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Thermogravimetric determination of the oxygen non-stoichiometry in $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ and $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$

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Abstract

Ni–Zn ferrite is a magnetic material that is used commercially in high-power devices, such as transformer and inductor cores. The important properties of this material are highly dependent on its oxygen non-stoichiometry. The processing of ferrites having the desired oxygen non-stoichiometry requires knowledge of the relationship between non-stoichiometry and the temperature and the partial pressure of oxygen.

Two Ni–Zn ferrites having compositions in the technologically important range were prepared by a spray-drying technique. The initial degree of oxidation was determined by coulometric titration. The PO_2 vs. temperature phase diagrams for these ferrites were then determined by thermogravimetry under atmospheres of varying PO_2, 2×10^{-4}–1 atm, in the 800–1400°C range. Isostoichiometric lines are shown on plots of log PO_2 vs. $1/T$. The heat of oxidation was calculated from the slopes of the isostoichiometric lines. © 1998 Elsevier Science B.V.

Keywords: Nickel–zinc ferrite; Oxygen non-stoichiometry; Spine

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1. Introduction

Oxygen non-stoichiometry plays an important role in the magnetic, electrical, and mechanical properties of ferrite materials. The oxygen non-stoichiometry varies with temperature and the partial pressure of oxygen. The desirable stoichiometries typically can be attained only at high temperatures. In addition, the desirable phase, spinel, is single phase only in a high-temperature region. Below this region, a second phase, hematite (α-Fe_2O_3), precipitates [1,2] and has an undesirable affect on the useful properties of the material. Though ferrites can be quenched in order to maintain the spinel structure having the proper oxygen non-stoichiometry, the intense thermal shock fractures most ferrites and, often, compositional gradients are set up within the ferrite. The preferred processing technique is, therefore, a slow cool in which the temperature and the partial pressure of oxygen are carefully controlled to maintain the proper phase and stoichiometry. The processing of ferrites, in this way, requires precise knowledge of the relationship between non-stoichiometry and the temperature and the partial pressure of oxygen. While these relationships are known for a wide variety of Mn–Zn ferrites [3–9], they are known only for a very limited number of Ni–Zn ferrite compositions [1,10].

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2. Experimental

2.1. Preparation of ferrites

Reagents used in the preparation of the nickel–zinc ferrite materials were $FeSO_4{\cdot}7H_2O$ (Allied Chemical), $NiSO_4{\cdot}6H_2O$ (Fisher Scientific), and $ZnSO_4{\cdot}7H_2O$ (Mallinckrodt). All reagents were assayed carefully for water content by thermogravimetry (Perkin–Elmer TGA7). The iron, nickel, and zinc sulfates were found to contain 33.23, 33.09, and 40.66 wt% water, respectively. These sulfates were carefully weighed into the proper proportions to make $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ and $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$. The sulfates were then dissolved in water and spray dried. The resulting powder was fired at 1000°C for ≈12 h under a flowing air atmosphere. The phase purity of the resulting ferrite was confirmed by powder X-ray diffraction (Scintag PAD-V).

The ferrite powder was ground in a mortar together with polyethylene glycol (8000 Powder NF, Union Carbide) to have a ferrite : polyethylene glycol mass ratio of 2 : 1. The ferrite/binder was pressed into pellets using a 0.500" diameter die under 1000 lb of pressure (∼5100 psi). The amount of ferrite/binder used for each pellet was 750 mg. The pellets were fired at 1000°C for 24 h under flowing air. Though samples appeared to be single-phase spinel by powder XRD, observation under an optical microscope revealed a second phase. which appeared as very small black areas in an otherwise brown pellet.

2.2. Thermogravimetry

Thermogravimetry (TG) was conducted using a Perkin–Elmer TGA7 thermogravimetric analyzer (TGA). The TGA was fitted with a sapphire hang down wire in order to eliminate the problem of platinum loss associated with a standard platinum hangdown wire at high temperatures and high oxygen partial pressures. A sample holder was fabricated from 0.2 mm diameter Pt-30% Rh wire in the form of a stirrup. Pt-30% Rh wire was chosen over 100% Pt wire in order to minimize platinum loss. This holder was made large enough to hold two, 500 mg ferrite pellets.

