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Quantitative Analysis of Zinc Vaporization from Manganese Zinc Ferrites

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Zinc vaporization of Mn-Zn ferrites was quantitatively characterized in terms of oxygen partial pressure P_{O_2}, temperature, grain size and sample geometry. The amount of zinc loss was measured as a function of time at various temperatures by a thermogravimetric method. The weight loss due to irreversible zinc vaporization showed a linear behavior with time and increased exponentially with temperature. The observed weight loss due to zinc evaporation at 1100°C was small, whereas a significant weight change was detected at 1200°C. The weight loss was even greater in a reducing atmosphere ($P_{O_2} = 5 \times 10^{-5}$). Below 1300°C, the diffusion of elemental zinc was sufficiently fast to compensate the zinc loss at the interface region, resulting in a linear dependence on time. At temperatures ≥1400°C, the weight change no longer followed the linear dependence and showed a rather parabolic behavior with a concave upward slope. The core shape and the gas flow around ferrite cores were important factors that affected the rate of zinc vaporization, but not the grain size.

I. Introduction

The zinc ion preferentially occupies the tetrahedrally coordinated A site of the spinel structure in Mn-Zn ferrites; the other cations occupy either A sites or octahedrally coordinated B sites. Nonmagnetic zinc ions consequently decrease the magnetic cancellation between A and B sites, leading to an increase in the net magnetic moment of Mn-Zn ferrites.[1] Thus, the addition of ZnO is an essential way to obtain the desirable high permeability of Mn-Zn ferrites; 18–23mol% of ZnO for high permeability materials and 8–13mol% for low-loss materials.[2]

Zinc vaporization has been recognized as troublesome during sintering of Mn-Zn ferrites, because ZnO is easily reduced and evaporates.[3] Slick and Basseches[4] reported that zinc vaporization is significant at low oxygen activities under high temperature. The reduction reaction and mass action expression of the zinc vaporization can be written as[5]

$$\mathrm{ZnO} = \mathrm{Zn}(g) + \tfrac{1}{2}\mathrm{O}_2(g) \tag{1}$$

$$P_{\mathrm{Zn}} = \frac{K}{\sqrt{P_{\mathrm{O}_2}}} \tag{2}$$

P_{Zn} and P_{O_2} are the zinc vapor pressure and the oxygen partial pressure, respectively. Consequently, zinc vaporization decreases the Zn content from the original ferrite formula, resulting in adverse effects on microstructures and electromagnetic properties. The concentration of ferric ions (Fe^{3+}) would be decreased to offset the zinc vaporization.[6] It was reported that the zinc vapor phase enhances grain growth and development of a duplex structure.[7] The initial permeability decreases with increasing zinc loss, whereas tan δ/μ_o and ferrous iron concentration increase.[8] It was also reported that the stacking condition of ferrite cores for sintering as well as the setter under ferrites have crucial effects on zinc loss and on electromagnetic properties.[9–12]

Although numerous problems due to zinc loss are recognized, little work has been done on quantitative analysis of zinc losses during sintering. Few experimental results have been on EDAX and EPMA studies of the subsurface region of ferrite cores.[8–11] This study will provide the *in situ* weight change at high temperature and quantitatively analyze the zinc loss. Zinc loss behavior will be also discussed in terms of sample geometry and oxygen activity.

