Corrosion related iron oxides: Cu, Mn and Cr doped hematite

G. Pérez*, C. Barrero*,**, A. Morales*,**, J. Tobon*, O. Arnache*, C. Rodríguez* and C. Arroyave**

Abstract We have obtained Cu, Mn, and Cr doped hematites, by a thermal treatment of doped goethites at 500 and 880 °C in air for 24 h. The goethites were prepared in the laboratory from iron chloride solutions in the presence of Cu^{2+}, Mn^{2+}, and Cr^{3+} ions. The samples are characterized by Mössbauer spectroscopy and X-ray diffraction. It is found that at 500 °C all the goethites have transformed into hematites. However, the thermal treatment at 880 °C produces hematites with better crystallinity.

Keywords Mössbauer spectroscopy. Thermal treatment. Goethite. Hematite. X-ray diffraction. Hyperfine parameters.

Óxidos de hierro relacionados con la corrosión: hematitas dopadas con Cu, Mn y Cr

Resumen Hemos obtenido hematitas dopadas con Cu, Mn y Cr, por un tratamiento térmico de goethitas dopadas a 500 y 880 °C en aire durante 24 h. Las goethitas fueron preparadas en el laboratorio a partir de soluciones de cloruro de hierro en presencia de iones de Cu^{2+}, Mn^{2+} y Cr^{3+}. Las muestras fueron caracterizadas por espectroscopía Mössbauer y difracción de rayos X. Se encontró que a 500 °C todas las goethitas se han transformado a hematitas. Sin embargo, el tratamiento térmico a 880 °C produce hematitas con mejor cristalinidad.

Palabras clave Espectroscopia Mössbauer. Tratamiento térmico. Goethita. Hematita. Difracción de rayos X.

1. INTRODUCTION

It is well documented in the literature that weathering steels produce a protective rust layer due to the presence of the alloying elements Cu, Mn, and Cr. The mechanisms for the corrosion resistance are not well known and studies that shed light into this problem are useful. One way to characterize rust products is Mössbauer spectroscopy where hyperfine parameters are needed to obtain good fits. Hyperfine parameters are modified by alloying elements present in the iron oxides. The knowledge of changes in hyperfine parameters is important to analyze corrosion products from weathering steels.

The transformation by heating under dry conditions, from goethite into hematite has been studied by several authors[1-4]. These studies reveal that the transition temperature usually depends on the crystallinity and the metal su bstitution of the starting material.

It is the purpose of the present investigation to prepare and characterize hematites that have been obtained from the thermal treatment of goethites at two different temperatures. The goethites (α-FeOOH) were synthetized from iron chloride solutions in the presence of Cu^{2+}, Mn^{2+}, and Cr^{3+} ions. This investigation also includes the influence of Cu, Mn, and Cr on the hyperfine parameters of the hematites.

2. EXPERIMENTAL

The goethites were synthetized according to the procedure described in references[1 and 5]. Table I summarizes the synthesis procedure to each sample.

The hematites were obtained by heating the goethites at 500 and 880 °C for 24 h in air. The

(*) Grupo de Estado Sólido, Dpto. de Física. Universidad de Antioquia, A.A. 1226, Medellín-Colombia.
(**) Grupo de Corrosión y Protección, Dpto. de Ingeniería de Materiales. Universidad de Antioquia, A.A. 1226, Medellín-Colombia.

Table I. Solutions used for the goethite synthesis

Tabla I. Soluciones usadas para la síntesis de las goethitas

Sample	Synthesis
GcF100	FeCl2 + NaHCO3
GcFcMn1	$FeCl_2$ + 1 %$MnCl_2$ + $NaHCO_3$
GcFcMn5	$FeCl_2$ + 5 %$MnCl_2$ + $NaHCO_3$
GcFcCu1	$FeCl_2$ + 1 %$CuCl_2$ + $NaHCO_3$
GcFcCu5	$FeCl_2$ + 5 %$CuCl_2$ + $NaHCO_3$
GcFcCr1	$FeCl_2$ + 1 %$CrCl_2$ + $NaHCO_3$
GcFcCr5	$FeCl_2$ + 5 %$CrCl_2$ + $NaHCO_3$

samples were analyzed by X-ray diffraction and Mössbauer spectroscopy.

