Nondestructive and Complete Analysis of Magnetite-Maghemite Solid Solutions by a Combined X-Ray Diffraction/Fluorescence Method

Masaaki IWATSUKI and Tsutomu FUKASAWA

Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University, Takeda, Kofu 400, Japan

This paper describes a nondestructive and complete analysis of magnetite($\text{FeO} \cdot \text{Fe}_2\text{O}_3$)-maghemite($\gamma\text{-Fe}_2\text{O}_3$) solid solutions including minor constituents: the proposed method consists of measurements of the lattice constant and X-ray fluorescent determination of the minor constituents. The diffraction angles of the solid solution were corrected using a silicon internal standard for calculation of the lattice constant, a_0 . Intensity ratios of Mn K_α /Fe K_α and Zn K_α /Fe K_α were measured for the determination of manganese and zinc and for the correction of the lattice constant due to the minor elements. The final analysis was done using the linear relation between a_0 and the sum total of converted mole percentages of divalent metal oxides. Differences between the analytical results obtained by the present method and those obtained by the wet methods were within 3.4 wt% for Fe_2O_3 , within 1.5 wt% for FeO, and within 0.08 wt% for MnO and ZnO. Time required for a complete analysis is about 30 min.

Keywords Magnetite, maghemite, solid solution, lattice constant, X-ray diffraction analysis, X-ray fluorescence analysis, manganese, zinc

In the previous paper¹, the authors have reported a linear relation between the mole percentage of Fe_2O_3 or the sum total of mole percentages of divalent metal oxides in magnetite($\text{FeO} \cdot \text{Fe}_2\text{O}_3$)-maghemite($\gamma\text{-Fe}_2\text{O}_3$) solid solutions and their lattice constants corrected for contents of minor constituents, MnO and ZnO. The present paper describes the use of the linear relation for a nondestructive and complete analysis of the solid solutions: the proposed method consists of measurements of the lattice constant and X-ray fluorescent (XRF) intensity ratios of Mn K_α /Fe K_α and Zn K_α /Fe K_α for the determination of the minor elements and for the correction of lattice constant according to their contents. The determination of Fe_2O_3 and FeO has been done so far only by wet methods² which require delicate techniques and are time-consuming and tedious, as is well known. Qualitative state analyses also have been studied before; for instance, Kanazawa *et al.*³ studied the relationship between the oxidation number of iron and the chemical shift of the Fe $K_{\beta 1,3}$ line from synthetic magnetite, maghemite and various ferrites by using a two-crystal type X-ray spectrometer; Mössbauer spectrometry also has been applied to the studies on iron oxides, for instance, photoelectrode⁴ and films.⁵ The proposed method, however, is quantitative, rapid and nondestructive. It is also a very unique method combining X-ray diffraction (XRD) analysis with XRF analysis.

Experimental Background

The lattice constant, a_c , which was corrected with contents of minor constituents, MnO and ZnO, has been found¹ to be represented by Eq. (1):

$$\begin{aligned} a_c &= a_\gamma + S X_{\text{Fe}_2\text{O}_3} \\ &= a_\gamma + S_a (X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{ZnO}}) \end{aligned} \quad (1)$$

where a_γ is the lattice constant of $\gamma\text{-Fe}_2\text{O}_3$; $X_{\text{Fe}_2\text{O}_3}$, X_{FeO} , X_{MnO} , and X_{ZnO} are mole percentages of oxides shown by suffix; S and S_a are the slopes of plots of a_c vs. mole percentage of Fe_2O_3 and a_c vs. sum total of mole percentages of divalent metal oxides, respectively.

This leads to the possibility that measurements of the lattice constant may reveal the contents of Fe_2O_3 and also FeO in the solid solution, provided that the contents of minor divalent metal oxides are known. If the XRF method allows the rapid and nondestructive determinations of minor divalent metals such as Mn and Zn in the samples, the combined XRD/XRF method will allow the nondestructive and rapid determination of Fe_2O_3 , FeO, and minor constituents such as MnO or ZnO.

