

PHYSICAL PROPERTIES OF AKAGANEITE OBTAINED BY HYDROLISIS OF Fe^{3+} IN THE PRESENCE OF Al^{3+} , Cr^{3+} , AND Cu^{2+}

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ABSTRACT

This paper deals with the influence of Al, Cr, and Cu ions on the formation of akaganeite. Powder samples were prepared by thermal hydrolysis of several mixtures of iron and the other cations solutions at 70°C during 48 hours. X-ray diffraction and Mössbauer spectrometry at 77 K and 300 K demonstrate that akaganeite is the only iron phase being formed. The X-ray patterns for all samples were adequately adjusted through Rietveld method with the monoclinic space group ($C2/m:b3$). This symmetry requires the existence of two distinct iron octahedral sites which is also confirmed by the Mössbauer spectrum in the paramagnetic state. No appreciable difference in the crystallographic parameters for all the samples were observed. The Mössbauer parameters both in the paramagnetic and in the magnetic states did not change appreciably. These results suggest that the metallic cations did not enter into the akaganeite's crystallographic structure in a detectable amount.

INTRODUCTION

For corrosion science and steel industry it is very important to understand the role played by the alloying elements upon the formation of the corrosion products in a given environment. This study can be done by exposing steels with varying chemical composition in an given environment or by performing accelerated corrosion tests. This way of working has the difficulty that several iron compounds are formed at the same time making difficult to discern the effect of the steel composition upon their formation. Another approach to do this investigation is to prepare in laboratory, under controlled conditions, the iron compounds in the presence of varying amounts of the alloying elements. This later type of investigation has been done extensively for goethite [1,2] and magnetite [2,3]. However, comparatively very few works have been reported for akaganeite [4]. In this paper we are studying the effect of Al^{3+} , Cr^{3+} , and Cu^{2+} ions upon the formation of akaganeite.

EXPERIMENTAL PART

Pure akaganeite, code-named Pak1, was obtained by thermal hydrolysis of 0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, which correspond to 53.8 g of the ferric salt dissolved in 2 liters of (twice distilled) water. All the solutions were hold in a 3 liters polypropilene closed vessels. During the reaction the pH drops from 1.7 to 1.2. The vessel with the solution was placed in an oven at 70°C during 48 hours. At the end of the reaction the solution was washed by dialysis. The doped samples were code-named as MAkX, in which M represents the metallic cations such as Cu, Cr, Al at X = 1, 5 and 10 mol% or the mixture Cu-Cr cations at X = 5 mol%. For example, AlAk5 means that this is the sample prepared by mixing 0.1M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution with 5% AlCl_3 , etc. The products were characterized by X-ray diffraction and Mössbauer spectroscopy. XRD patterns were

obtained using a D500 Siemens diffractometer equipped with a Cu ($K\alpha$) radiation; data were collected in the 15° - 120° 2θ range with a 0.02° step and a counting time of 10 s per point. XRD pattern was analyzed using a program called MAUD which combines the Rietveld method and a Fourier transform analysis, well adapted especially in presence of broadened Bragg peaks [5]: this program allows thus to derive crystalline cell parameters, average crystallite size as well as microstrains. The initial structural model used was that reported by Post and Buchwald [6]. The scale factor, sample displacement, unit cell, five-order polynomial background, and the average crystallite size were refined. The average crystallite size and the texture were assumed to be isotropic and arbitrary respectively in the present study. 300 K and 77 K Mössbauer spectra were collected in a time-mode spectrometer working in the transmission geometry using a constant acceleration drive with triangular reference signal. Calibration was achieved from a standard α -iron foil at 300 K. The spectra were analyzed using a program called MOSFIT which is based on non-linear least squares fitting procedures assuming lorentzian Mössbauer lines while the isomer shift value is quoted to that of α -Fe at 300 K.

