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Short Communication

DETERMINATION OF Fe^{2+} CONTENT OF NiZnCo IRON-EXCESS FERRITES BY THERMOGRAVIMETRY

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Experimental results are reported on the determination by thermogravimetry of the iron(II) content of the NiZnCo ferrite with the molar ratio $Fe_2O_3:NiO:ZnO:CoO = 59.0:19.5:20.5:1.0$.

In a previous paper a gravimetric method of determining the Fe^{2+} content of iron-excess ferrites was outlined, and the basic analytical expressions were derived [1]. In the following, we report some tentative experimental results on a NiZnCo ferrite with a molar ratio $Fe_2O_3:NiO:ZnO:CoO$ of 59.0 : 19.5 : 20.5 : 1.0.

In a mixture of oxides with a given molar ratio of α NiO, β ZnO, c CO and $(2-\gamma)$ Fe_2O_3, where $\gamma = \alpha+\beta+c<1$, the fact that a certain amount of Fe^{3+} is transformed to Fe^{2+} during the synthesis of the ferite may be expressed as

$$Fe_2^{3+}O_3 \leftrightarrow 2\theta Fe^{2+}O + \frac{\theta}{2}O_2(g) \tag{1}$$

If the conditions of electroneutrality, mass conservation and crystalline structure invariance (no oxygen vacancies) are considered, the ferrite chemical formula may be expressed as:

$$\left(\frac{m}{4}\right) Ni_pZn_qCo_rFe_y^{2+}Fe_z^{3+}[V]_\delta O_4 + \frac{\theta}{2}(g) \tag{2}$$

where [V] means a cation vacancy, $p = 4\alpha/m$, $q = 4\beta/m$, $r = 4c/\mathrm{m}$, $y = 8\theta/m$, $z = 8(2-\gamma-\theta)/m$, $\delta = (2-2\gamma-3\theta)/m$ and $m = 6-2\gamma-\theta$. The number of "moles" formed is $m/4$. For the molar ratio given above, $\alpha = 0.39$, $\beta = 0.41$, $c = 0.02$ and $\gamma = 0.82$. After the ferrite is formed, the Fe^{2+} content may change

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according to

$$\frac{3}{8}[V]+Fe^{3+}+\frac{1}{2}O_F \leftrightarrow Fe^{2+}+\frac{1}{4}O_2(g)$$

where O_F = is the oxygen in the ferrite lattice. However, Eq. (1) must hold for the final equilibrium state in every case, since the only source of Fe^{2+} is through the disappearance of Fe^{3+}, at least in the type of NiZnCO ferrite analysed here.

The value of θ is related to the weight change in the sample during the synthesis procedure by the equation

$$\theta = \frac{PM_i}{8PM(O_2)}(3-\gamma)\left(1-\frac{m_f}{m_i}\right) \tag{3}$$

m_i and m_f being the weights of the unreacted and reacted material, respectively, $PM(O_2)$ the molecular weight of oxygen and

$$PM_i = 8\left\{\frac{2}{3-\gamma}[\alpha PA(Ni)+\beta PA(Zn)+cPA(Co)+\right.$$
$$\left.+\frac{4(2-\gamma)}{3-\gamma}PA(Fe)+4PA(O)\right\}$$

where PA(Ni) is the atomic weight of Ni, and so on [1].

The mixed raw materials, calcined at 950° and milled, were formed into 30 g toroidal samples at 2.5 ton/cm², with the addition of polyvinyl alcohol, heated slowly to 700° and maintained for 8 h at this temperature, in order to eliminate the polyvinyl alcohol and any Fe^{2+} formed at 950° [2]. No weight changes were detected in the samples when the treatment was repeated. Afterwards, the samples were sintered in air for 1 h, in pairs. In every case, one of the samples was cooled rapidly in the air, while the other was allowed to remain in the furnace, being cooled slowly to room temperature during not less than 24 h. The results obtained are shown in the following Table: m_i is the initial weight, m_f the final weight, and T_s the sintering temperature.

T_s, °C	m_i, g	m_f, g	θ	y
		(fast cooling)		
1200(a)	28.534	28.421	0.062	0.115
1200(b)	28.660	28.540	0.066	0.123
		(slow cooling)		
1160	28.567	28.510	0.315	0.058
1200(a)	28.852	28.797	0.0340	0.063
1200(b)	28.516	28.462	0.0299	0.055

The agreement in the values of the parameter y, which denotes the Fe^{2+} content, is reasonable if we take into account the simplicity of the method as compared with the usual chemical analysis of Fe^{2+} content [3]. However, some objections to the method are that both unsintered and sintered samples have a strong tendency to absorb water from the atmosphere, and that when the samples are cooled rapidly they usually crack or break. These features tend to distort the weight measurements, and must be carefully controlled to obtain good results. Much better results can be expected in an automatic thermobalance with continuous recording.

The fair the agreement in the case of the slowly cooled samples, even for the different sintering temperatures, suggests that the oxygen interchange with the atmosphere become negligibly small at about the same temperature for all samples, and that the kinetics of oxygen interchange at higher temperatures is fast enough, relative to the established cooling rate, to maintain a virtual oxygen equilibrium between the sample and the atmosphere.

If the mean value of θ is taken for the slowly cooled samples (0.0318) and the above equations are used, the chemical formula of this ferrite, sintered in air and cooled slowly to room temperature, may be written with fairly good approximation as

$$Ni_{0.36}Zn_{0.38}Co_{0.018}Fe^{2+}_{0.06}Fe^{3+}_{2.12}[V]_{0.6}O_4$$

In iron-excess NiZnCo ferrites, the possibility of Ni^{3+} or Co^{3+} being present is excluded [4]. In other iron-excess systems, e.g. MnZn ferrites, the analysis of the results may become more involved, because of the "electron hopping" $Fe^{3+} + Mn^{2+} \leftrightarrow Fe^{2+} + Mn^{3+}$ [5].

References

1 A. González Arias, Latin Am. J. of Met. and Mat., 6 (1986) 2.

2 A. Morita and A. Okamoto, Proc. Int. Conf. Ferrites, Japan, 1980.

3 J. G. M. de Lau, Philips Res. Rpts. Suppl. No. 6, 1975.

4 J. G. M. de Lau and A. B. von Groenou, J. de Phys., Coll. C1, Suppl. A, 38, c1–17, 1977.

5 S. Krupička and P. Novák, Oxide spinels, Ch. 4 in "Ferromagnetic Materials", Vol. 3, North Holland Publ. Co., 1982.