust converters.

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