RESULTS AND DISCUSSION

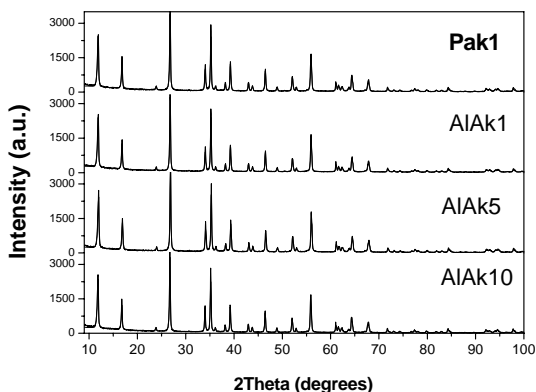


Figure 1. XRD patterns of pure akaganeite (Pak1), and akaganeite prepared in the presence of 1 mol% Al, 5 mol% Al and 10 mol% Al.

expect a reduction in the cell parameters, because of the smaller ionic radius of Al^{3+} (0.535 Å) in comparison to Fe^{3+} (0.645 Å) [2]. The same results were obtained for the other metallic cations. On the other hand, two doublets with $\delta_1 = 0.37$ mm/s, $\Delta E_{Q,1} = 0.54$ mm/s, area (A_1) of 65% and $\delta_2 = 0.37$ mm/s, $\Delta E_{Q,2} = 0.97$ mm/s, area (A_2) of 35% were used to fit the 300 K Mössbauer spectrum of the pure sample (Pak1). These data are in agreement with those reported in the literature [2,8,9]. The origin of these two sites is related to the two symmetrically different iron sites required by the monoclinic structure [6,8]. The 300 K Mössbauer spectra for the other

Figure 1 shows the XRD patterns of samples Pak1, AlAk1, AlAk5, and AlAk10. The patterns were adjusted by introducing only one single phase, akaganeite (PDF: 80-1770) [7] with the $C2/m:b3$ monoclinic space group. In the case of pure sample, the fit gives unit cell values of $a = 10.5238(6)$ Å, $b = 3.0343(1)$ Å, $c = 10.5415(6)$ Å and $\beta = 90.110(6)^\circ$, while the average crystallite grain size is estimated at about 46(6) nm [8]. The unit cell parameters as well as the average crystallite grain size did not change appreciably for the other samples. These results imply that Al did not substitute Fe in the crystallographic structure in an appreciable way to be measured, otherwise we should

samples were adjusted in the same way with two doublets and the derived parameters were similar to the ones reported for Pak1. These results support the XRD findings.

Figure 2 shows the Mössbauer spectra collected at 77 K for samples Pak1, AlAk1, AlAk5, and AlAk10. Next, figure 3 shows the Mössbauer spectra collected at 77 K for samples Pak1, CrAk5, CuAk5, and CuCrAk5. These spectra were adjusted introducing three sextets (a fit with four sextets is also possible [8]). We can see that the shape of the spectra did not change appreciably from sample to sample. The derived hyperfine parameters for the three sextets fit are very similar to the ones reported in the literature [2,9]. No appreciable differences in the hyperfine parameters were also observed for the akaganeites prepared in the presence of the other metallic cations. These results imply that Fe for cation substitution is very small or absent, otherwise we should expect appreciable variation in some of the hyperfine parameters. Moreover, these cations did not promote the formation of other iron phases as have been reported in the case of goethite [1] and magnetite [3]. Again, these results support XRD and 300 K Mössbauer spectrometry findings. The observed results could be explained by the fact that the metallic ions exhibit very different hydrolysis constants as compared to Fe^{3+} in the reaction $Me^{n+} + H_2O \leftrightarrow Me(OH)^{(n-1)+} + H^+$, in which Me is the metal [4].

