JOURNAL OF MATERIALS SCIENCE 25 (1990) 1813–1815

Chromium substitution and crystallinity changes in γ-FeOOH

J. MORALES, J. L. TIRADO, C. VALERA
Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba, 14004, Spain

Cr-substitution in γ-FeOOH takes place with changes in the unit cell parameters and a marked decrease in crystallinity. The γ-FeOOH structure is maintained up to 5.0 atomic % with a progressive diminution of crystallite size, as shown by X-ray line broadening analysis and electron microscopy. The dehydroxilation of the Cr-substituted oxyhydroxide to γ-sesquioxides and the phase transition $\gamma \rightarrow \alpha$ sesquioxide take place at lower temperatures than in γ-FeOOH, due to the lower crystallinity.

1. Introduction

Trivalent metal substitution in iron oxyhydroxides has been extensively studied in synthetic goethite [1–3] as there are various isostructural oxyhydroxides (α-AlOOH, α-MnOOH) with the goethite type structure. In these studies, an increase in crystallite size with increasing manganese or aluminium substitution in goethite was evidenced by X-ray diffraction line broadening analysis. δ-FeOOH-type solid solutions have also been prepared with compositions $Fe_{1-x}M_xO_{1-x}(OH)_{1+x}$ (M: Ca, Mg, Cd and Zn) [4, 5] with M ions in octahedral sites. For lepidocrocite these studies are less frequent, although some trivalent cations give isostructural phases. This is the case of chromium which has a green isostructural γ-oxyhydroxide [6].

In this paper, the preparation of chromium-substituted γ-FeOOH is described. Additionally, it is known that crystallinity has a significant effect on the thermal behaviour and decomposition products of γ-FeOOH [7–9]. Thus, crystal imperfections in Cr-substituted lepidocrocite and its thermal decomposition products are also studied.

2. Experimental procedure

Synthetic lepidocrocite was prepared according to the method reported by Giovanoli and Brutsch [10]. Cr-substituted samples were obtained in the presence of known amounts of $CrCl_3$ by the same procedure. The precipitates were washed by centrifugation until chloride ion was undetected and dried at 80° C.

Atomic Cr/Fe ratios were determined alternatively by electron microprobe and atomic absorption spectrometry measurements. X-ray diffraction was carried out with a Siemens D500 apparatus provided with CuK_α radiation, graphite monochromator and digital processing unit. The determination of unit cell parameters was effected from the 020, 021, 151 and 132 diffraction lines. Line broadening analysis was carried out from profiles recorded by the step-scan procedure (step-size 0.02°2θ). Differential scanning calorimetry (DSC) traces were obtained with a Mettler TA3000 apparatus previously calibrated with an indium metal sample. The electron micrographs were obtained with a JEOL 200CX microscope with side entry stage.

3. Results and discussion

The XRD patterns of the products obtained with Cr contents x (100.Cr/(Cr + Fe)): 1.2, 3.0, 5.0, 7.0 and 9.0 are compared with that of lepidocrocite in Fig. 1. As Cr content increases up to 5.0, a progressive change in peak position and broadening is detected although the patterns can be indexed as an orthorhombic phase analogous to γ-FeOOH. The diffractogram for a value of $x = 7.0$ shows significant differences as the absence of a clear 020 reflection and the occurrence of other lines close to spinel phase reflections. For $x = 9.0$, the product is almost amorphous but maintains highly-broadened reflections probably belonging to the spinel phase. These results show that the presence of chromium contents higher than 5.0 may inhibit the formation of a γ-oxyhydroxide phase, probably due to the higher tendency to form spinel ferrites.

The analysis of the diffraction data yielded the parameters shown in Table I. The evaluation of unit cell parameters was only possible for those samples with $x = 0$ and $x = 1.2$ since an important broadening of the lines occurs at higher chromium contents. This fact may mislead the values obtained for the cell dimensions. The values in Table I show that the Cr-containing sample has higher a and lower b

TABLE I Unit cell parameters and crystallite size for Cr-substituted γ-FeOOH

x	a (nm)	b (nm)	c (nm)	V (nm^3)	Crystallite size (nm)	
					(020)	(021)
0.0	0.308_8	1.245_7	0.387_9	0.1492	6.7	9.8
1.2	0.312_8	1.235_6	0.388_7	0.1502	6.4	8.9
3.0	–	–	–	–	5.1	8.0
5.0	–	–	–	–	5.2	6.3

