Synthesis and Mössbauer characterization of Cu and Cr doped magnetites

C.A. Barrero*,**, A.L. Morales*,**, J. Mazo-Zuluaga*, F. Jaramillo**, G. Pérez*,
D.M. Escobar**, C. Arroyave**, J. Tobón*, P.M. Montoya**, L. Osorio**,
R.E. Vandenberghe*** and J.M. Greneche****

Abstract

A detailed Mössbauer investigation of magnetites prepared under different hydrothermal conditions and doped with Cu and Cr is presented. The samples were characterized by means of room temperature Mössbauer spectrometry, infrared spectroscopy, and X-ray diffraction. Mössbauer results show that the hydrothermal method produces highy stoichiometric and relativelly well-crystallized magnetites. The results suggest that the best samples are obtained when the alkaline solution is added quickly to the ferrous solution. It was also found that mixing the solutions under constant ultrasonic stirring produce magnetites with slightly better crystallinity and stoichiometry than the samples produced under magnetic or nitrogen bubbling stirring. The effect of the Cu and Cr on the hyperfine parameters is also presented and discussed.

Keywords

Cu- and Cr- magnetites. Hydrothermal synthesis. Mössbauer spectrometry. Infrared spectroscopy. Corrosion product.

Síntesis y caracterización Mössbauer de magnetitas dopadas con Cu y Cr

Resumen

Se presenta una investigación Mössbauer detallada de magnetitas preparadas bajo diferentes condiciones hidrotermales y dopadas con Cu y Cr. Las muestras fueron caracterizadas utilizando la espectrometría Mössbauer a temperatura ambiente, espectroscopía infrarroja y difracción de rayos X. Los resultados Mössbauer muestran que el método hidrotermal produce magnetitas altamente estequiométricas y relativamente bien cristalizadas. Los resultados sugieren que las mejores muestras se obtienen cuando la solución alcalina se añade rápidamente a la solución ferrosa. Se encontró que la mezcla de las soluciones bajo agitación ultrasónica constante produce magnetitas con cristalinidad y estequiometría levemente mejores que las muestras producidas bajo agitación magnética o por burbujeo de nitrógeno. También se presentan y se discuten los efectos del Cu y del Cr en los parámetros hiperfinos.

Palabras clave

Magnetitas de Cu y Cr. Síntesis hidrotermal. Espectrometría Mössbauer. Espectroscopía infrarroja. Producto de corrosión.

1. INTRODUCTION

Magnetite, Fe_3O_4, is one of the most important products of the corrosion of iron and steel[1-3]. It is usually found in the nonstoichiometric form. Besides, due to the presence of some alloying elements in the steel, such as Cu and Cr, it is also expected to find doped magnetites in the corrosion products[1-3]. In order to understand the origin of these oxides in the corrosion of steel, it is of primary importance to fully characterize their structural properties. Because the corrosion products usually consist of complex combinations of several iron oxides and oxihydroxides, it is easier to characterize the magnetites prepared in the laboratory. In that respect the hydrolysis method is interesting, because in that way it is possible to simulate the corrosion process under atmospheric conditions. The results obtained from such investigations should lead to an analytical framework for the characterization of magnetites originating from corrosion products.

(*)   Grupo de Estado Sólido. Departamento de Física.
(**)   Grupo de Corrosión y Protección. Departamento de Ingeniería Metalúrgica y de Materiales. Universidad de Antioquía. A.A. 1226. Medellín (Colombia).
(***)   NUMAT. Department of Subatomic and Radiation Physics. University of Gent. B-9000. Gent (Belgium).
(****) Laboratoire de Physique de l'Etat Condensé. UMR CNRS 6087. Université du Maine. 72085 Le Mans. Cedex 9 (France).

