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Note

THE APPLICATION OF MÖSSBAUER SPECTROSCOPY TO THE STUDY OF THE INTERACTION OF THE SYSTEMS $CuO—Fe_3O_4$, $Cu_2O—Fe_3O_4$ AND $CuO—ZnO—Fe_3O_4$

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In the hydrometallurgical processing of zinc concentrates the more effective recovery of copper and iron is being impeded by the increase in ferrite formation [1,2]. The determination of the phase content of the product after the concentrate has been roasted is of decisive importance, as is the investigation of the interactions between the zinc, copper and iron oxides. The chemical and X-ray structural analyses and infrared spectroscopy do not always allow the identification of the available phases. The use of Mössbauer spectroscopy for these purposes is of great interest. It has proven advantages, compared with the other methods of investigation of complex metallurgical products [3—5] mentioned.

It is well known that $ZnFe_2O_4$ and $CuFeO_2$ are paramagnetic at room temperature [6—9]. The Neel temperature (T_N) for $ZnFe_2O_4$ is 10.3 K [8] and for $CuFe_2O_4$ it is 14.06 K [6]. Zinc ferrite has a typical normal spinel structure, all octahedral places being occupied by iron ions. If the Mössbauer spectrum shows two lines at room temperature, this allows an accurate measurement of the quadrupole splitting. Usually, the quadrupole splitting increases with the increase [7] in the number of impurities. The $CuFeO_2$ spectrum at room temperature is a doublet with a quadrupole splitting [10] of 0.63 ± 0.003 mm s^{-1}. The $CuFe_2O_4$ and $CuFe_5O_8$ spectra are typical ferrite spectra. The copper ions occupy mainly the octahedral places (B), while the iron ions occupy both the octahedral and the tetrahedral (A) places [11] in the spinel $CuFe_2O_4$. The Neel temperature for $CuFe_2O_4$ is 1063 K [12].

The application of Mössbauer spectroscopy allows the identification of iron containing the phases: α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, $CuFeO_2$ and $ZnFe_2O_4$, which are obtained by the interaction of the systems containing copper, zinc and iron [5—7,10]. The determination of $CuFe_2O_4$ is complicated by the coincidence of its lines with those of α-Fe_2O_3 [12].

EXPERIMENTAL

The conditions for heating the oxide systems and the results from the X-ray structural analyses and the metal solubility in 7% sulphuric acid solution are represented in an earlier work [13] of ours.

The Mössbauer spectra are taken on a standard Mössbauer spectrometer working under conditions of constant acceleration and using a multichannel analyser. The error in setting the velocity and the non-linearity of the impulse are smaller than 0.01 min s^{-1}. Co^{57m} is used as a source in a Pd matrix of 20 mCi activity. The isomer shift for all the spectra is given by using the one for $Na_2Fe(CN)_5NO \cdot 2\,H_2O$ as a standard. The Mössbauer lines of the standard, using our device, have a width of 0.23 mm s^{-1}. The samples represent powder-pressed tablets made from the substance under study and polyvinylalcohol of density 20 mg cm^{-2}.

The Mössbauer spectra obtained are processed graphically and the overlapping of the individual phase spectra are reported.

RESULTS

On heating the mixture of CuO and Fe_3O_4 in the ratio 25.57% CuO and 74.43% Fe_3O_4 the phases α-Fe_2O_3, Fe_3O_4 and $CuFeO_2$ are observed. Fig. 1(a) shows the spectrum (at 293 K) for the system after heating in an inert atmosphere at 1023 K for 18×10^3 s.