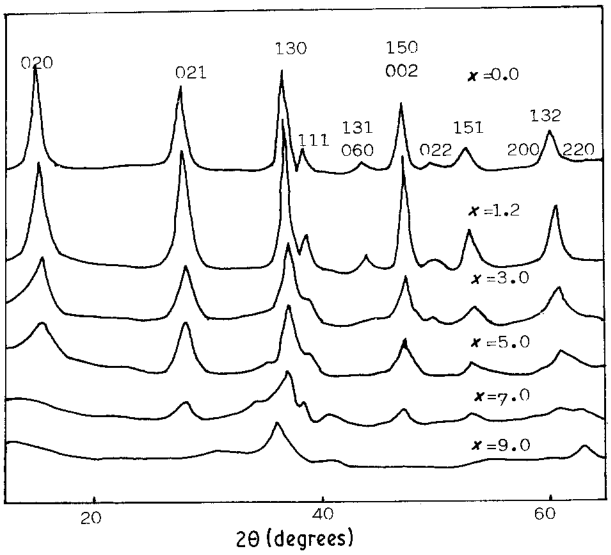

Figure 1 X-ray diffraction patterns of the products of γ-FeOOH preparation in the presence of Cr(III) ions.

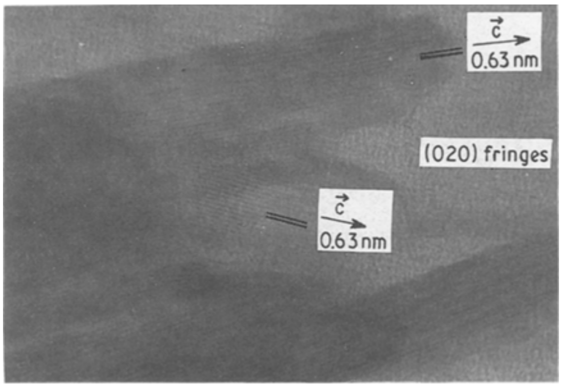

Figure 2 Electron micrograph of a Cr-substituted γ-FeOOH sample (x = 1.2).

parameters, while the differences are less pronounced along the c axis. On the other hand, the cell volume increases slightly with Cr-content as a consequence of the larger ionic radius of Cr(III). These changes may indicate that Cr-substitution has taken place in γ-FeOOH. Additionally, the undetectability of other phases in the X-ray diffractograms of Fig. 1 and the results of the electron microprobe analysis showed a high uniformity in chemical and phase composition below x values of 5.0.

The results of X-ray diffraction line broadening analysis showed a clear and progressive increase in the values of full width at half maximum (FWHM) and integral breadths (β) for all the crystallographic directions studied. This behaviour is in contrast with aluminium [1, 2] and manganese [3] substituted goethites that show an increase in crystallinity as substitution increases. This fact may reflect the lower stability of γ-CrOOH as compared with the rhombohedral α and orthorhombic β phases. On the other hand, the ratio FWHM/β is close to the theoretical value for a lorentzian profile. This fact reflects that line broadening is mainly ascribable to a low size of the coherently diffracting domains [11]. The values of crystallite size computed by the Scherrer equation (Table I) show that Cr-substitution inhibits progressively the development of γ-oxyhydroxide domains, probably originated by the difficulty for accommodating the chromium ions in the lattice. The electron microscopy observation of the samples (Fig. 2) is in agreement with the above results. Substituted samples show lath-like domains composed of ∼ 15 020 lattice planes. These crystallites do not show additional contrast effects that could be ascribed to stacking faults or dislocations.

The evolution of these samples with temperature was followed by the DSC traces of the γ-oxyhydroxide samples (Fig. 3). These data showed that the peak temperature of the endothermal dehydroxylation of γ-FeOOH initially lowered with Cr-substitution, in contrast with other metal substitutions [2, 3]. This cannot be ascribed to a change in the dehydroxilation product as the X-ray diffractograms of the decomposed products at 290°C (Fig. 4) are indexable in a γ-sesquioxide phase with a limited content in α-phase, behaviour commonly found in γ-FeOOH [12]. The decrease in crystallite size with Cr-substitution may be responsible for the decrease in temperature by facilitating the loss of hydroxyl groups.