62

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

C.A. Barrero, A.L. Morales, J. Mazo-Zuluaga, F. Jaramillo, G. Pérez, D.M. Escobar, C. Arroyave, J. Tobón, P.M. Montoya, L. Osorio, R.E. Vandenberghe and J.M. Greneche

Magnetite has the inverse spinel structure. The unit cell contains 8 Fe^{3+} ions on the tetrahedral sites (or A sites) and 16 Fe ions on the octahedral sites (or B sites), 8 of which are Fe^{2+} and the other 8 are Fe^{3+}. The chemical formula of non-stoichiometric magnetite can be written as $Fe_{3-x}O_4$, where the oxidation parameter x can, in principle, vary continously from zero (stoichiometric magnetite) to 1/3 (maghemite). However, this formula can better be represented as $(Fe^{3+})_A[Fe^{2+}_{(1-3x)}Fe^{3+}_{(1+2x)}\square_x]_B O^{2-}_4$, where $\square$ stands for a vacancy. This latter formula assumes both that there are no vacancies on the A sites, and that the rapid hopping of electrons between the Fe^{2+} and Fe^{3+} ions occurs only on the B sites, leading to the well known "$Fe^{2.5+}$" ionic state and leaving some Fe^{3+} ions on the B sites[4-7]. The chemical formula can also be rewritten as $(Fe^{3+})_A[Fe^{2.5+}_{(2-6x)}Fe^{3+}_{5x}\square_x]_B O^{2-}_4$. Room temperature Mössbauer spectrometry can be used to determine the oxidation parameter x. In order to calculate it, the Mössbauer spectra are usually fitted with two sextet components. The first sextet, which will be called Fe^{3+} component, is due to the contributions coming from both $(Fe^{3+})_A$ and $[Fe^{3+}_{5x}]_B$, which have very similar hyperfine fields[4-6]. The second sextet comes from the $[Fe^{2.5+}_{(2-6x)}]_B$ ions, and therefore will be called the $Fe^{2.5+}$ component. The ratio R of the subspectral area of the Fe^{3+} component, $A(Fe^{3+})$, to the subspectral area of the $Fe^{2.5+}$ component, $A(Fe^{2.5+})$, can be written as:

$$R = \{ A(Fe^{3+}) \} / \{ A(Fe^{2.5+}) \} = \{ n(Fe^{3+}) \cdot f(Fe^{3+}) \} / \{ n(Fe^{2.5+}) \cdot f(Fe^{2.5+}) \}$$
$$= \{ [n(Fe^{3+}_A) \cdot f(Fe^{3+}_A)] + [n(Fe^{3+}_B) \cdot f(Fe^{3+}_B)] \} / \{ n(Fe^{2.5+}_B) \cdot f(Fe^{2.5+}_B) \} \quad (1)$$
$$= \{ \{ n(Fe^{3+}_A) \cdot [f(Fe^{3+}_A) / f(Fe^{2.5+}_B)] \} + \{ n(Fe^{3+}_B) \cdot [f(Fe^{3+}_B) / f(Fe^{2.5+}_B)] \} \} / \{ n(Fe^{2.5+}_B) \}$$
$$= \{ 1.06 + 5.3 \, x \} / \{ 2 - 6 \, x \}$$

In this equation we have considered the well known relation $A(Fe^i_j) \cdot f(Fe^i_j)$, in which (Fe^i_j) is the number of iron atoms of a given i valence state, belonging to a given j site, and $f(Fe^i_j)$ is the corresponding Mössbauer fraction. Additionally, we have considered the reported values of $[f(Fe^{3+}_A) / f(Fe^{2.5+}_B)] = [f(Fe^{3+}_B) / f(Fe^{2.5+}_B)] \approx 1.06$ for sotichiometric magnetite[5]. By solving x from equation (1) we get the following relation, which can be used to determine the oxidation parameter:

$$x = \{2 R - 1.06 \} / \{ 5.3 + 6 R \} \quad (2)$$

On the other hand when Cu or Cr replaces Fe in the structure, $Fe_{3-y}Cu_yO_4$ and $Fe_{3-y}Cr_yO_4$ can represent the chemical formula for the doped magnetite.

It is the purpose of the present investigation to determine the degree of stoichiometry and the crystallinity of the magnetites prepared using the hydrolysis method. Moreover, it is considered the effect of introducing some variables to this synthesis procedure in the final product. The principal technique used for this characterization is Mössbauer spectrometry, which is able to distinguish Fe atoms with different strcutural and magnetic environment and with different valence state. In this respect, the degree of stoichiometry is determined from the oxidation parameter x, and the degree of crystallinity is calculated from the values of both the magnetic hyperfine field and the peak broadening. The Mössbauer results are complemented by means of X ray diffraction and infrared spectroscopy techniques. This study also includes the effects of adding dopants to the crystalline structure on the hyperfine parameters derived from the Mössbauer spectra.