Equation (1) can be transformed into Eq. (2), representing the observed lattice constant, a_0 , for convenience in practical use:

$$\begin{aligned} a_0 &= a_\gamma + S_a (X_{\text{FeO}} + c_{\text{MnO}} X_{\text{MnO}} + c_{\text{ZnO}} X_{\text{ZnO}}) \\ &= a_\gamma + S_a (X_{\text{FeO}} + 2.84 X_{\text{MnO}} + 1.80 X_{\text{ZnO}}) \end{aligned} \quad (2)$$

where c_{MnO} and c_{ZnO} are conversion factors of X_{MnO} and X_{ZnO} , respectively: the factors express the magnitude of the effect of their replacements on the lattice constant. Namely, $c_{\text{MnO}}X_{\text{MnO}}$ and $c_{\text{ZnO}}X_{\text{ZnO}}$ are "converted mole percentage" for each constituent, and $(X_{\text{FeO}} + c_{\text{MnO}}X_{\text{MnO}} + c_{\text{ZnO}}X_{\text{ZnO}})$ means "total mole percentage converted as FeO". The factors were calculated from the following equations using the lattice constants of magnetite (8.3967 Å)⁶, maghemite (8.341 Å)⁷, jacobite ($\text{MnO} \cdot \text{Fe}_2\text{O}_3$, 8.499 Å)⁸ and franklinite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, 8.4411 Å):⁹

$$c_{\text{MnO}} = (a_{\text{MnO} \cdot \text{Fe}_2\text{O}_3} - a_{\gamma}) / (a_{\text{FeO} \cdot \text{Fe}_2\text{O}_3} - a_{\gamma}) = 2.84$$

$$c_{\text{ZnO}} = (a_{\text{ZnO} \cdot \text{Fe}_2\text{O}_3} - a_{\gamma}) / (a_{\text{FeO} \cdot \text{Fe}_2\text{O}_3} - a_{\gamma}) = 1.80.$$

On the other hand, XRF analysis is expected to give linear relations between the K_{α} intensity ratios, R_{Mn} and R_{Zn} , of minor constituents Mn and Zn against the main constituent Fe and their mole ratios. And the following relations may be obtained:

$$R_{\text{Mn}} = S_{\text{Mn}}X_{\text{MnO}} / (2X_{\text{Fe}_2\text{O}_3} + X_{\text{FeO}}) \quad (3)$$

$$R_{\text{Zn}} = S_{\text{Zn}}X_{\text{ZnO}} / (2X_{\text{Fe}_2\text{O}_3} + X_{\text{FeO}}) \quad (4)$$

where S_{Mn} and S_{Zn} are the slopes of plots of R_{Mn} or R_{Zn} vs. the mole ratios shown.

Furthermore, the sum total of mole percentages of all constituents should be equal to 100:

$$X_{\text{Fe}_2\text{O}_3} + X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{ZnO}} = 100. \quad (5)$$

The mole percentages of the oxides can be obtained by solving Eqs. (2) – (5) as follows:

$$X_{\text{Fe}_2\text{O}_3} = (A + AB - 100C - 100) / (C - 2B - 1) \quad (6)$$

$$X_{\text{FeO}} = (200C - A - 2AB) / (C - 2B - 1) \quad (7)$$

$$X_{\text{MnO}} = R_{\text{Mn}}(A - 200) / S_{\text{Mn}}(C - 2B - 1) \quad (8)$$

$$X_{\text{ZnO}} = R_{\text{Zn}}(A - 200) / S_{\text{Zn}}(C - 2B - 1) \quad (9)$$

where $A = (a_0 - a_{\gamma}) / S_a$, $B = R_{\text{Mn}} / S_{\text{Mn}} + R_{\text{Zn}} / S_{\text{Zn}}$, and $C = 2.84R_{\text{Mn}} / S_{\text{Mn}} + 1.80R_{\text{Zn}} / S_{\text{Zn}}$.

The discussion described above can be extended also to the solid solutions which contain some other minor constituents replaced in the lattice.

Experimental

Samples

Seven synthetic powder samples shown in Table 1 were used.

Chemical analysis

Determination of Fe(II) and Fe(III).² A sample was decomposed with H_2SO_4 (1+1) and HF (46%) in CO_2 atmosphere. After being mixed with a boric acid solution, it was titrated with a KMnO_4 standard solution to determine Fe(II) in the same atmosphere. After reduction of Fe(III) to Fe(II) in a zinc-amalgam reductor, the sample solution was titrated with the same KMnO_4 standard solution to determine the amount of total iron, from which the amount of Fe(III) was calculated as total iron minus divalent iron. The analyses were carried out after careful training using mixed solutions of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_4$.

