Synthesis and Sintering of Active Manganese(II) Zinc Ferrite Powders[†]

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Manganese(II) monoxide which is spontaneously oxidized in air is stabilized by solid solution with zinc oxide and then employed as a raw material in the synthesis of manganese(II) zinc ferrites in an inert atmosphere, giving thereby no chance for Mn^{2+} to get oxidized. Sintering is done in a static controlled atmosphere created by the thermal dissociation of pellets of active iron(III) oxide kept in oxygen-free nitrogen along with the ferrite toroids. The ferrite formation and the sintering are performed at 950 and 1150 °C respectively by employing active oxide raw materials.

The synthesis of manganese(II) zinc ferrites is complicated by the need to have all the manganese as Mn^{2+}, while a small amount of Fe^{2+} is also needed in order to reduce the magnetocrystalline anisotropy or magnetostriction.[1,2] It is not possible to employ manganese(II) monoxide directly as the raw material since this oxide is not stable in air. Conventional methods employ a higher stable oxide of manganese as the raw material[3] or allow the manganese(II) monoxide to get oxidized during the initial calcination.[4] The reduction of Mn^{2+} is subsequently performed by a current of an inert gas such as nitrogen that sweeps off the oxygen produced by the thermal dissociation of the ferrite at the sintering temperature which is usually between 1200 and 1300 °C. Calculated small concentrations of oxygen are mixed with the nitrogen current in order to effect the optimum thermal reduction of Fe^{3+} to Fe^{2+}. This oxygen concentration has to vary with temperature during the sintering cycle so as to cope with the temperature variation of the partial pressure of oxygen in thermal equilibrium with the ferrite.

Quite apart from the complexity and expense of maintaining the flowing current of the controlled atmosphere with varying oxygen concentrations at different temperatures, it is difficult to know in such a process the stage at which the reduction of Mn^{3+} to Mn^{2+} is complete. Even if this reduction is complete, the Mn^{2+} may or may not be situated completely at the correct lattice sites in the spinel. The Mn^{2+} can enter the spinel lattice only after it is formed by the thermal reduction of Mn^{3+}; but the possibility of harmful non-spinel forming solid state reactions before such a reduction cannot be ruled out. The site-preference for Mn^{3+} is obviously different from that for Mn^{2+} during the solid state reaction among the component oxides. The manganese has to move to the correct lattice site in the ferrite spinel after the subsequent reduction of Mn^{3+} to Mn^{2+}; but this migration in the solid matrix may or may not be complete during the sintering run. One can then expect a considerable degree of non-reproducibility in the final properties of the ferrite even when all the synthetic parameters have been apparently kept constant; and in fact this non-reproducibility of properties is a bugbear in the synthesis of these ferrites.

This difficulty has been overcome in the present investigation by stabilizing the MnO by solid solution with ZnO. It is then possible to prepare the ferrite without oxidation of Mn^{2+}. There is subsequently no need to maintain a running current of the controlled atmosphere in order to reduce the Mn^{3+}. The controlled atmosphere is now necessary only to prevent the oxidation of Mn^{2+} as well as an undue thermal reduction of Fe^{3+}. A static controlled atmosphere suffices for this purpose; and this can be easily obtained by an inert gas in the presence of suitable metallic oxides placed in the high temperature zone. These oxides can supply the required oxygen to the ambient atmosphere by thermal dissociation.

Experimental

(1) Preparation of Raw Materials. Manganese(II) oxalate precipitated from filtered solutions of manganese(II) chloride (AnalaR) and ammonium oxalate (Laboratory Reagent) was washed free from chloride and dried in vacuum. Zinc oxalate prepared similarly could be dried in air at 70°C due to its greater thermal stability. Iron(III) oxide was prepared by adding a concentrated purified iron(III) nitrate solution into an excess of aqueous ammonia. After decanting the supernatent liquid, the precipitate was heated to 250 °C to give pure and active iron(III) oxide. These pure raw materials could be easily estimated gravimetrically; manganese as $MnSO_4$, zinc and iron as the respective oxides by direct ignition.

(2) Preparation of MnO-ZnO Solid Solution. The oxalates of manganese and zinc were mixed in the required proportion and decomposed in a flowing current of oxygen-free nitrogen obtained by passing the cylinder gas through a column of heated reduced copper.[5] The carbon monoxide was disposed off by direct burning. After the evolution of gases ceased, the powder was degassed at 750 °C in order to remove carbon monoxide in particular that is tenaciously chemisorbed by MnO.[6] The system was cooled before taking out the charge which had a fine orange colour and could be safely exposed to air. Chemical analysis revealed the presence of manganess fully as Mn^{2+}.

(3) Preparation of the Ferrite Powder. The above powder containing ZnO and MnO was thoroughly mixed with the requisite amount of iron(III) oxide, pressed as such into pellets and then heated to 950 °C for 8 h in a static atmosphere of pure nitrogen. After cooling, the pellets were found to have become strongly magnetic. They were ground and ball-milled.