Purge gases were directed first through a drying column containing anhydrous calcium sulfate, a mass-flow controller, the balance chamber of the TGA, and the furnace tube. The oxygen partial pressure of the exiting gas was measured using a zirconia-based oxygen analyzer (Illinois Instruments Model 3000). Prior to each analysis the appropriate gas, either 100% oxygen, air, 2% oxygen/balance nitrogen, or 0.2% oxygen/balance nitrogen, was purged through the TGA until the oxygen partial pressure of the exiting gas, as measured by the oxygen analyzer, matched that of the entering gas. The gas-flow rate was then set to 10 ml min^{-1} on the mass-flow controller where it remained for the duration of the analysis.

After taring the balance, two of the previously prepared ferrite pellets (500 mg each) were placed on the sample holder. The sample was maintained at room temperature under flowing atmosphere until thoroughly dehydrated and a constant mass was attained. Before starting the furnace program, verification was made that the oxygen partial pressures of the entering and exiting gas streams were identical.

The temperature programs used for the analyses varied with ferrite composition and partial pressure of oxygen in the atmosphere. It was determined that 800°C was the lowermost temperature at which equilibrium could be attained in a reasonable amount of time for any ferrite under any atmosphere. Thus, all thermal programs started with an initial isotherm near 800°C. Subsequent isotherms were programmed in 50°C increments to an upper limit of 1400°C. In some cases, where the rate of platinum and zinc loss became extremely high at temperatures below 1400°C, the upper temperature limit was decreased. The furnace was subsequently programmed to cool with isotherms at 50°C decrements falling at temperatures between the isotherms reached during heating. Thus, when heating and cooling data were combined, equilibrium mass data were collected every 25°C between ≈800 and 1400°C. The furnace was ramped to the initial isotherm at a rate of 20°C min^{-1}. All subsequent isotherms were reached by heating or cooling at a rate of 5°C min^{-1}.

Samples were maintained at isotherms until reaching an equilibrium mass. Equilibrium was defined as the point after which there was no measurable change in mass for a 10-minute period. In cases where platinum and/or zinc losses occurred, equilibrium was defined as the point where the rate of mass loss became constant. An equilibrium point (mass, temperature, time) was recorded for each isotherm. For isotherms during which platinum and/or zinc loss occurred, two, additional equilibrium points were recorded for later determination of the rate of platinum/zinc loss.

Samples of each ferrite composition were run under each of the four different atmospheres. Separate but identical pellets were used under each atmosphere.

2.3. Fe^{2+} analysis

Fe^{2+} content was determined by coulometric titration using chlorine [11].

3. Results and discussion

The equilibrium masses determined from TG experiments were corrected for buoyancy using the ideal gas law, and then corrected for platinum and zinc loss. Platinum and/or zinc loss was assumed to have occurred if a sample reached a state of constant mass loss during an isotherm. At each of these isotherms, the rate of mass loss (mg/min) was calculated using two mass vs. time points. This rate of mass loss represented the combined rates of platinum and zinc loss. Rates of platinum and zinc loss during heating and cooling steps were taken as the average rate of mass loss between the preceding and following isotherms. The cumulative platinum/zinc loss could then be calculated based on how long the sample spent at each temperature. The cumulative platinum/zinc loss at each equilibrium point was then added to the buoyancy-corrected mass at that point.

The corrected masses were converted to mass percent, and an excess oxygen coefficient, γ, was assigned to each mass percent value. The corrected masses were simply divided by the initial sample mass in order to obtain mass percent. Values of γ were assigned based on the following oxidation reaction for stoichiometric ferrite:

$$\begin{aligned} &M^{2+}_{1-x}Fe^{2+}_{x}Fe^{3+}_{2}O^{2-}_{4} + \gamma/2O_2 \\ &\rightleftarrows M^{2+}_{1-x}Fe^{2+}_{x-2\gamma}Fe^{3+}_{2+2\gamma}O^{2-}_{4+\gamma} \end{aligned} \quad (1)$$

where x=0.250 and M_{1-x}=$Ni_{0.375}Zn_{0.375}$ or $Ni_{0.563}Zn_{0.188}$.