Determination Mn¹⁰ and Zn.¹¹ A sample was decomposed with a mixed acid of nitric, sulfuric, and phosphoric acids. After oxidation of manganese ions to permanganate with trace silver ions and ammonium peroxydisulfate, Mn was determined by spectrophotometry. Zinc was determined by atomic absorption spectroscopy, after the decomposition with hydrochloric and nitric acids.

Measurements of lattice constants

A Rigaku X-ray diffractometer equipped with an iron tube was used for the measurements of lattice constants under the conditions in Table 2. A sample of about 0.5 g was mixed with silicon powder of nominal 99.9% purity and 100 mesh as internal standard at the ratio of 2:1, packed in a standard sample holder and analyzed. The XRD lines of (511), (440), (533) or (731) from the solid solution to be analyzed and (311) or (422) from silicon standard as shown in Table 3 were recorded twice on a chart at a slow scanning rate. Each XRD angle was estimated from the center of gravity of a triangle approximating the line profile and corrected using the standard angle of the silicon to calculate the lattice constant.

XRF analysis

A Philips PW1410 semiautomatic XRF spectrometer

Table 1 Samples and their analytical results (wt%)

Sample	Fe_2O_3	FeO	MnO	ZnO	Total
A : high-purity Fe_3O_4 , 99.9%	75.1	24.8	0.00	0.00	99.9
B : reagent of Fe_3O_4	74.7	24.3	0.81	0.25	100.1
C : reagent of Fe_3O_4	75.6	24.8	0.28	0.01	100.7
D : needle-shaped magnetite	84.2	13.3	0.27	0.87	98.6
D' : sample D kept at 110°C, 3 h	87.8	10.2	0.27	0.87	99.1
E : needle-shaped maghemite	96.6	0.0	0.26	0.88	97.7
F : needle-shaped maghemite	97.2	0.2	0.26	0.04	97.7

Table 2 Conditions of XRD

Target	Fe
Voltage/kV	35
Current/mA	10
Filter	Mn
d. and s. slit/deg	1
r. slit/mm	0.3
Time constant/s	4
Scanning speed/deg min ⁻¹	1/4
Chart speed/mm min ⁻¹	20

Table 3 XRD lines measured

Sample		Silicon (standard)	
<i>hkl</i>	<i>2θ</i> /deg	<i>hkl</i>	<i>2θ</i> /deg
511	73.7–74.2	311	72.539
440	81.5–82.1	422	121.675 ^a
533	98.4–99.4		
731	125.1–126.2		

a. For Fe K_{α1}. Others for Fe K_α.

Table 4 Conditions of measurements of XRF intensity ratios

Target	W
Voltage/kV	25
Current/mA	4
Anal. crystal	LiF
Path	vacuum
Collimator	fine
Detector	FC+SC
Scanning speed/deg min ⁻¹	1/4
Time constant/s	4

equipped with a tungsten tube was used for the qualitative analysis and the measurements of XRF intensity ratios of Mn K_α/Fe K_α and Zn K_α/Fe K_α. The sample powder of about 0.5 g was placed in a small bag made of 6 μm Mylar film, and analyzed under the conditions of Table 4. In order to prevent counting losses arising from very high intensities of Fe K_α, an aluminum filter 0.3 mm thick, attached to the apparatus, was inserted between the tube window and sample. The Fe K_α intensities without the filter were calculated by using the absorption coefficient of the filter measured with a smaller iron-containing sample.

Results and Discussion

Qualitative and chemical analyses

The results of the XRF analysis showed that the samples other than "A" contained small amounts of Mn and Zn, and trace amounts of Cr which were negligible for the discussion here. Table 1 shows results of chemi-

cal analysis.

Relationships between XRF intensity ratios and mole ratios of MnO and ZnO against (2Fe₂O₃+FeO)

Linear relationships were obtained between Mn K_α/Fe K_α or Zn K_α/Fe K_α intensity ratios and mole ratios of MnO or ZnO against (2Fe₂O₃+FeO) with relative standard deviations (RSD) of 12% for MnO and 8% for ZnO at the mole ratio of 0.005, as shown in Fig. 1. The slopes, *S*_{Mn} and *S*_{Zn}, of the regression lines for Mn and Zn were 1.63 and 0.87, respectively.