(4) Sintering. The sintering of toroids pressed with this ferrite powder could also be done without allowing the Mn^{2+} to get oxidized. The powder was pressed into toroids —3.6 cm o.d., 1.6 cm i.d., 1 cm thickness, employing a

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Table 1. Measurements on sintered manganese(II) zinc ferrite toroids made by the technique described in the paper

Sr. No.	Composition (mol %)			μ_i(initial permeability)		Loss factor $\frac{\tan\delta}{\mu_i}\times 10^6$ at 4 kHz	Curie point °C	Density g cm^{-3}	D.F.[a] × 10^6	T.F.[b] × 10^6
	Fe_2O_3	ZnO	MnO	at 4 kHz	at 100 kHz					
1	51.75	20.25	28	2640	2621	1.15	135	4.72	0.87	1.06
2	51.71	23.13	25.26	2800	2762	1.72	125	4.72	0.45	1.74
3	52.00	19.25	28.75	2720	2701	1.53	150	4.77	1.09	1.42
4	53.06	17.8	29.14	2729	2571	2.7	160	4.82	1.08	0.13

a) D.F.: Disaccommodation factor defined as $(\mu_1-\mu_2)/\mu_1^2 \log(t_2/t_1)$ where μ_1 and μ_2 are the initial permeabilities at 10 min (t_1) and 100 min (t_2) respectively after demagnetization at 23 °C. b) T.F.: Temperature factor defined as $1/\mu^2\, d\mu/dT$ where T is the temperature.

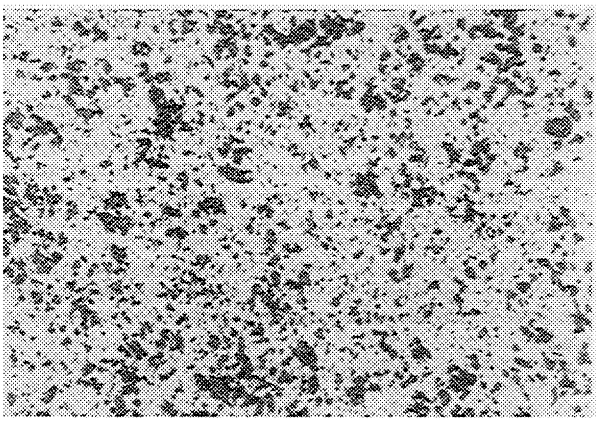

Fig. 1. Photomicrographs of ferrites (present technique) sintered at 1150 °C. Magnification × 100.

volatilizable binder such as camphor. The binder was distilled off in a current of purified nitrogen. The sintering was then done as per the technique given below.

It was however also possible to employ a binder such as polyvinyl alcohol that needs to be burnt out. The Mn^{2+} did of course get oxidized in the process, but subsequent satisfactory reduction could be effected in a run at 1050 °C for eight hours in a static atmosphere of oxygen-free nitrogen and in the presence of a calculated amount of iron powder (pressed as such into pellets) in the closed system. The iron in the hot zone got oxidized by the oxygen given out by the thermal dissociation of the oxidized ferrite; and the reduction of Mn^{3+} back to Mn^{2+} could be effected quantitatively as checked by subsequent chemical analysis. The amount of iron needed in the above reduction was not very critical and a little excess was found to do no harm. After cooling, the toroids contained all the manganese as Mn^{2+}.

These toroids were then sintered in static nitrogen at 1150 °C for 12 h in the presence of iron(III) oxide pellets meant to generate the required partial pressure of oxygen in the closed system. Here again it was found that the quantity of iron(III) oxide to be kept was not very critical so long as it exceeded a certain minimum amount depending on the quantity of ferrite to be sintered. This could be easily determined by slight trial. The temperature of 1150 °C proved to be the correct sintering temperature to give satisfactory grains (Fig. 1). The furnace was cooled after sintering, at a rate of about 25 °C per hour till about 500 °C when the power was switched off. The toroids were taken out after cooling to room temperature and examined for their properties (Table 1). Each of the compositions given in the table was repeated four times and the variation in any of their properties was never more than ±15% of the mean values given in the table. No additives were tried in order to reduce the losses still further.