As coulometric experiments showed that the starting ferrites contained no Fe^{2+}, γ values of 0.125 were assigned to mass%=100.000%. The molar masses of Ferrite 316 and Ferrite 226 with γ values of 0.125 were calculated to be 238.19 and 237.00 g, respectively. The molar masses of stoichiometric (γ=0.000) $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ and $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$ are 236.19 and 235.00 g, respectively. Thus, γ=0.000 was assigned to 99.160% (236.19 g/238.19 g×100%) for $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ and 99.156% (235.00 g/237.00 g×100%) for $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$. Intermediate values of mass percent for each ferrite were then assigned γ values by interpolation.

Values of gamma and mass percent were plotted as a function of temperature and are shown in Figs. 1 and 2. These figures can be divided into two regions based on the reversibility of the weight change: a high-temperature reversible range and a low-temperature irreversible range. The high-temperature range represents the single-phase spinel region of the phase diagram, while the low-temperature range represents the two-phase (spinel and α-Fe_2O_3) region [1]. The spinel phase is metastable change below the phase boundary; therefore, the mass change is irreversible. Had the ferrite reverted entirely to the same phases in the same proportion that existed in the starting material, the mass changes would be completely reversible. This metastability is very important, since it allows the desired spinel phase to be maintained at room temperature. If, however, the ferrite is maintained for an extended period at a relatively high temperature (>700°C) that is below the phase boundary, α-Fe_2O_3 will slowly precipitate.

The γ vs. temperature plots for both ferrites were fitted to fourth-order polynomials (Tables 1 and 2) using Table Curve® 2D (Jandel Scientific Software) curve-fitting software. A fourth-order polynomial was chosen because of its consistently good fit between the various plots and because of its simplicity. Slightly higher order polynomials (i.e. fifth or sixth order) did not produce a significantly better fit.

For each PO_2, fitted curves of γ vs. temperature data were used to determine the temperatures at which a predetermined set of γ values occurred. The points for each value of γ were then plotted on a log PO_2 vs. $1/T$ diagram (Figs. 3 and 4). Isopleths were drawn by a least-squares fit to the log PO_2 vs. $1/T$ data for each value of γ.

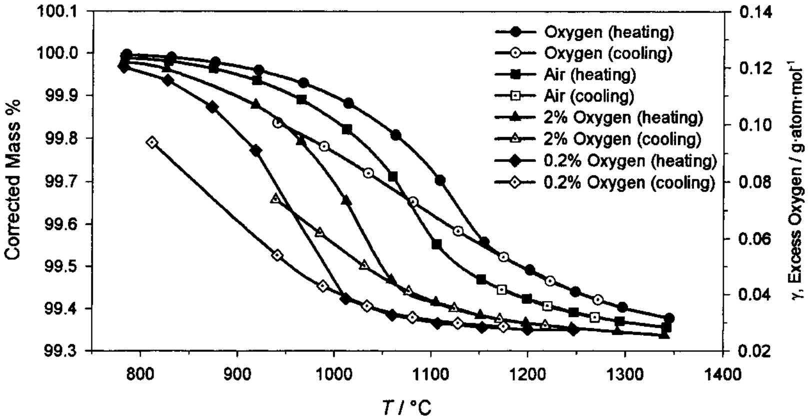

Fig. 1. Excess oxygen coefficient and corresponding mass percent as a function of the temperature and the partial pressure of oxygen for $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$.

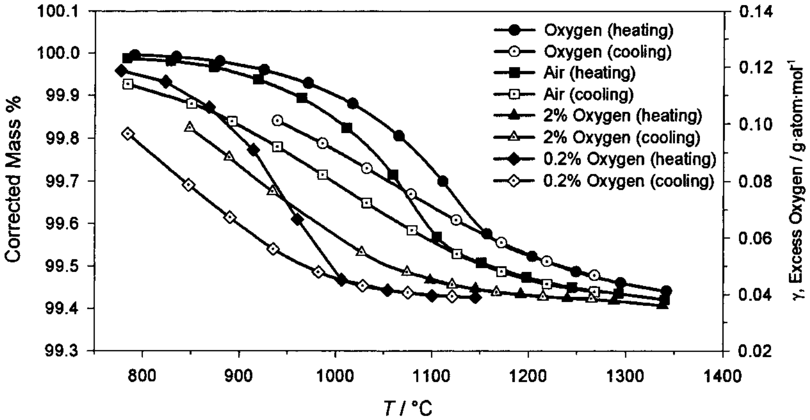

Fig. 2. Excess oxygen coefficient and corresponding mass percent as a function of the temperature and the partial pressure of oxygen for $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$.