II. Experimental Procedure

Mn-Zn ferrites of a composition $\mathrm{Mn_{0.72}Zn_{0.22}Fe_{2.06}O_4}$ were prepared by a conventional ceramic processing technique. The ingredient raw materials were mixed in a planetary mill, calcined at 950°C for 3 h, and then pulverized to obtain a mean particle size of ~1.2 μm. The granulated powder was formed into various shapes as shown in Table I. A thermobalance (Model D101, Cahn, Madison, WI) was used to measure zinc evaporation from Mn-Zn ferrites. The sample was hung with Pt wire in a vertical furnace and then heated to the measurement temperatures with the heating rate of 250°C/h. A mixture of air and nitrogen gas ($P_{\mathrm{O}_2} = 5 \times 10^{-5}$ atm (5 Pa)) was used to obtain the desired oxygen activity. An overall gas flow of 400 cm^3/min was used to maintain constant P_{Zn} and P_{O_2} because the oxygen activity might change the concentration of the gas phase on the solid surface. The thermobalance coupled with a vertical tube furnace (4.5 cm i.d. and 60 cm length) was designed for sample weights up to 100 g and is sensitive to detect weights as small as 1 μg. In fact the balance sensitivity was limited, at high temperatures, to ~50 μg due to convection currents. This was sufficient to detect the weight change of full size ferrite cores at the elevated temperature range.

III. Results and Discussion

Figure 1 shows the *in situ* weight change of cylindrically pressed compacts of ZnO powder as a function of heating time under air ($P_{\mathrm{O}_2} = 0.21$) and nitrogen ($P_{\mathrm{O}_2} = 5 \times 10^{-5}$) at various

Table I. Weight, Surface Area, and Specific Surface Area for Specimens of Different Geometries

Shape	Weight (g)	Surface area (cm^2)	Specific surface area (cm^2/g)
Toroid	15	27.8	1.85
	8	15.1	1.88
	8	18.5	2.31
	3	8.67	2.89
Cylinder	40	32.7	0.82
	10	7.89	0.79

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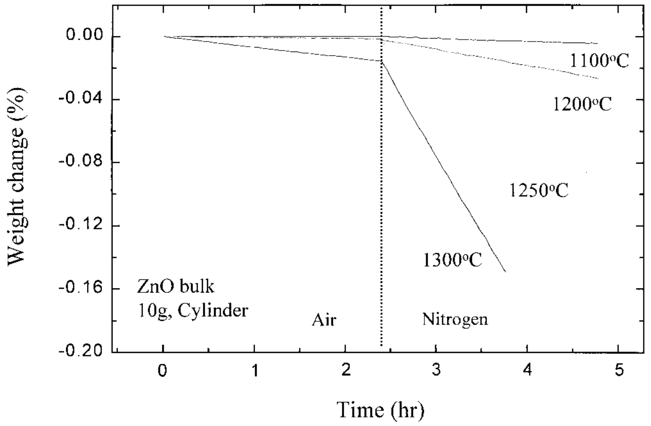

Fig. 1. Weight losses from pure ZnO compacts as a function of time for various temperatures.

temperatures. The weight decreases linearly with time and the slope of weight change versus time depends on the process temperature and oxygen activity. A small weight loss was observed at 1100°C in nitrogen, whereas there was a significant change in the slope at 1300°C when the zinc evaporation rate was ~ 0.1 wt% per hour. These results are in good agreement with the zinc vapor pressure expressed in Eq. (2), which is inversely proportional to the square root of oxygen partial pressure and proportional to the equilibrium constant, i.e., increasing exponentially with temperature. The zinc vapor pressures, 9.66×10^{-6} atm (966 kPa) and 1.63×10^{-3} atm (163 Pa) were calculated at 1100° and 1300°C, respectively. The linear dependence of weight change on time implies that the vaporization rate was independent of diffusion processes such as zinc migration to the sample surface, and the zinc vapor pressure on the surface of specimens was maintained at a constant value. This result is acceptable because the vertical process tube (~950 cm^3) was flushed with enough gas (450 cm^3/min) to ensure the constant ambient pressure condition.