2. EXPERIMENTAL PROCEDURE

Eleven magnetites were considered in the present work. Ten of them were prepared following the hydrothermal method described by Schwertmann and Cornell[8]. The other sample was obtained in the market (AGFA). In order to find adequate conditions of synthesis, some relevant variables have been considered in the preparation of the pure magnetites, and these are listed in table I. Besides, 1, 5 and 10 % of mole Fe, in the nominal composition, was substituted by Cu and Cr.

Room temperature (RT) Mössbauer spectra were obtained in the transmission mode using a constant acceleration drive. A $^{57}Co/Rh$ source with initial activity of 25 mCi was used. Velocity was regularly calibrated by taking spectra of standard hematite. All absorbers were prepared by mixing the material with very pure sugar in order to achieve an homogeneous thickness of about 10 mg Fe/cm². The spectra were adjusted using programs MOSF and DIST3E[9 and 10]. The MOSF program is based on a nonlinear least-squares fitting procedure assuming lorentzian line shapes, whereas the DIST3E program is based on a model-independent distribution of hyperfine fields and/or quadrupole splittings. The XRD measurements were performed on a D501 Siemens diffractometer equipped with a

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

63

Table I. Variables considered in the sample preparation of the magnetites

Tabla I. Variables consideradas en la preparación de las magnetitas

Sample name	Synthesis conditions
MCF100	The alkaline solution is added dropwise but quickly to the ferrous chloride solution (for about 5 min) under constant magnetic stirring.
MCF100TC	The alkaline solution is added dropwise and slowly to the ferrous chloride solution (for about 15 min) under constant magnetic stirring.
MCF100AU	Both solutions are mixed slowly (for about 15 min) under constant ultrasonic stirring.
MCF100SAM	Agitation is produced by bubbling nitrogen and the solutions are mixed slowly for about 15 min.
MCFCrX	X mole percentage of the total ferrous chloride solution is replaced by chromium chloride solution.
MCFCuX	X mole percentage of the total ferrous chloride solution is replaced by copper chloride solution.

Cu (K_α) radiation, Ni filter and a proportional detector. The scans were done in the range 15 ° - 70 ° (2θ) using a step size of 0.08 ° (2θ) and a mean time of 2 s per step. FTIR spectra were collected on a Perkin-Elmer spectrometer operating in the transmission mode between 4000 and 50 cm^{-1}. KBr pellets in a relation 100/2 were employed.

In order to obtain the relevant Mössbauer parameters, two fitting models were applied. In the first model, which employs the MOSF program, two symmetric lorentzian shaped sextets were used to fit the spectra of the pure and the lowest substituted (1 % Cu, 1% Cr) magnetites. For each sextet B_{hf}, δ, the intensity of the second line (3:x:1), two width parameters and the area fraction were adjusted. The quadrupole shift of both sites were fixed to zero. The two width parameters are $\Gamma \neq$ and $\Delta\Gamma$, which can be used to calculate the width of six lines of a given sextet by $\Gamma_1 = \Gamma_6 = \Gamma + 2\Delta\Gamma$, $\Gamma_2 = \Gamma_5 = \Gamma + \Delta\Gamma$, and $\Gamma_3 = \Gamma_4 = \Gamma\ae$. In the second model, which uses the DIST3E program, the spectra of the highest substituted magnetites were fitted by using the model-independent hyperfine field distributions, assuming linear correlations in the B site between B_{hf} on the one hand and d on the other hand. Again, the quadrupole shift of both sites were fixed to zero.