Table 1
Curve-fit parameters for γ vs. temperature plots for $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$

	$y=a+bx+cx^2+dx^3+ex^4$					
Atmosphere	a	b	c	d	e	r^2
Oxygen	−2.558	9.147e-03	−1.125e-05	5.845e-09	−1.097e-12	1.0000
Air	11.07	−3.289e-02	3.704e-05	−1.868e-08	3.553e-12	0.9996
2% Oxygen	−3.335	1.415e-02	−2.091e-05	1.320e-08	−3.039e-12	0.9995
0.2% Oxygen	−2.450	1.184e-02	−1.938e-05	1.338e-08	−3.349e-12	0.9995

The enthalpies of oxidation of the ferrites (Eq. (3)) were calculated using the slopes of the isopleths.

$$4Fe^{2+}_{(s)} + O_{2(g)} \rightarrow 4Fe^{3+}_{(s)} + 2O^{2-}_{(s)} + \tfrac{3}{2}V_c \qquad (2)$$

$$\log PO_2 = \Delta H/(2.303RT) + \Delta S/R \qquad (3)$$

The slopes of the isopleths in the log PO_2 vs. $1/T$ plots are equal to ($\Delta H/2.303R$), as shown in Eq. (3).

Table 2
Curve-fit parameters for γ vs. temperature plots for $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$

	$y=a+bx+cx^2+dx^3+ex^4$					
Atmosphere	a	b	c	d	e	r^2
Oxygen	−2.909	1.064e-02	−1.359e-05	7.423e-09	−1.483e-12	0.9999
Air	−2.310	9.225e-03	−1.263e-05	7.347e-09	−1.556e-12	0.9997
2% Oxygen	−3.008	1.303e-02	1.960e-05	1.258e-08	−2.946e-12	0.9998
0.2% Oxygen	−4.604	2.096e-02	−3.393e-05	2.370e-08	−6.081e-12	0.9999

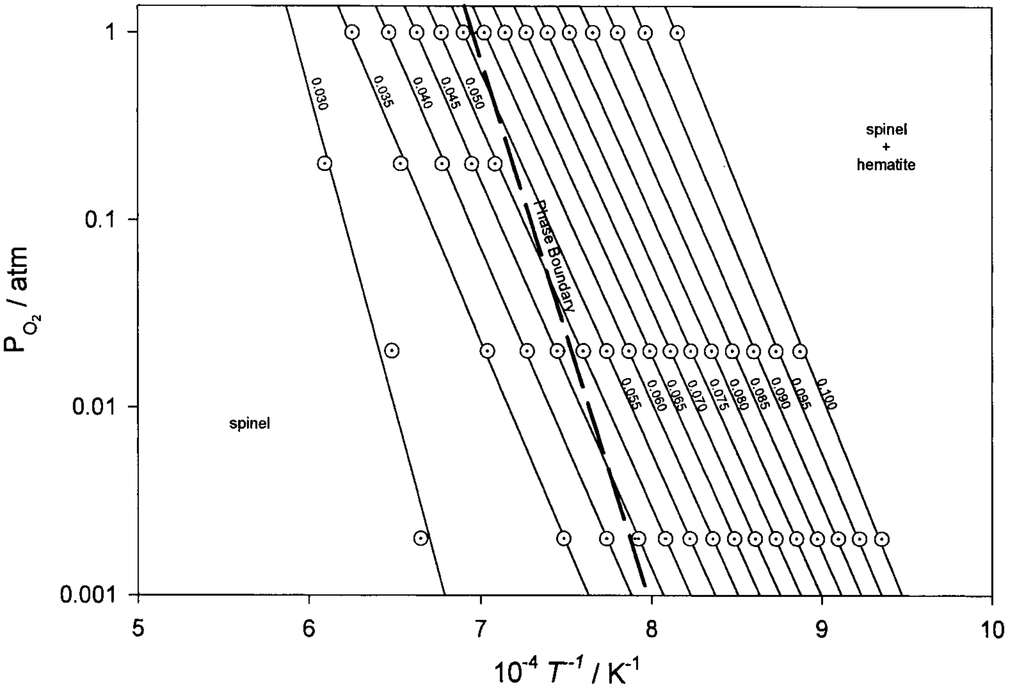

Fig. 3. Isocompositional phase diagram for $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$. Values for γ are shown on isopleths.