X-ray diffraction measurements were performed with a RIGAKU Miniflex 2005 diffractometer equipped with a Cu (Kα) cathode and filter. The scans were done in the range of 5 ° to 60 ° (2θ) at a speed of 2° per minute.

The Mössbauer Spectra were obtained by means of a conventional transmission spectrometer, with constant acceleration, with a ^{57}Co/Rh source of 25 mCi of initial activity. For the analysis the Mössbauer spectra two computer programs were used: MOSF for the hematite samples and DISTS3E[6] for the goethites.

3. RESULTS AND DISCUSSION

Figure 1 shows the room temperature Mössbauer Spectra of the pure goethite and the products of its thermal treatment at 500 and 880 °C. The last spectrum in the figure is that of a commercial hematite, which has been used as a reference sample. It is seen fitting the spectra with a sextet of Lorenzians lines reproduce the experimental data quite reasonably. The derived hyperfine parameters are listed in table II. It is possible to deduce that already at 500 °C the goethite transforms completely into hematite, but the heating process at 880 °C produces hematite with better crystallinity. This latter statement is based on the fact that the line broadening is lower and the hyperfine field is higher in the spectra on the samples heated at 880 °C as compared to the ones treated at 500 °C. It is also worth mentioning that the spectrum of the sample heated at 880 °C is quite similar to that of the commercial hematite.

Figure 2 shows the Mössbauer Spectra of the Mn and Cr goethite before and after the thermal treatment at 880 °C. The spectra of the products with 1 % of each dopant, were reasonably adjusted

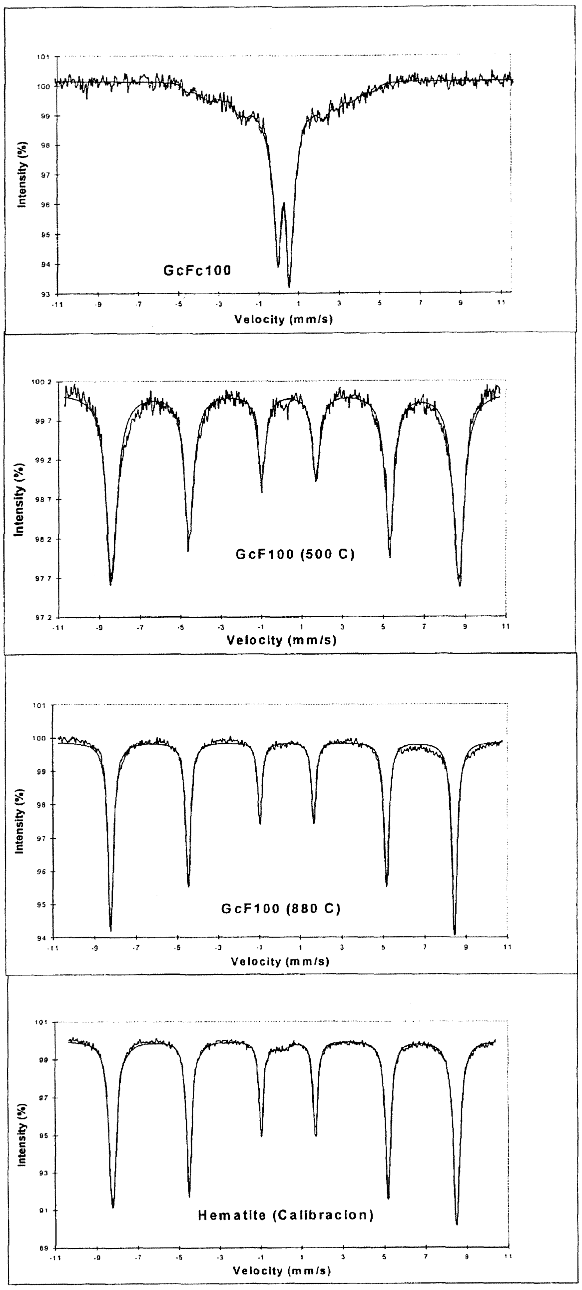

Figure 1. Mössbauer spectra of goethite GcF100 and its thermal treatment products.