3. RESULTS AND DISCUSSION

Figure 1 shows the Mössbauer spectra of some selected samples. It is possible to see that the fitting model reproduces the experimental data quite reasonably as commonly found by other reports[3-7]. Thus the samples seem to consist of pure magnetites. However, in order to improve the fitting procedure, it was necessary to introduce another component to all the spectra. This component, which accounts from 1 % to 2 % of the total absorption area, has also been observed in other similar synthetic magnetites[3, 4 and 8]. Owing to the small absorption, the errors related to the derived Mössbauer parameters are very high. However, for the purpose of the present investigation, this component can be treated as an impurity, without affecting the conclusions. The origin of this impurity, which was reasonably adjusted with a doublet with quadrupole splitting of 0.55 mm/s, isomer shift of 0.035 mm/s, and a peak width of 0.5 mm/s, could not be clearly established. The hyperfine parameters for this impurity phase were always kept fixed. The Mössbauer parameters of the AGFA sample, which is a well crystallized magnetite[4], have been used as a reference to the values determined for the other samples.

From table II, it is possible to deduce that the hydrothermal method produces relatively well-crystallized samples. Besides, it seems that the samples prepared when the alkaline solution is added quickly to the ferrous solution, exhibit slightly better crystallinity than the samples obtained by slowly mixing both solutions. This observation is based on the fact that both the peak width and the incremental broadening of sample MCF100TC have slightly larger values than the ones determined for sample MCF100. Additionally, the latter sample is more stoichiometric than former one. These results are, as expected, in full line with the work by Schwertmann and Cornell[8]. Another important observation is that mixing the solutions under constant ultrasonic stirring produce magnetites with slightly better crystallinity and stoichiometry than the ones produced under magnetic or nitrogen bubling stirring. However, to our experience, the ultrasonic agitation remains more difficult to handle than the magnetic one.

The preparation of the samples in the presence of chromium or copper chloride solutions results in magnetites with poorer crystallinity. This effect is more pronounced as the amount of chromium or
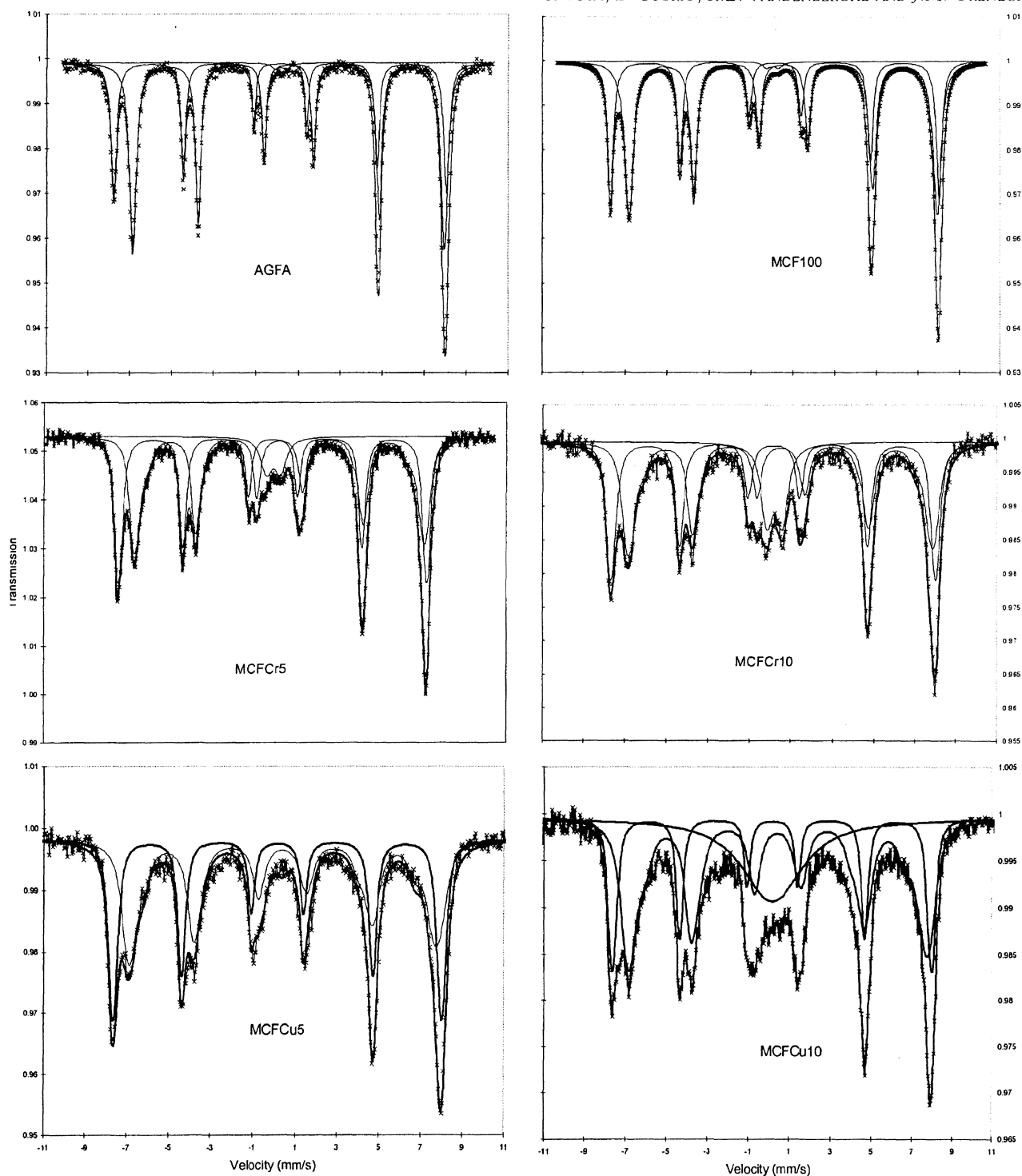
64