Mn-Zn ferrites are nonstoichiometric oxides consisting of transition-metal ions and their ionic state is easily changed. The oxidation state of these specimens could be affected by temperature and oxygen partial pressure (P_{O_2}). Thus, the weight change due to oxidation–reduction during sintering should be taken into account. The related equation can be written as:[13]

$$\frac{2}{3}\,\mathrm{Fe}^{3+} + \frac{1}{3}\,\mathrm{Mn}^{3+} + \frac{3}{8}\,V_{\mathrm{C}} + \frac{1}{2}\,\mathrm{O_O}^{2-} = \frac{2}{3}\,\mathrm{Fe}^{2+} + \frac{1}{3}\,\mathrm{Mn}^{2+} + \frac{1}{4}\,\mathrm{O}_2 \qquad (3)$$

V_{C} and $\mathrm{O_O}$ represent the cation vacancy and the oxygen ion on the normal oxygen lattice site, respectively. The forward direction represents the reduction reaction; half mole of oxygen releases from the spinel crystal together with the corresponding disappearance of cation vacancies. Thus, the forward reaction results in weight loss, the reverse reaction leading to weight gain.

Figure 2 shows the weight change of ferrite cores after switching from air to nitrogen at 1100°–1300°C. Unlike the weight change of ZnO as shown in Fig. 1, no weight change was observed in air even at 1300°C, and drastic weight changes occurred just after switching to nitrogen, followed by a linear weight change with time. The abrupt weight change is presumably due to the reduction reaction as described in Eq. (3). It should be noted that the abrupt weight change (%) at 1100°C is greater than at 1200° and 1300°C. This is in good agreement with the previous result that there is an abrupt change of slope in the equilibrium ferrite weight change with temperature as the temperature is lowered.[14] At 1100°C, in a nitrogen atmosphere, the specimen gets to an equilibrium state within a reasonable period of time (<3 h). However, equilibrium states were not attained under nitrogen at 1200° and 1300°C. Such a continuous weight change is attributed to zinc loss. The oxidation–reduction reaction is reversible, whereas the zinc loss is irreversible. Thus, the net weight loss due to the zinc evaporation could be separated from the total weight change. The reversible process does not develop any permanent weight change, but the zinc evaporation would result in permanent weight losses.

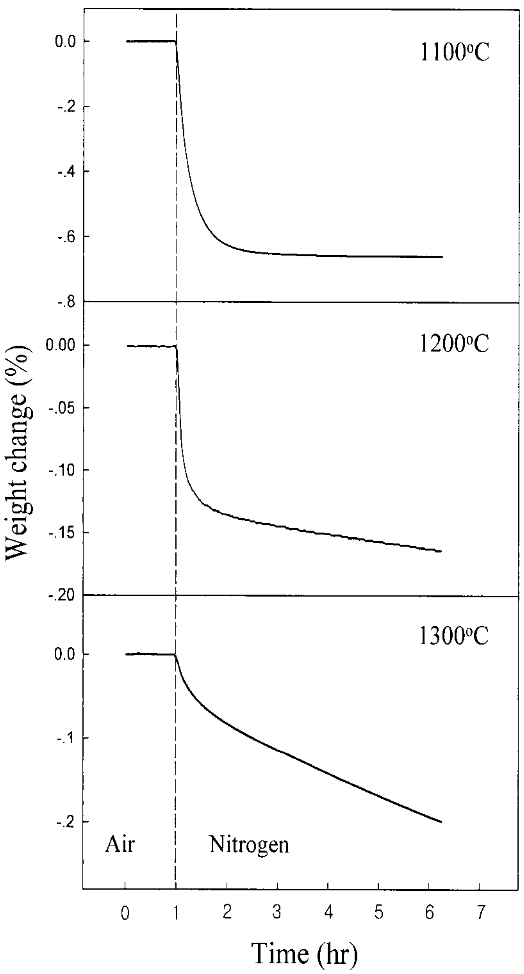

Fig. 2. Weight losses from pure Mn-Zn ferrites as a function of time for various temperatures.

Figure 3 shows a sequential weight change of a ferrite core at two different levels of oxygen activity, air and nitrogen ($P_{O_2} = 5 \times 10^{-5}$ atm) at 1100° and 1200°C as a function of sintering time. The specimen attained an equilibrium state within a reasonable period of time at 1100°C. After switching to air, the specimen gained the weight and recovered its original state with a slight weight loss. However, the specimen did not recover its previous state at 1200°C, leaving behind a permanent weight change of ~0.05%, which is equal to the linear weight loss followed by the abrupt change due to the reduction reaction. This confirms that the compositional deviation of Mn-Zn ferrites after heating is attributable to zinc evaporation.