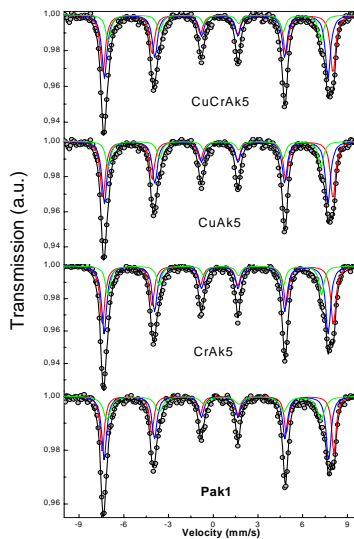
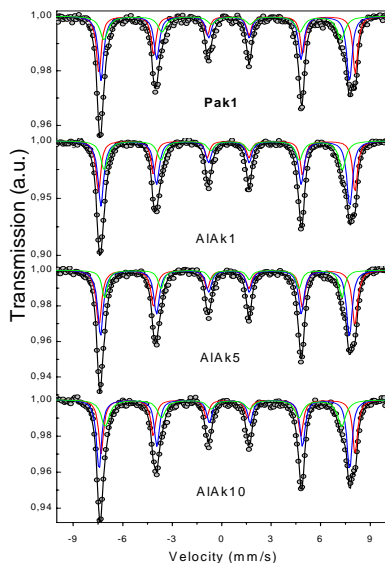


Figure 2. Mössbauer spectra at 77 K of pure akaganeite (Pak1), and akaganeite prepared in the presence of 1 mol% Al, 5 mol% Al and 10 mol% Al. The spectra were fit with three sextet components

Figure 3. Mössbauer spectra at 77 K of pure akaganeite (Pak1), and akaganeite prepared in the presence of 5 mol% Cr, 5 mol% Cu and 5 mol% Cu-Cr. The spectra were fit with three sextet components.

CONCLUSIONS

Akaganeite was prepared by hydrolysis of FeCl_3 solutions in the presence of Al^{3+} , Cr^{3+} , Cu^{2+} and the mixture of Cr^{3+} with Cu^{2+} ions. XRD and Mössbauer spectroscopy show that only akaganeite is formed. No appreciable differences in the crystallographic and the Mössbauer parameters for all the samples were observed. These results suggest that the physical properties of the akaganeites studied in this work are not noticeably affected by the presence of these cations. None of these cations entered into the crystallographic structure in detectable amount if any. The present results implies that in the design of a steel meant to alter the properties or even to inhibit the akaganeite formation, the Al, Cr, and Cu are not appropriate metallic cations for this purpose. Also akaganeite forms in large quantities in high chloride environments with large particle size preventing the formation of protective rust layer.

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REFERENCES

- [1]. A. Morales, C.A. Barrero, P. Morales, F. Jaramillo, C. Arroyave and J.M. Greneche, *Hyperfine Interactions* 148-149 (2003) 135.
- [2]. U. Schwertmann and R.M. Cornell, *Iron oxides in the laboratory*. Second edition, VCH, Weinheim, Germany, 2000.
- [3]. C.A. Barrero, A.L. Morales, J. Mazo-Zuluaga, F. Jaramillo, G. Pérez, D.M. Escobar, C.E. Arroyave, J. Tobón, P.M. Montoya, L.F. Osorio, R.E. Vandenberghe, and J. -M Greneche, *Rev. Metal. Madrid*, Vol. Extr. (2003) 62.
- [4]. T. Ishikawa, R. Katoh, A. Yasukawa, K. Kandori, T. Nakayama, and F. Yuse, *Corrosion Science* 43 (2001) 1727.
- [5]. MAUD, materials analysis using diffraction by L. Lutteroti. Version: 1.84 (2002).
- [6]. J.E. Post and V.F. Buchwald., *Am. Mineral.* 76 (1991) 272.
- [7]. JCPDS, X-ray diffraction data cards of the joint committee on powder diffraction standars, (2001).
- [8]. K.E. Garcia, A.L. Morales, C.A. Barrero, C.E. Arroyave, and J.M. Greneche, *Physica B* (2004) in press.
- [9]. E. Murad, *Clay Minerals* 14 (1979) 273.