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

Figure 1. Mössbauer spectra of some selected samples. The stars represent the experimental data and the solid lines the subspectral component.

Figura 1. Espectros Mössbauer de algunas muestras seleccionadas. Las estrellas representan los puntos experimentales y las líneas sólidas las componentes espectrales.

copper solutions is increasing (see Table III). These are perhaps indications that copper and chromium have entered into the crystalline structure, but it is difficult to establish unambiguously at which site.

The increments of Cr or Cu in the solutions also increase the presence of an impurity phase in the case of Cr, the hyperfine parameters for this phase (quadrupole splitting of about 0.5 mm/s and an isomer shift of about 0.33 mm/s) resemble those of a poorly crystalline, probably doped, goethite and/or lepidocrocite. In fact, XRD measurements and infrared spectra points to the presence of goethite in

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

65

Table II. Mössbauer parameters derived from the spectra using the symmetric lorentzian shaped sextets model

Estimated errors are 0.1 T for B_{hf}, 0.01 mm/s for δ, 0.003 for x, and 0.01 mm/s for both Γ and ΔΓ

Tabla II. Parámetros Mössbauer derivados de los ajustes de los espectros utilizando el modelo de sextetos con formas de líneas lorentzianas

Sample	$B_{hf,A}$ (T)	$δ_A$ (mm/s)	$Γ_A$ (mm/s)	$ΔΓ_A$ (mm/s)	$B_{hf,B}$ (T)	$δ_B$ (mm/s)	$Γ_B$ (mm/s)	$ΔΓ_B$ (mm/s)	X	A (%)
	±0.1	±0.01	±0.01	±0.01	±0.1	±0.01	±0.01	±0.01	±0.003	±0.1
AGFA	49.0	0.26	0.23	0.04	45.9	0.66	0.25	0.07	0.009	1
MCF100	48.8	0.27	0.28	0.02	45.7	0.65	0.32	0.08	0.016	1
MCF100TC	48.8	0.27	0.35	0.05	45.9	0.65	0.39	0.13	0.050	2
MCF100AU	48.8	0.26	0.30	0.03	45.7	0.66	0.32	0.08	0.028	2
MCF100SAM	48.9	0.28	0.32	0.07	45.7	0.65	0.33	0.12	0.075	1
MCFCu1	48.7	0.28	0.39	0.02	45.6	0.63	0.43	0.12	0.78*	3
MCFCr1	48.7	0.27	0.32	0.03	45.7	0.64	0.40	0.14	0.66*	2

$B_{hf,A}$: Hyperfine field for the A site; $δ_A$: Isomer shift for the A site relative to the isomer shift of α-iron at room temperature; $Γ_A$: width of the third peak, $ΔΓ_A$: incremental broadening of the peaks; $B_{hf,B}$: Hyperfine field for the B site; $δ_B$: Isomer shift for the B site relative to the isomer shift of α-iron at room temperature; $Γ_B$: width of the third peak; $ΔΓ_B$: incremental broadening of the peaks; x: oxidation parameter. * These are not x values but the R parameters. A: subspectral area belonging to the impurity doublet.