Figure 4 shows a series of weight changes under a periodic atmosphere control: alternating oxygen activities with a fixed pattern of 9.5 h reduction in nitrogen and 6 h oxidation in air at 1200°C. The repeated oxidation processes made the ferrite cores completely oxidized and recovered to their previous state except for the zinc evaporation during the reduction step. It should be noted that the maximum points after oxidation and the minimum points after reduction lie on the straight lines with the same slope. This result supports the assumption that the oxidation–reduction reaction does not cause any permanent weight change and the alternating P_{O_2} switch does not change the rate of Zn-evaporation. However, as the sintering time increases at 1200°C, the density and microstructure of ferrite cores would change because of the

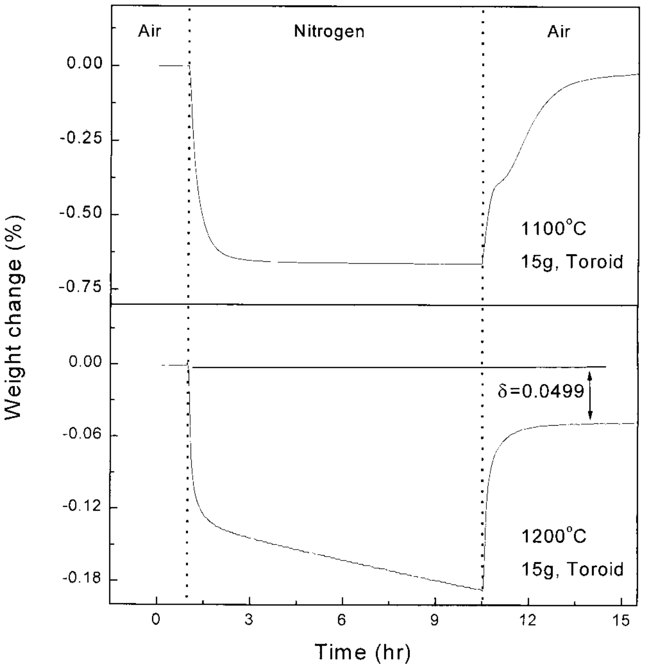

Fig. 3. Weight change of a ferrite core under periodic atmosphere control at the 1100° and 1200°C isotherms.

progress of sintering. Figures 5(a) and (b) show the microstructures of the specimens sintered for 1 h and 35 h, respectively, at 1200°C,. An obvious difference can be seen between them in densification amounts with significant grain growth. The specimen shown in Fig. 5(b) was sintered under the alternating oxygen activity for 35 h as scheduled in Fig. 4. It is an interesting result that microstructural developments such as grain growth and densification do not affect the zinc loss kinetics as well as the oxidation–reduction reaction rate, the maximum and minimum points lying on the straight line.

The weight change due to zinc losses shows a linear time dependence at 1200°C as shown in Fig. 2. This result implies that the diffusion of elemental zinc from bulk to surface is sufficiently fast to compensate the zinc loss at the specimen surface, similar to water evaporation in swimming pools. At 1400°C the weight change no longer follows a linear dependence as shown in Fig. 6. The rate of weight change decreases with time, showing a rather parabolic behavior, and the abrupt weight change, which normally occurs just after switching to a nitrogen atmosphere, is not observed. The weight change due to the reduction reaction on switching from an air to a nitrogen atmosphere seems negligibly small compared with the zinc loss. The disappearance of the abrupt weight change is attributed to the trivial change in the oxidation degree as reported in the phase equilibrium diagram of Mn-Zn ferrites.[14] The fast evaporation rate depreciates the ZnO concentration at the surface region, lowering the amount of vaporization. The evaporation rate depends on the ZnO content; the more the