The ratio of the phases obtained is α-Fe_2O_3 : Fe_3O_4 : $CuFeO_4$ = 2.8 : 1 : 1. It is determined approximately by the line intensity of the individual phases, assuming equal probability for each effect (Table 1). The parameters of the spectra α-Fe_2O_3 and Fe_3O_4 which were determined initially agree with the literature values [10]. The composition of the heated oxide mixtures are

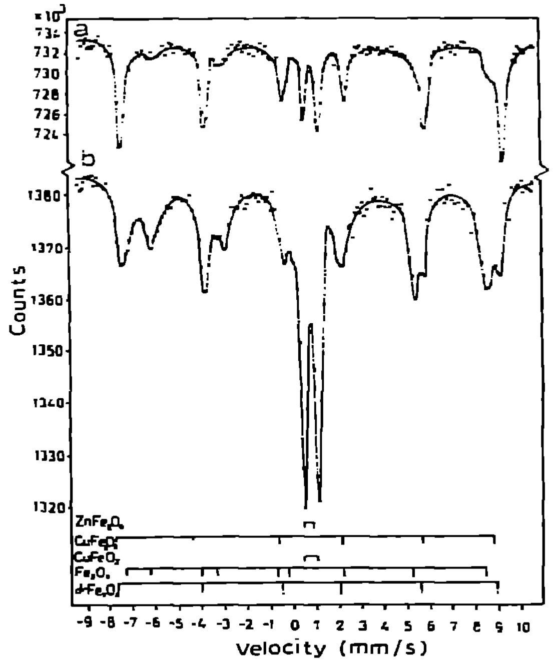

Fig. 1. Mössbauer spectra (at 293 K) for the systems (a) CuO—Fe_3O_4 and (b) Cu_2O—Fe_3O_4 after heating in an inert atmosphere for 18×10^3 s.

TABLE 1

Mössbauer spectra parameters of the oxide systems

System	Components	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Intrinsic magnetic field (kOe)
CuO : Fe_3O_4 = 1 : 1	α-Fe_2O_3	0.70 ± 0.05	0.20 ± 0.05	520 ± 3
	Fe_3O_4 a	0.63 ± 0.05	0.00 ± 0.05	497 ± 3
	Fe_3O_4 b	0.88 ± 0.05	0.00 ± 0.05	466 ± 3
	$CuFeO_2$	0.69 ± 0.05	0.62 ± 0.05	0
Cu_2O : Fe_3O_4 = 1 : 1	α-Fe_2O_3	0.72 ± 0.05	0.65 ± 0.05	0
	Fe_3O_4			
	$CuFeO_2$			
	$CuFe_2O_4$			
(CuO + ZnO) : Fe_3O_4 = 1 : 1	α-Fe_2O_3			
	Fe_3O_4			
CuO : ZnO = 1 : 1	$ZnFe_2O_4$	0.67 ± 0.005	0.38 ± 0.05	0
	Mixed spin.	0.88 ± 0.10	0.14 ± 0.05	378 ± 5
CuO—ZnO—Fe_3O_4	α-Fe_2O_3			
Cu : Zn : Fe = 17 : 34 : 26	Fe_3O_4			
	$ZnFe_2O_4$	0.68 ± 0.05	0.44 ± 0.05	0

determined on the basis of these values. The ratio of the components shows that a comparatively small part of the iron is combined with the copper in the form of $CuFeO_2$. This explains the high solubility of the copper from the heated mixture (82.0%) in a 7% sulphuric acid solution, which is very close to the solubility of Cu_2O obtained from the heating of CuO [13].

The amount of $CuFeO_2$, obtained by the interaction of Cu_2O and Fe_3O_4 is much greater, except that the experimental spectrum [Fig. 1(b)] shows the presence of a fourth component, which most probably belongs to a tetragonal $CuFe_2O_4$. The $CuFe_2O_4$ spectrum is a complex one and consists of two 6-line patterns [10]. One of them has parameters very close to that of α-Fe_2O_3. That is why it is very difficult to distinguish this ferrite from α-Fe_2O_3 on the Mössbauer spectrum. The ratio of the phases obtained is $CuFeO_2$: Fe_3O_4 : α-Fe_2O_3 : $CuFeO_2$ = 3.5 : 1.7 : 1 : 0.7. This explains why the copper solubility in a 7% sulphuric acid solution decreases abruptly and is 54.5% for the given case. This shows that CuO dissociation is a comparatively slower process and longer heating is necessary to obtain $CuFeO_2$. Perhaps the greater ion radius [14] of Cu^+ also affects the formation of $CuFeO_2$, impeding its diffusion in the solid phase reaction.

