Preparation of manganous zinc ferrites*

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Abstract. Active manganous oxide prepared *in situ* is mixed in a closed system with a coprecipitated mixture of zinc and ferric oxides, and then heated in an inert atmosphere to 800°C to form the manganous zinc ferrite at this relatively low temperature. A volatilizable binder employed for pressing is first distilled off in an inert atmosphere and the sintering is then carried out in a controlled static atmosphere. The formation of the spinel with total absence of Mn^{3+} far below the sintering temperature, and the subsequent sintering without any possibility of oxidation of Mn^{2+} at any stage result in improved properties.

Keywords. Manganous zinc ferrites; sintering.

1. Introduction

High permeabilities combined with low losses have made manganous-zinc ferrites the most interesting and important of ferrites. The preparation of these ferrites has always been a bit of a challenge. Raw materials have to be very pure (Tebble and Craik 1969) and their physical texture is also important (Natansohn and Baird 1969). For example, spherical particles are preferred over needle shaped ones for these ferrites. All the manganese has to be in the bivalent state (Smit 1971). Besides, a calculated small amount of Fe^{2+} ion is very necessary to reduce the magnetostriction or magnetocrystalline anisotropy of the ferrite (Ohta 1963). Conventional techniques start with a stable higher oxide of manganese as the raw material (Strivens and Chol 1971). Alternatively, manganous carbonate (Shichizo *et al* 1964) is also used but even this compound gives some higher oxide of manganese during its decomposition due to the oxidizability of manganous oxide by the carbondioxide itself (Sidgwick 1950). This higher valency of manganese gets reduced to Mn^{2+} at sintering temperatures in the neighbourhood of 1250°C, especially in a flowing current of inert gas. Since the spinel cannot form until the reduction to Mn^{2+} has taken place, it follows that spinel formation and sintering are not two separate and well-defined steps in such a process. It is also difficult in this kind of process to make sure of the completeness of reduction to Mn^{2+}. A technique in which we have bivalent manganese even to start with is very much to be preferred since we do not then have to wait for the high-temperature reduction of the higher valency of manganese as a prerequisite for the ferrite formation. The temperature of the solid state reaction to give the ferrite can then be decreased considerably below the sintering temperature *per se* by employ-

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ing freshly precipitated active raw materials. However, a technique of this type has not been popular because of the difficulty of handling the oxygen-sensitive manganous oxide (Hayward and Trapnell 1964). The present investigation is an attempt to solve this problem and prepare manganous zinc ferrites with ease.

2. Experimental

2.1. *Preparation of raw materials*

All the required raw materials of requisite purity and texture were prepared for the purpose and as an integral part of the ferrite preparation. This eliminated many uncertain parameters especially in view of the fact that active oxides do not keep well and undergo some room-temperature sintering (Gregg 1961).

2.1.1. Manganous oxalate was precipitated by double decomposition of manganous chloride AR and ammonium oxalate LR in filtered solution. The precipitate was washed free from chloride, then washed with acetone and dried in vacuum. The MnO content in the powder was estimated.

2.1.2. A co-precipitated mixture of zinc oxide and ferric oxide was prepared as follows (Murthy and Sinha 1968). Zinc (AR) was dissolved in nitric acid and the concentrated solution was filtered and analysed. The required amount of this solution was mixed with a calculated quantity of analysed, filtered and concentrated ferric nitrate solution and this mixture was added gradually under stirring to an excess of cooled, concentrated and filtered aqueous ammonia prepared afresh from the cylinder gas. Zinc dissolved as ammine while the ferric hydroxide was precipitated. This mixture was evaporated to dryness and then decomposed at 200°C to 250°C. Mixing the residual powder with a small amount of ammonia and heating at this temperature were repeated to complete the conversion of the metal nitrates to the hydrated oxides. The oxide mixture so prepared was again analysed and any marginal adjustments needed for obtaining the required ratio of ZnO to Fe_2O_3 were made by mixing an appropriate small quantity of the required oxide prepared similarly. We will refer to this mixture as M.