Table III. Mössbauer parameters derived from the spectra using the model-independent hyperfine field distribution model

Tabla III. Parámetros Mössbauer derivados de los ajustes de los espectos utilizando el método de la distribución de campos hiperfinos independiente de un modelo teórico

Sample	$B_{hf,A}$ (T)	$δ_A$ (mm/s)	$σ_A$ (kOe)	$B_{hf,B}$ (T)	$δ_B$ (mm/s)	$σ_B$ (kOe)	R	A (%)
	±0.1	±0.01	±0.1	±0.1	±0.01	±0.1	±0.05	±1
MCFCu5	48.7	0.18	6	45.5	0.46	23	0.8	3
MCFCu10	48.6	0.18	7	45.5	0.47	25	0.47	25
MCFCr5	48.8	0.17	6	45.8	0.53	20	0.9	7
MCFCr10	48.8	0.18	7	45.6	0.52	19	0.83	14

$B_{hf,A}$: Hyperfine field of maximum probability for the A site; $δ_A$: Average isomer shift relative to the isomer shift of α-iron at room temperature; $σ_A$: standard deviation of the hyperfine field distribution; $B_{hf,B}$: Hyperfine field for the B site; $δ_B$: Isomer shift corresponding to the maximum hyperfine field for the B site relative to the isomer shift of α-iron at room temperature; $σ_B$: standard deviation of the hyperfine field distribution; R: area ratio; A: subspectral area belonging to the impurity doublet.

the case of Cu, the existence of other phases, such as superparamagnetic and/or highly Cu doped magnetites can be proposed. Jaen *et al.*[11] have found $CuFeO_2$ in the final products of the hydrolysis of iron in the presence of Cu. However, it was not possible to detect the presence of this phase by XRD.

The sample prepared under the presence of 5 wt. % Cr solution contains more impurities than the sample prepared with 5 wt. % of Cu solution. This observation is based on the larger area values determined for sample MCFCr5 as compared to that value for sample MCFCu5 (see Table III). In contrast, the MCFCu10 has larger impurity area values than MCFCr10. On the other hand, the

magnetic hyperfine parameter for both sites as well as their corresponding standard deviations seems to be lower and larger respectively for the Cu doped magnetites than for the Cr doped magnetites.

These observations could imply that the Cu doped magnetites have poorer crystallinity than the Cr-magnetites. However, this statement should be taken with extreme precaution, because measurements are needed in order to establish both the amount of dopant incorporated into the structure and the particle sizes of the magnetites. These measurements are in progress.

Figure 2 shows the infrared spectra of some selected samples. It is possible to notice that
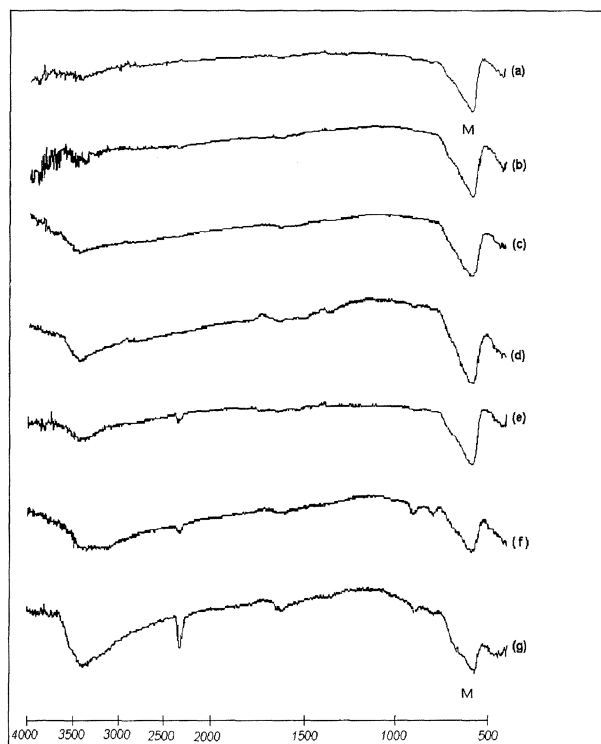
66

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

Figure 2. Infrared spectra of some selected samples.
a) MCF100, b) MCFCu1, c) MCFCu5, d) MCFCu10,
e) MCFCr1, f) MCFCr5, and g) MCFCr10.