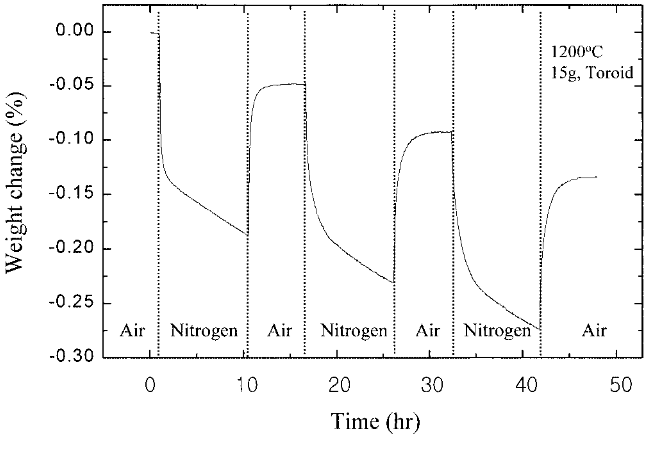

Fig. 4. Weight change of a ferrite core under periodic atmosphere control at the 1200°C isotherm.

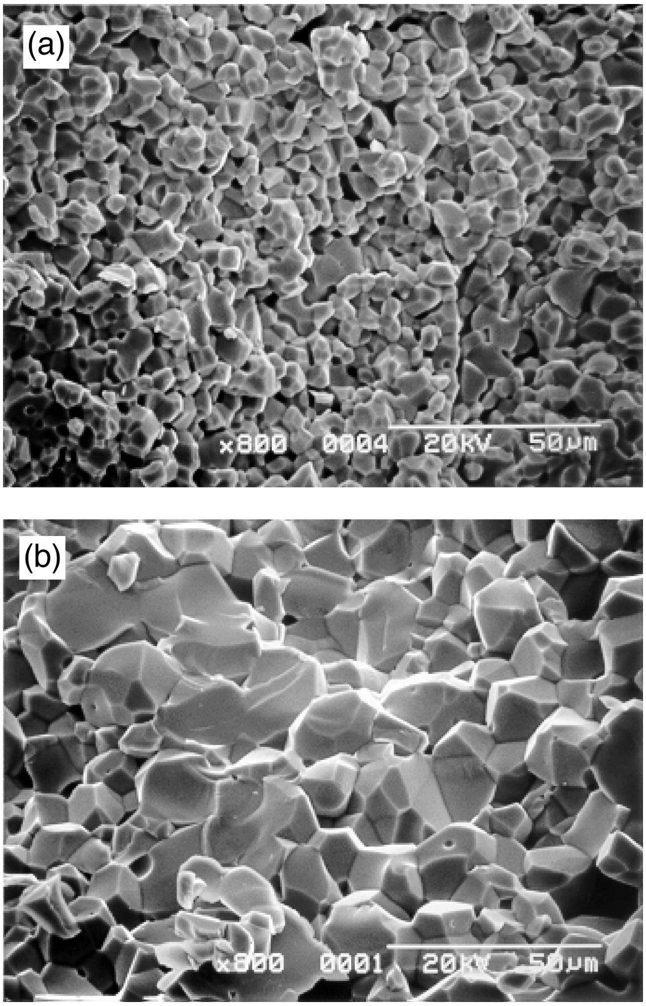

Fig. 5. SEM micrographs showing microstructures of fractured surfaces of Mn-Zn ferrites sintered at 1200°C for (a) 1 and (b) 35 h.