2.2. *Preparation of the ferrite powder*

The ferrite was made out of manganous oxide prepared by the decomposition of manganous oxalate in an atmosphere of oxygen-free nitrogen obtained by passing the gas through a heated column of reduced copper (Schenk 1963). Since heating of the manganous oxalate along with ferric and zinc oxides in an inert atmosphere causes a reduction of ferric oxide to ferrous, it was necessary to decompose the manganous oxalate separately at 400°C in the silica reactor B (figure 1), degas MnO, cool and then add the mixture M from the retort like unit D (attached at the joints O_1 and O_3). The opening H helps in isolating the reactor B or connecting it through O_1 either to D or to the mercury manometer C by a suitable rotation of B inside the joint G_1. G_2 and G_3 are spherical joints through which connection can be made with a vacuum-cum-nitrogen purification train not shown in the figure. S_1 and S_2 are sintered glass pieces meant to arrest any chance suction of powder.
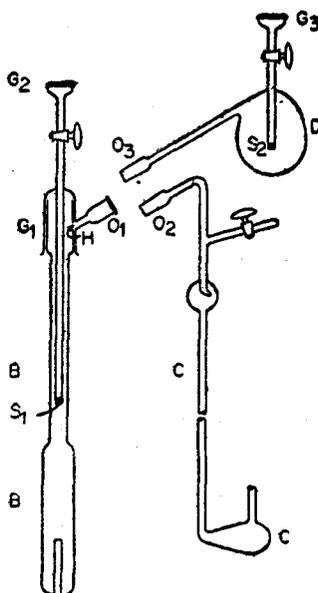
Figure 1. Unit for synthesizing manganous zinc ferrite. O_1 can accommodate O_2 (leading to the manometer unit) or O_3 (leading to the unit containing $ZnO+Fe_2O_3$). B made of silica can be closed or opened to O_1 as desired, by rotation against the female joint G_1. MnO formed by the decomposition of manganous oxalate in an inert atmosphere in B is mixed without exposure to air with the oxide mixture in D by rotating the latter around O_1. G_2 and G_3 are spherical joints which may be connected to a vacuum-cum-nitrogen purification train (not shown in the figure).

Unit B along with the joint assembly of G_1 at the top could be totally detached and shaken well in order to mix the manganous, zinc and ferric oxides in it. The powder mixture was then heated to 750°C for 8 hr in an atmosphere of pure nitrogen with the manometer-cum-mercury seal C attached at O_1. On cooling, the powder in B was found to have become magnetic and could be safely handled in air. Chemical analysis of this powder also revealed complete absence of Mn^{3+}. This powder pressed as such into pellets was heated to 850°C for 8 hr in pure nitrogen, cooled and ball-milled.

2.3. *Sintering of toroids*

The sintering of toroids pressed with the above material could also be done without any chance of oxidation of Mn^{2+} at any stage. The ferrite powder was mixed and granulated with 2% of its weight of camphor dissolved in acetone and pressed into toroids—3·6 cm OD, 1·6 cm ID, 1 cm thickness under a pressure of 4 tons/cm². The binder was then distilled off in a current of nitrogen. Sintering was then done at 1200°C to 1300°C in a controlled atmosphere. This controlled atmosphere was however a static and not a flowing one as in a conventional method. The results in table 1 were obtained with the following sintering cycle: Heating in a static atmosphere of pure nitrogen during the entire heating cycle up to 1290°C, sintering at 1290°C for 4 hr in a static atmosphere of 0·6% oxygen, the rest being nitrogen; cooling from

1290°C to 1190°C in the same sintering atmosphere; cooling from 1190°C to 1100°C in an atmosphere of 0·3% oxygen; cooling from 1100°C to 1000°C in 0·1% oxygen; cooling below 1000°C in pure nitrogen. Both the heating and cooling were done with a programme of 25°C per hour between 900°C and 1290°C. Heating and cooling between room-temperature and 900°C were done without any programme. These conditions of sintering could however be easily adjusted in some details for different requirements of ferrite properties.

2.4. *A conventional technique for comparison*

As a comparison to the above, manganous oxalate was straightway mixed with the required amount of mixture M and fired to 1100°C in air for 12 hr. The resultant powder was ball-milled, mixed with 1% polyvinyl alcohol and pressed into toroids of the same dimensions as before. The toroids were slowly heated in air up to 800°C at which the temperature was held steady for 4 hr to complete the combustion of the binder. The air was then replaced by a flowing current of pure nitrogen in the same sintering unit as before and the temperature was slowly brought to 1290°C at the rate of 25°C per hour. At this temperature the controlled atmosphere was switched on as before and the sintering completed just as before; with however one difference that the atmosphere now was a flowing and not a static one as before. The central assumption behind this conventional technique is that Mn^{3+} gets reduced at high temperatures in a flowing current of an inert gas which sweeps off the oxygen in thermal equilibrium with the higher oxide of manganese.