The enthalpy of oxidation for $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ was −164.8 kJ/mol^{-1} for γ=0.030 and averaged −99.4 kJ/mol^{-1} for γ=0.035 to 0.100. The enthalpy of oxidation for $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$ was −115.3 kJ/mol^{-1} for γ=0.040 and averaged −93.4 kJ/mol^{-1} for γ=0.045 to 0.100. A change in the nature of the defects for non-stoichiometry is evident from the abrupt change in slope on going from γ=0.030 to 0.035 in $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ (Fig. 3) and from γ=0.040 to 0.045 in $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$ (Fig. 4). The fact that this change occurs over a different range of γ for the two ferrites is consistent with the previous observation [9] that this change is compositionally dependent.

4. Conclusions

1. Isocompositional phase diagrams were developed for two Ni–Zn ferrite compositions, $Ni_{0.563}Zn_{0.188}Fe_{2.25}O_{4+\gamma}$ and $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$, in the range 700–1400°C and in the PO_2 range 2×10^{-3}–1 atm.

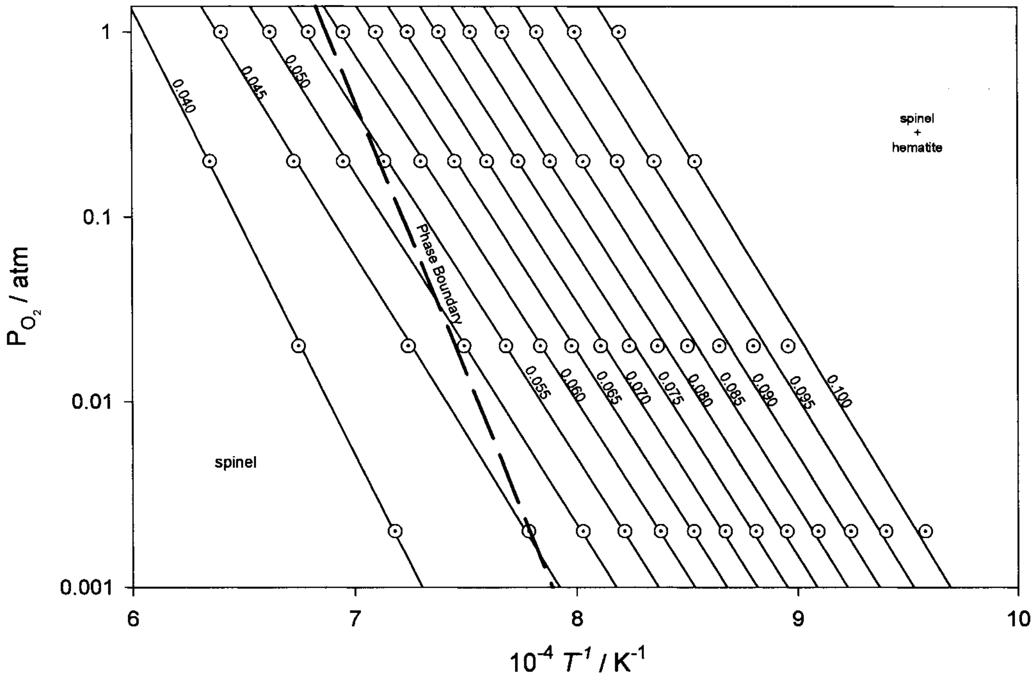

Fig. 4. Isocompositional phase diagram for $Ni_{0.375}Zn_{0.375}Fe_{2.25}O_{4+\gamma}$. Values for γ are shown on isopleths.

2. Enthalpies of oxidation and cation vacancy formation were determined for both ferrites. They fell into two ranges based on the degree of non-stoichiometry.
3. The phase boundary between the single-phase spinel and the two-phase spinel/hematite regions was established for both ferrites.

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