*Figura 2. Espectros infrarrojo de algunas muestras
seleccionadas. a) MCF100, b) MCFCu1, c) MCFCu5,
d) MCFCu10, e) MCFCr1, f) MCFCr5, y g) MCFCr10.*

magnetite (bands located at about 581 cm^{-1}) is the principal phase in all the samples. The bands typical of goethite (800 cm^{-1} and 900 cm^{-1}) are observed only in the highest doped samples. These results are in line with the findings by the other techniques. Another interesting feature of the infrared spectra is that the goethite bands are more pronounced in the spectra of samples with Cr than with Cu, this characteristic being more apparent for the 5 wt. % Cr than for the 10 wt. Cr. An impurity band located at about 1600 cm^{-1} could indicate the presence of $FeCl_2$. The XRD patterns of the pure and the smallest substituted samples demonstrates again the presence of magnetite. The goethite peaks are only visible in the highest subtituted samples, as found by the other techniques.

4. CONCLUSIONS

It has been confirmed that the hydrothermal method produces magnetites with relatively good crystallinity and stoichiometric. Some variables in the synthesis procedure, such as ultrasonic stirring

and a fast mixing of the solutions, seem to introduce improvements in the final product. The degree of crystallinity and the presence of impurities in the samples are greatly influenced by the presence of Cr and Cu. However, this effect seems to be opposite in each case. In that respect, the increment of the Cr solutions appears to introduce more goethite in the final product than the increment of the Cu solutions do. Nevertheless, it seems that large amount impurities are present in the solutions with the highest Cu content. On the other hand, the degree of crystallinity of the magnetites seems to be worse in the Cu doped samples than in the Cr ones.

Acknowledgements

REFERENCES

[1] T. ISHIKAWA, H. NAKAZAKI, A. YASUKAWA, K. KANDORI and M. SETO, *Corros. Sci.* 41 (1999) 1.665-1.680.

[2] S. NASRAZADANI and A. RAMAN, *Corros. Sci.* 34 8 (1993) 1.355-1.365.

[3] A.L. MORALES, H. MOSQUERA and C. ARROYAVE, *Hyp. Interac.* (C) 4 (1999) 43-47.

[4] G.M. DA COSTA, E. DE GRAVE, P.M.A. DE BAKKER and R.E. VANDENBERGHE, *Clays Clay. Miner.* 34 6 (1995) 656-668.

[5] R.E. VANDENBERGHE and E. DE GRAVE, *Mössbauer Spectroscopy Applied to Inorganic Chemistry,* G.J. Long and F. Grandjean (eds.), Plenum Press, New York, 1989, pp. 59-182.

[6] F.C. VOOGT, T. HIBMA, G.L. ZHANG, M. HOEFMAN and L. NIESEN, *Surf. Sci.* 331-333 (1995) 1.508-1.514.

[7] J.M.D. COEY and A.H. MORRISH, *J. Phys.* 23 2-3 (1971) C1-271 - C1-273.

[8] U. SCHWERTMANN and R.M. CORNELL, *Iron Oxides in the Laboratory,* 1rst ed., VCH mbH, Weinheim (Germany), 1991, p. 136.

[9] R.E. VANDENBERGHE, E. DE GRAVE and P.M.A. DE BAKKER, *Hyp. Interac.* 83 (1994) 29-49.

[10] E. DE GRAVE, R.M. PERSOONS and R.E. VANDENBERGHE, *Proc. XXXII,* Zakopane School of Physics, Görlich, E.A., Latka, K. (eds.), Jagiellonian University and Niewodniczanski Institute, Krakow, 1997, pp. 178-238.

[11] J.A. JAEN, J. DÁVALOS and J.R. GANCEDO, *Hyp. Interac.*(C) 3 (1998) 81.

Rev. Metal. Madrid Vol. Extr. (2003) 62-67

67