Relationship between composition and lattice constant of the solid solutions

Figure 2 shows the relationship between the observed

Fig. 1 Relationships between XRF intensity ratios and mole ratios of manganese or zinc oxides against iron oxides (2Fe₂O₃+FeO). Equation for MnO: $y=1.63x$, $\sigma(x)=0.0006$ (12% in RSD at $x=0.005$); for ZnO: $y=0.87x$, $\sigma(x)=0.0004$ (8% in RSD at $x=0.005$).

Fig. 2 Relationship between observed lattice constant (*a*₀) and sum total of converted mole percentages of divalent metal oxides ($X_{\text{FeO}}+2.84X_{\text{MnO}}+1.8X_{\text{ZnO}}$). $y=8.342+0.001135x$, $\sigma(x)=1.6$ mol%.

Table 5 Comparison between the results of wet and X-ray analyses

Sample	Fe ₂ O ₃ , mol%		FeO, mol%		MnO, mol%		ZnO, mol%	
	Wet	X-Ray	Wet	X-Ray	Wet	X-Ray	Wet	X-Ray
A	57.7	60.3	42.3	39.7	0.00	0.00	0.00	0.00
B	57.0	58.6	41.2	39.9	1.39	1.29	0.37	0.29
C	57.5	56.8	42.0	42.6	0.48	0.59	0.01	0.00
D	72.5	70.6	25.5	27.3	0.53	0.58	1.47	1.44
E	97.6	97.4	0.0	0.0	0.59	0.73	1.75	1.90
F	98.9	98.3	0.4	1.0	0.60	0.69	0.08	0.09

lattice constants a_0 and the total mole percentage as FeO, which was shown by $(X_{\text{FeO}} + c_{\text{MnO}}X_{\text{MnO}} + c_{\text{ZnO}}X_{\text{ZnO}})$ in Eq. (2). The regression line was expressed by the formula: $y = 8.342 + 0.001135x$, $\sigma(x) = 1.6 \text{ mol\%}$, which can be universally used for the analysis of the solid solution.

Comparison between analytical results by the present and wet methods

The observed values of R_{Mn} , R_{Zn} and a_0 were substituted in Eqs. (6) – (9) to obtain mole percentages of the constituents. Table 5 shows analytical results, which are given as mole percentages for convenience in construction of chemical formulas. The differences between the values obtained by the two methods were within 2.6 mol% or 3.4 wt% (4.5% in relative error) for Fe₂O₃, within 2.6 mol% or 1.5 wt% (6.2% in relative error) for FeO, and within 0.15 mol% or 0.08 wt% for MnO and ZnO, which were minor constituents. These relative errors or differences are negligible for the construction of their chemical formulas. The present method is nondestructive and does not include any painstaking procedures such as those needed in the wet analysis. Time required for a complete analysis of a sample is about 30 min, including the calculation time.

References

1. T. Fukasawa, M. Iwatsuki and M. Furukawa, submitted to *Anal. Chim. Acta*.
2. I. Iwasaki, T. Katsura, M. Yoshida and T. Tarutani, *Bunseki Kagaku*, **6**, 211 (1957).
3. J. Kanazawa, H. Maekawa and T. Yokogawa, "X-ray *Bunseki no Shimo* (Adv. in X-ray Anal., Japan)", **13**, 9 (1982).
4. K. Nomura, Y. Ujihira, K. Itoh and K. Honda, *Thin Solid Films*, **128**, 225 (1985).
5. M. Fujinami and Y. Ujihira, *Hyperfine Int.*, **29**, 1475 (1986).
6. JCPDS 19 – 629, 1969.
7. JCPDS 25 – 1402, 1975.
8. JCPDS 10 – 319, 1960.
9. JCPDS 22 – 1012, 1972.
10. Nippon Gakujutsu Shinkoukai (The Japan Association for the Advancement of Science), "Tekkou Kagaku *Bunseki Zensho* (Chemical Analysis of Iron and Steel: A Comprehensive Treatment, in Japanese)", new ed., Vol. 9, p. 38, Nikkan Kougyou Shimbunsha, Tokyo, 1963.
11. JIS M 8124, "Methods for Determination of Zinc in Ores", Japanese Industrial Standards Committee, Tokyo, 1979.

(Received August 14, 1992)

(Accepted November 24, 1992)