Discussion

The above technique virtually enables us to use MnO itself as the raw material in the preparation of manganese(II) zinc ferrites. In fact, it was found that even 1 mol % of ZnO in MnO stabilizes the lattice in air[7] so that such an analysed solid solution can be prepared once and for all, and used regularly as a raw material for the synthesis of this ferrite, adding the required balance of ZnO along with the Fe_2O_3 afterwards. It is therefore possible to effect the spinel formation at a relatively low temperature and then sinter the ferrite at a higher temperature just as in the case of nickel zinc or any other ferrite. In a conventional technique on the other hand these two processes are combined into one since the thermal reduction of Mn^{3+} to Mn^{2+} at the sintering temperature is a prerequisite for the spinel formation. Since manganese is present as Mn^{2+} right from the start, the spinel formation occurs at the lowest temperature at which the component oxides can at all react with one another; and it is possible to lower this temperature considerably by employing very active oxides produced by the effervescent decomposition of precipitated compounds at low temperatures —MnO and ZnO by the decomposition of their respective precipitated oxalates, and Fe_2O_3 during the effervescent decomposition of ammonium nitrate produced at the time of precipitation from iron(III) nitrate with ammonia. The preparation of the ferrite powder could be accomplished even at a temperature lower than 950 °C used here. This temperature was employed in order to get the bigger particles necessary for a higher pressed density. The burning of the binder at 800 °C—while it oxidizes the Mn^{2+} and renders the burnt toroids totally nonmagnetic—can be expected not to disturb the various ions from their lattice sites. Subsequent reduction at 1050 °C in a closed system filled with pure nitrogen and in the presence of iron powder in the hot zone effects an *in situ* reduction of Mn^{3+} to Mn^{2+}. The iron gets oxidized by the oxygen given out by the thermal dissociation of the oxidized ferrite and thereby reduces all the manganese to Mn^{2+}. It is obvious from the above that the Mn^{2+} should be expected to

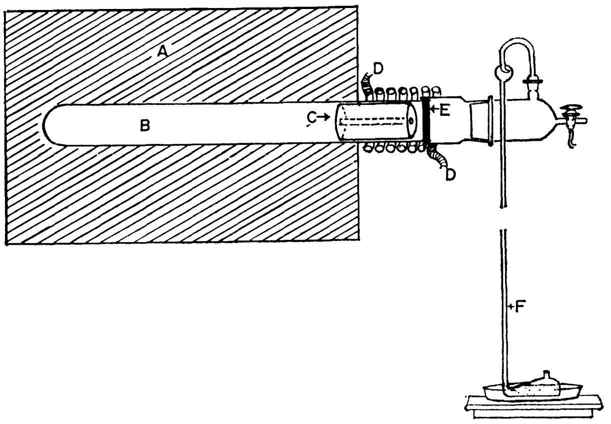

Fig. 2. Experimental arrangement for sintering manganese(II) zinc ferrites.
(A) Furnace; (B) sintering chamber in a recrystallized alumina tube; (C) cylindrical firebrick piece (with an axial bore) to act as a radiation shield on the glass joints; (D) coil for circulation of water to cool the outer end of the furnace tube; (E) attachment of the alumina tube to a ground glass joint with an epoxy resin; (F) manometer-cum-mercury seal.

be fully present at the appropriate lattice sites in the spinel, thereby eliminating an important cause of uncertainty of the results. A little excess iron can obviously do little harm since reduction, if any, of Fe^{3+} to Fe^{2+} at this stage can be easily corrected during the final sintering at 1150 °C in the presence of an excess of active iron(III) oxide pellets. This iron(III) oxide dissociates at the sintering temperature into Fe_3O_4 and oxygen, thereby providing the correct partial pressure of oxygen required to leave an optimum small concentration of Fe^{2+} in the sintered ferrite. The relatively lower temperatures of processing minimise the loss of zinc oxide from the ferrite. Since the dissociation pressure of iron(III) oxide is independent of the quantity of the oxide and depends only on the temperature, the quantity of iron(III) oxide to be placed in the hot zone of the sintering furnace is not very critical provided however, it is sufficient to maintain the correct dissociation pressure of oxygen in the sintering chamber. The mercury seal (Fig. 2) employed during the sintering run and the previous reduction serves to release the pressure during the heating. Since the dissociation pressure of oxygen in equilibrium with the ferrite varies with temperature in the same way as for the iron(III) oxide, the composition of the ambient atmosphere during the entire sintering run adjusts itself automatically at each temperature. The concentration of Fe^{2+} in the sintered ferrite is therefore fixed only by its composition and sintering temperature but not the vagaries of an externally controlled atmosphere; thereby eliminating one uncertain and sensitive parameter determining the ferrite properties. These properties can be varied in other ways such as variation of composition. This simplifies the technique considerably in every way. As mentioned in the introduction, sintering in a static controlled atmosphere whose composition adjusts itself automatically at each temperature is a great advantage over a flowing current of gas whose composition has to be externally adjusted from time to time.

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References

1) G. Winkler, "Magnetic Properties of Materials," ed by J. Smit, McGraw Hill, New York (1971), p. 52.
2) Keizo Ohta, *J. Phys. Soc. Jpn.*, **18**, 685 (1963).
3) M. A. Strivens and G. Chol, "Ferrites," ed by Y. Hoshino, S. Iida, and M. Sugimoto, Univ. of Tokyo Press, Tokyo (1971), p. 239.
4) Y. Schichijō, G. Asano, and E. Takama, *J. Appl. Phys.*, **35**, 1646 (1964).
5) P. W. Schenk, "Handbook of Preparative Inorganic Chemistry," 2nd ed, ed by George Brauer, Translation ed by R. F. Riley, Academic Press, New York (1963), Vol. I, p. 458.
6) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworths, London (1964), p. 85, Table 8.
7) C. E. Deshpande, L. M. Pant, and M. N. Sankarshana Murthy, *Indian J. Chem.*, **16A**, 251 (1978).