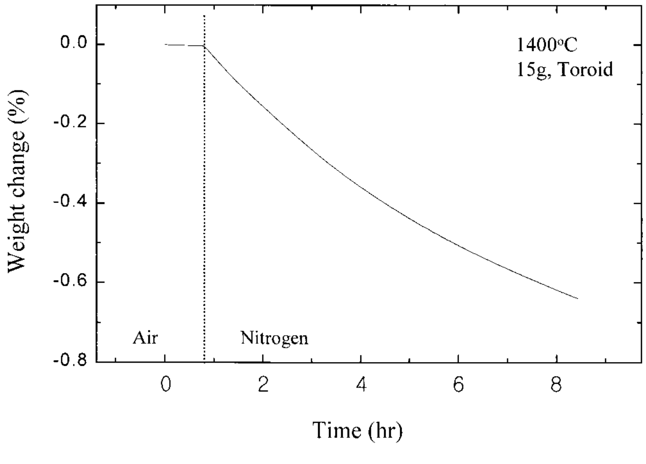

Fig. 6. Weight loss from Mn-Zn ferrites with time at 1400°C.

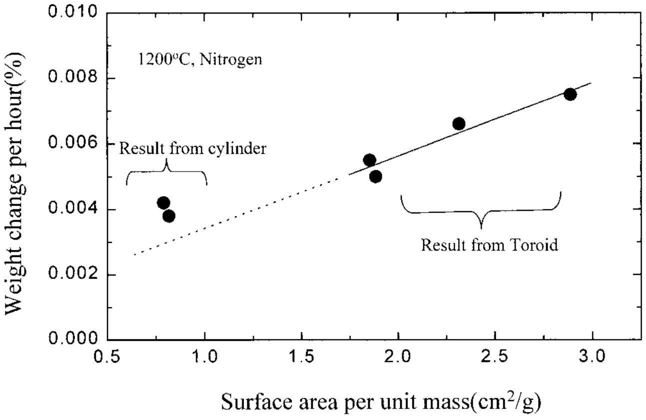

Fig. 7. Weight loss per hour (%) as a function of specific surface area for toroidal and cylindrical ferrite cores.

ZnO on the surface area the higher the rate of weight loss. It thus leads to a parabolic behavior of zinc vaporization because the bulk diffusion of ZnO to the surface area controls the evaporation kinetics. However, weight loss due to zinc evaporation, obtained from the total weight change less that due to the reduction reaction, still has an important meaning from a practical point of view. A processing condition as severe as heating at 1400°C is not common in real sintering processes.

Figure 7 shows the weight change per hour as a function of specific surface area of toroidal and cylindrical ferrite cores. As summarized in Table I, the surface area of specimens per gram depends on sample geometry. It is interesting that the cylindrical specimen shows larger weight changes than those estimated from the extrapolation of toroidal specimens. The vapor pressure depends on the surface curvature. Toroidal specimens have a concave surface (inner radius) as well as a convex surface (outer radius), whereas cylindrical specimens have only a convex surface. In addition, the gas flow would be stagnant at the inner side of the toroid cores. The bare specimens showed five times greater evaporation rate than cores put in an alumina crucible. These results indicate that the core shape and gas flow around ferrite cores are important factors affecting zinc vaporization.

IV. Conclusion

Zinc vaporization from Mn-Zn ferrites was quantitatively analyzed by a thermogravimetric technique. The amount of zinc loss was determined by a periodic change of atmosphere. As the zinc vaporization is an irreversible reaction, it was possible to separate the net amount of zinc weight loss by subtracting the weight change due to oxidation–reduction from the total weight change. Thus, the irreversible process results in permanent weight losses. At 1100°C a negligibly small weight loss was observed with zinc evaporation, whereas at 1200°C a significant weight change due to zinc loss was detected. The weight loss stemming from zinc vaporization increased exponentially with temperature. Below 1300°C, the weight loss was a linear function of time, indicating that the diffusion of elemental zinc to the surface of specimens is fast enough to compensate the zinc loss at the interface region. However, at 1400°C the weight change no longer followed the linear dependence and showed a rather parabolic behavior with a concave upward. It was confirmed that the rate of zinc vaporization is strongly influenced by the core shape and the gas flow around ferrite cores but is not affected by the grain size.

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