In the interaction of CuO and Fe_3O_4, the Cu^{2+} ions substitute the Fe^{2+} ions in the tetrahedral position (B) in Fe_3O_4 forming $CuFe_2O_4$. In addition, the Fe^{2+} quantity decreases due to their oxidation by the oxygen liberated in the CuO dissociation. These are the reasons for the decrease in intensity of the 6-line pattern for Fe^{2+}.

When Cu_2O interacts with Fe_3O_4 the intensity of Fe^{2+} lines remains relatively high compared with that found from the interaction of CuO and Fe_3O_4. In this case Cu_2O interacts with Fe_2O_3 from the magnetite, forming $CuFeO_2$. The result of this is the doublet $CuFeO_2$ and the relatively weak lines in the 6-line pattern of Fe^{3+}. The narrowing of the Fe^{2+} 6-line pattern due to the fading of the intrinsic magnetic field because of the change of the Fe^{2+} environment is proof of this.

The situation is very different when there is ZnO in the systems studied. Figure 2 shows the Mössbauer spectra of the system $CuO—ZnO—Fe_3O_4$ on heating for 18×10^3 s (a) at 1023 K; (b) at 1223 K (taken at 293 K); (c) at 1223 K (taken at 173 K).

At the oxide ratio mentioned the doublet $ZnFe_2O_4$ is observed with an isomer shift 0.67 ± 0.05 mm s^{-1} and a quadrupole splitting of 0.38 ± 0.05 mm s^{-1} (Table 1). Regarding the isomer shift and the quadrupole splitting, those obtained for $ZnFe_2O_4$ at 1023 K agree with the reference data [7]. A new phase, small in quantity, which was characterized by a smaller intrinsic magnetic field compared with that of $CuFe_2O_4$ — 378 ± 5 kOe, is obtained in the spectrum shown in Fig. 2(a). This phase increases quantitatively at higher heating temperatures [Fig. 2(b)]. The positions of the new phase absorption lines are: -5.1 ± 0.2; -2.0 ± 0.2; -0.1 ± 0.1; $+1.7 \pm 0.1$; $+3.7 \pm 0.2$; $+7.0 \pm 0.2$ (mm s^{-1}). The isomer shift is 0.88 ± 0.1 mm s^{-1} and the quadrupole split-

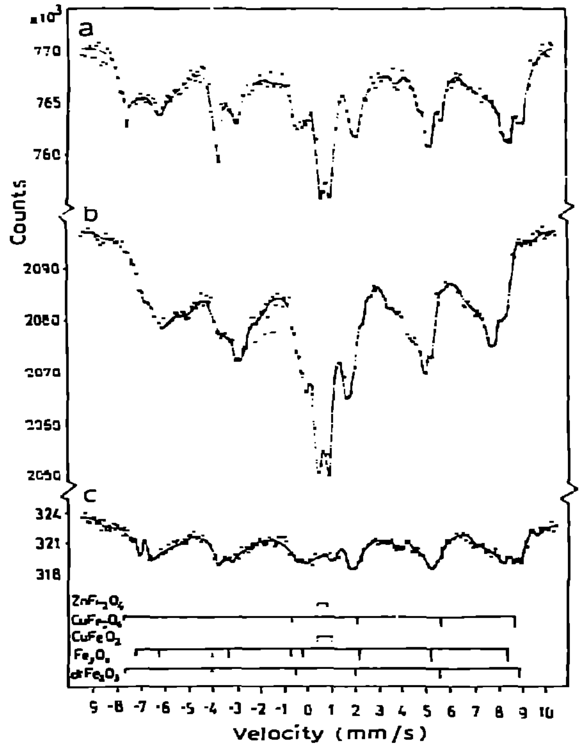

Fig. 2. Mössbauer spectra for the system $CuO—ZnO—Fe_2O_3$ (a) after heating at 1023 K for 18×10^3 s; (b) after heating at 1223 K for 18×10^3 s (taken at 293 K); (c) after heating at 1223 K for 18×10^3 s (taken at 173 K).