Figura 1. Espectros de Mössbauer de la goethita GcF100 y sus productos de tratamiento térmico.

with only one sextet. The derived parameters are summarized in table II. It is again observed that the spectra of all the products as well as their derived hyperfine parameters are quite similar to those of the commercial hematite. This means that at 880 °C all the doped goethites have transformed into hematites with good crystallinity. It is important to mention that all the derived hyperfine parameters for the hematites at 1 % of dopant are within the experimental errors the same. The Mössbauer

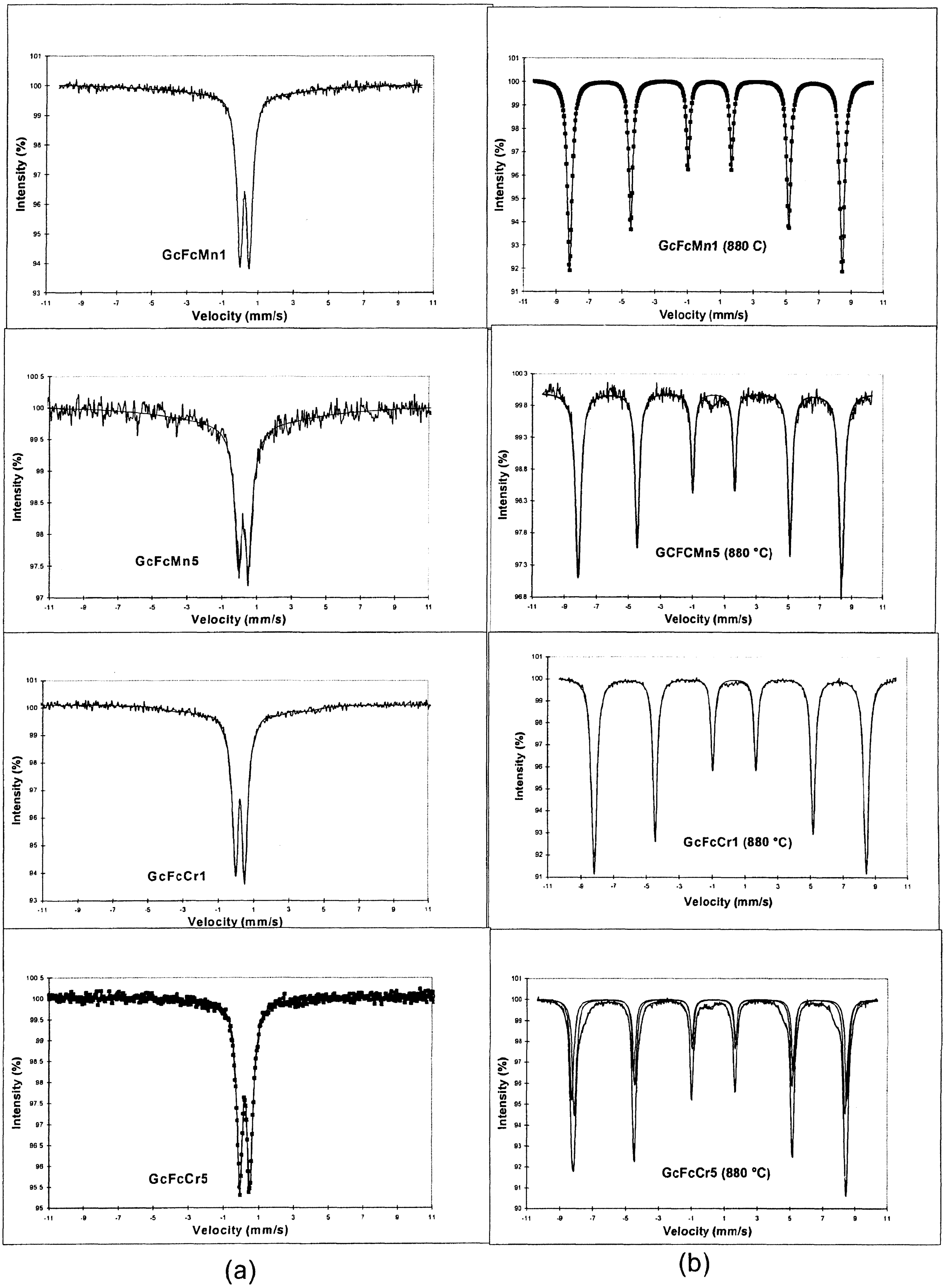

Figure 2. Mössbauer spectra of goethites with Mn and Cr a) Unheated, b) Heated at the 880 °C.