3. Results, discussion and conclusions

Table 1 gives the results obtained on two separate compositions employing the specific techniques given in this paper. The figures in parentheses are the results on the same compositions processed according to a conventional technique, also described above. There are clear differences between the two. It is obvious from the preparative details given earlier that the present technique deals with Mn^{2+} throughout, so that the formation of the spinel structure is easy and in fact takes place as soon as any solid state reaction at all occurs among the component oxides. This temperature is minimized by employing very active oxides prepared by precipitation followed by effervescent thermal decomposition:

$$Fe(NO_3)_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4NO_3$$

$$NH_4NO_3 = N_2O + 2H_2O.$$
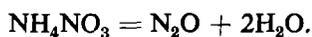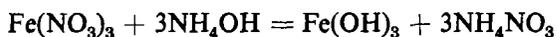
The escaping gases increase the surface area of the oxides and render them very reactive. Since the ammonium nitrate was mixed with so much inert material the above decomposition did not become violent at 200°C at least on the 500 g scale on which the work was done. Larger quantities could be handled conveniently by the use of a double drum drier (Nissan and McMurray 1963) provided with doctor blades, so that the amount of ammonium nitrate decomposing at any one time is always small. The preliminary reaction at 750°C protects the Mn^{2+} from spontaneous

Table 1. Results on manganese zinc ferrite toroids prepared by the special technique. Figures in parantheses are those on ferrites of the same composition but prepared by a conventional technique.

No.	Composition (molar)		Initial permeability μ_i at 4 kHz	Temp. factor $\times 10^6$ (25–70°C)	Curie temp. °C	Loss factor $\dfrac{\tan \delta}{\mu_i} \times 10^6$	Dis-accommodation factor $\times 10^6$	Density gms/cc.
1.	Fe_2O_3 ZnO MnO	52% 18% 30%	3178 (2091)	1·7728 (4·59)	160 (165)	1·4651 (8·55)	4.77 (16.01)	4·912 (4·62)
2.	Fe_2O_3 ZnO MnO	52% 19·1% 28·9%	3903 (3304)	0·476 (2·854)	150 (140)	1·922 (19·95)	0·5672 (3·0)	4·71 (4·617)

oxidation in air at room temperature. The powder in fact becomes magnetic even at this stage showing that the spinel formation has already taken place. Subsequently the powder becomes easy to handle in air. Pressing and heating it at 850°C virtually completes the solid state reaction and enables bigger particles to be formed. These bigger particles are necessary in order to get a sufficient density in the final sintered product (Hancock 1970; Herdon 1960). Subsequent ball-milling, compacting and sintering the material which has already fully attained the spinel structure should naturally result in a very homogeneous spinel. The large difference in temperature between reaction and sintering made possible in this technique offers a clear advantage over the conventional technique of combining the sintering with the spinel formation after the Mn^{3+} gets reduced to Mn^{2+} in a flowing current of inert gas at the sintering temperature. The static controlled atmosphere during sintering is not for reducing Mn^{3+} to Mn^{2+} since there is no Mn^{3+} at all at any stage of the process. The atmosphere prevents the oxidation of Mn^{2+} which is already there, while the small partial pressure of oxygen only helps to prevent undue reduction of Fe^{3+} to Fe^{2+} by loss of oxygen from the spinel lattice at the sintering temperature. The controlled atmosphere therefore need only be a static and not a flowing one. The partial pressure of oxygen in the controlled atmosphere has to correspond to the dissociation pressure of oxygen in equilibrium with the ferrite; and hence should vary with the temperature as mentioned above. In a conventional technique however of the type sketched above, the spinel formation can be complete only when all the Mn^{3+} is fully reduced to Mn^{2+} by the *flowing* current of inert gas at the higher temperature. We do not have a clear difference here between the two steps of reaction at a lower temperature and sintering at a much higher temperature with all the advantages noted above. The reduction of Mn^{3+} may or may not be complete in the flowing current of inert gas; and since the spinel can only be formed after the above reduction, and harmful non-spinel forming high temperature reactions among the oxides even before such a reduction is complete cannot obviously be ruled out, the final ferrite formation may not be as complete, homogeneous and satisfactory as in the particular technique described above. Last but not least, the large amount of purified inert gas which has to be kept flowing so long in a conventional technique is saved.

The details of experimental manipulation for the preparative method on the bench scale described in this paper get very much simplified on a larger scale employing metal reactors and vacuum valves. Transferring powder through glass stopcocks

and valves is not feasible and therefore needs complicated alternative techniques of the type described here; but this is quite easy through metal valves. The preparative technique therefore, using the same principle is much simpler with metal units on a larger scale.

Acknowledgements

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