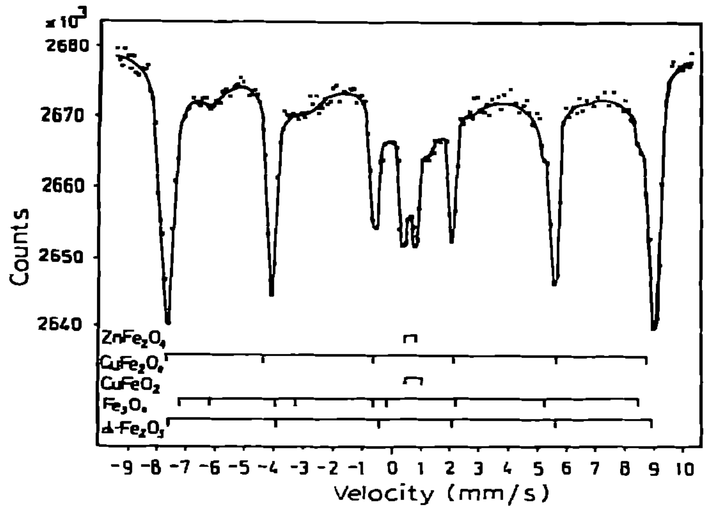

Fig. 3. Mössbauer spectra for the system $CuO—ZnO—Fe_3O_4$ (Cu : Zn : Fe = 17 : 34 : 26) taken at 293 K.

ting is 0.14 ± 0.05 mm s^{-1}. Most probably this phase represents a mixed spinel having the general formula $Cu_xZn_yFe_{3-x-y}O_4$, where $x + y \geqslant 1$.

Copper content in the mixed spinel increases with the increase in heating temperature and the spectrum approaches that of $CuFe_2O_4$. That is confirmed by the fact that in the interval 293—173 K the doublet passes to a line split six times, which shows that the T_N of the spinel is in this interval.

When the heating temperature is increased, the Mössbauer spectra show non-stoichiometric $CuFe_2O_4$ and $ZnFe_2O_4$, containing impurities of substitution. Obtaining a spinel phase, the content of which depends directly on the diffusion rate and the crystallization in the individual grains, is also observed by other authors [15].

With the increase in copper and zinc content compared with that of iron (Cu : Zn : Fe = 17 : 34 : 26) the interactions in the system $CuO—ZnO—Fe_3O_4$ lead to an increase in the quantity of α-Fe_2O_4 and the formation of $ZnFe_2O_4$ (Fig. 3). The ratio of α-Fe_2O_3, $ZnFe_2O_4$ and Fe_3O_4 is 4.6 : 1.3 : 0.8. The decrease in the solubility of copper shows that $CuFe_2O_4$ exists as well as the phases mentioned. The quantity of $ZnFe_2O_4$ obtained is relatively small and so zinc has comparatively high solubility (~95%) in a 7% sulphuric acid solution.

CONCLUSIONS

The processes which take place during the heating of the oxide systems $CuO—Fe_3O_4$, $Cu_2O—Fe_3O_4$ and $CuO—ZnO—Fe_3O_4$ are studied, using Mössbauer spectroscopy. The analysis of the Mössbauer spectra and the interaction products allows us to make the following conclusions.

(1) In the interaction between CuO and Fe_3O_4, the oxygen liberated as a result of the CuO dissociation oxidises the Fe^{2+} from Fe_3O_4. The product of

the dissociation (Cu_2O) interacts with the product of oxidation (Fe_2O_3) and $CuFeO_2$ forms. In the interaction of Cu_2O and Fe_3O_4 the copper oxide interacts with the Fe_2O_3 from the magnetite, forming $CuFeO_2$.

(2) On heating the system CuO—ZnO—Fe_3O_4, a zinc spinel is predominantly formed ($ZnFe_2O_4$). On increasing the heating temperature, mixed zinc and copper spinels are obtained. Their T_N is significantly higher than those of $ZnFe_2O_4$ and $CuFeO_2$. T_N is between 173—293 K, depending on their copper and zinc ratios.

(3) The conditions for the formation of a minimum quantity of ferrites can be established, using the Mössbauer spectra of the calcines produced in the roasting of zinc and copper—zinc concentrates. This is of great importance for improving the results of the hydrometallurgical processing of the oxide products obtained.

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