Figura 2. Espectros Mössbauer de Goethitas dopadas con Mn and Cr. A) Sin calentar, b) Calentadas a 880°C.

Table II. Mössbauer parameters of samples heated at 500 and 880 °C

Tabla II. Parámetros Mössbauer de las muestras calentadas a 500 y 880 °C

Sample	T (°C)	W (mm/s)	H (koe)	Q (mm/s)	IS (mm/s)	A (%)
Hematita comercial	–	0.26	516	-0.20	0.36	100
GcF100	500	0.60	507	-0.20	0.36	100
	880	0.25	516	-0.24	0.34	100
GcFcCu1	880	0.26	519	-0.20	0.37	100
GcFcCu5	880	0.25	514	-0.21	0.36	100
GcFcM1	880	0.24	516	-0.21	0.36	100
GcFcM5	880	0.26	515	-0.21	0.33	100
GcFcCr1	880	0.27	515	-0.21	0.36	100
GcFcCr5	880	0.22	519	-0.22	0.31	36
		0.22	512	-0.20	0.35	46
		0.34	477	-0.07	0.28	15

H: Hyperfine field; IS: Isomer shift referred to α-Fe; Q: Quadrupole splitting and Area (%): percentage relative of the areas of the subspectros.

Spectra of the samples with 5 % Cu and 5 % Mn were acceptably adjusted with one sextet and one doublet; this doublet was reasonably adjusted with a quadrupole splitting of 0.55 mm/s, isomer shift of 0.035 mm/s, and a peak widht of 0.5 mm/s. These parameters were allways kept fxed. However, the origin of this doublet could not be established. In contrast the spectra of sample synthetized in the presence of Cr ions with 5 % and heated at 880 °C seems to become more complex.

A good fit was obtained with 3 sextets. However more measurements are needed, in order to fully identify each one of these components.

Figure 3 shows the X-ray difractogram of the hematite obtained from the sample GcF100 after heating at 880 °C. This difractogram confirms the presence of hematite in good agreement with the Mössbauer results.

4. CONCLUSIONS

The procedure to obtain pure and substituted hematite with Cu, Mn and Cr by means of thermal treatment of goethites at temperatures of 500 and 880 °C for 24 h. is reproducible. The Mössbauer parameters have confirmed that in the transformation of goethite into hematite at 880±12 °C for 24 h, the final product is a well crystallized hematite having a line width and hyperfine parameters similar to that of the commercial hematite. The presence of Cr ions perhaps induces a distribution of particles in the hematite, due possibly to the structural substitution of octahedral Fe^{III} for Cr^{3+} in the structure. The X-ray diffraction confirms that all samples thermally treated a 880 °C become hematite.

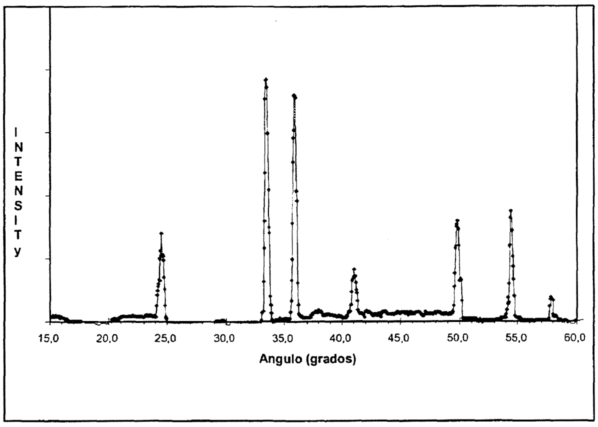

Figure 3. X ray diffractogram of GcF100 heated for 24 h at 880 °C.

Figura 3. Difractrograma de rayos X de la muestra GcF100 calentada durante 24 h a 880 °C.

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