On the other hand, previous studies on the thermal behaviour of γ-(Fe$_{1-x}$Cr$_x$)$_2$O$_3$ [13, 14] show that the γ to α transformation temperature increases with Cr-substitution when no other effect is present. However the DSC curves in Fig. 3 show that the peak temperature of the exothermal γ to α phase transformation is lower for substituted samples. Again, it should be emphasized that crystal perfection may play an important role in the thermal evolution of the γ-mixed oxides [7–9]. Fig. 4 shows the progressive diminution in the crystallinity of the γ-sesquioxide below x = 7.0. This effect and the stabilization of the γ-phase by Cr-substitution may condition the observed temperature sequence for x = 0 to 5.0. For Cr contents higher than 5.0, the pattern changes, and an

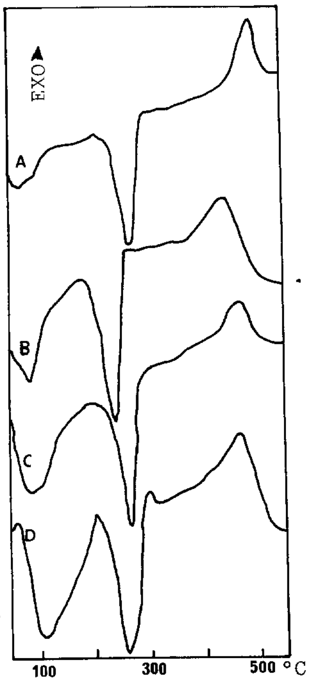

Figure 3 DSC curves of Cr-substituted γ-FeOOH. A: x = 0, B: x = 1.2, C: x = 3.0, D: x = 5.0.

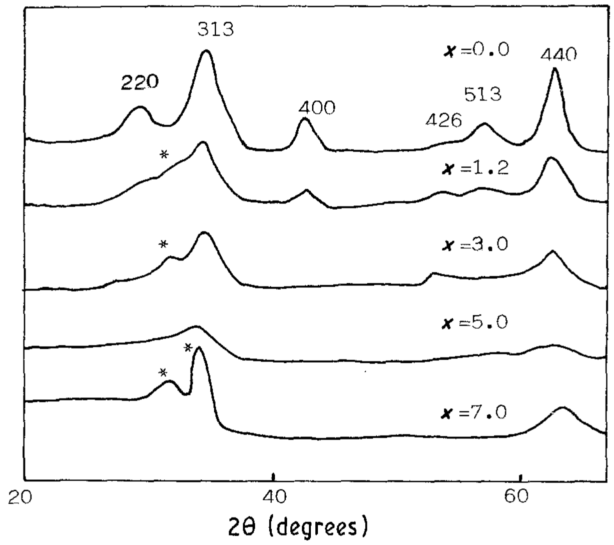

Figure 4 X-ray diffraction patterns of Cr-substituted γ-FeOOH after thermal treatment at 290°C. *Probable α-sesquioxide reflections.

amorphous product is found at $x = 7.0$, and an α-phase at $x = 9.0$ as a consequence of the inhibition of the occurrence of γ-oxyhydroxide.

Acknowledgement

This work was carried out with the financial support of CAICYT (contract no. 982/84). The authors acknowledge Mrs M. C. Mohedano for the drawing of the figures.

References

1. R. THIEL, *Z. Anorg. Allg. Chem.* **326** (1963) 70.
2. D. G. SCHULZE and U. SCHWERTMANN, *Clay Min.* **19** (1984) 521.
3. W. STIERS and U. SCHWERTMANN, *Geochim. Cosmochim. Acta* **49** (1985) 1909.
4. O. MULLER, R. WILSON and W. KRAKOW, *J. Mater. Sci.* **14** (1979) 2929.
5. O. MULLER, R. WILSON, H. COLIJN and W. KRAKOW, *ibid.* **15** (1980) 959.
6. F. HUND, *Naturwissenschaften* **46** (1959) 320.
7. R. GIOVANOLI and R. BRUTSCH, *Thermochim. Acta* **13** (1975) 15.
8. J. SUBRT, F. HANOUSEK, V. ZAPETAL, J. LIPKA and M. HUCL, *J. Thermal Anal.* **20** (1981) 61.
9. R. GOMEZ-VILLACIEROS, L. HERNAN, J. MORALES and J. L. TIRADO, *Mater. Res. Bull.* **22** (1987) 513.
10. R. GIOVANOLI and R. BRUTSCH, *Chimia* **28** (1974) 188.
11. TH. H. DE KEIJSER, E. J. MITTEMEIJER and H. C. R. ROZENDAAL, *J. Appl. Cryst.* **16** (1983) 309.
12. R. GOMEZ-VILLACIEROS, L. HERNAN, J. MORALES and J. L. TIRADO, *J. Colloid Interface Sci.* **101** (1984) 329.
13. A. ROUSSET, J. PARIS and P. MOLLARD, *Ann. Chim.* **7** (1972) 119.
14. P. S. SIDHU, *Clay Min.* **36** (1988) 31.

Received 15 November 1988
and accepted 26 April 1989