Bull. Mater. Sci., Vol. 6, No. 1, February 1984, pp. 65–70.


# Dependence of microstructure on process variables in manganese zinc ferrites

N VENKATARAMANI, R AIYAR*, P S SEKHAR** and C M SRIVASTAVA*

Advanced Centre for Research in Electronics, *Department of Physics, **Materials Science Centre, Indian Institute of Technology, Bombay 400 076, India

**Abstract.** The dependence of microstructure on sintering conditions during hot pressing have been investigated and the densification mechanisms have been used to explain the observed results. The effect of addition of excess ZnO content over stoichiometry on permeability has been studied in the normal sintered Mn–Zn ferrites.

**Keywords.** Hot pressing; manganese zinc ferrites; densification mechanism; sintering.

## 1. Introduction

The initial permeability of manganese zinc ferrites is a sensitive function of the microstructure. To achieve high permeability the microstructure has to be controlled. In hot pressed ferrites this can be controlled by the sintering conditions (temperature and pressure) employed in a modified technique developed earlier (Venkataramani *et al* 1982). In normal sintered ferrites the evaporation of Zn during sintering alters the stoichiometry and affects the microstructure and permeability. Thus excess ZnO must be taken to offset this loss due to evaporation. Here we discuss the effect of varying this excess ZnO over stoichiometric content from 0 to 10% on the microstructure.

## 2. Experimental procedure

### 2.1 *Hot pressing*

The composition chosen for this study was 53 mol% $Fe_2O_3$, 27 mol% MnO and 20 mol% ZnO. The powders were processed by the usual ceramic technique. During hot pressing the presintered compact was initially soaked at a lower temperature (1100°C) under pressure ($\sim$20 MPa) and subsequently the temperature was increased to the final temperature (1200°C) maintaining the temperature constant, for various sintering times shown in table 1. This was followed by the ejection of the sample at the final temperature and the sintered pellet was cooled in $N_2$ atmosphere. For comparison we have prepared another pellet by directly heating to 1275°C (without soak) and cooling within the die. To evaluate the mechanism involved during the final stages of sintering, the time of sintering was varied from 0 to 4 hr at the final temperature.

### 2.2 *Normal sintering*

From the phase diagram for permeability by Roess (1970) the starting composition was chosen as 53 mol% $Fe_2O_3$, 23 mol% MnO and 24 mol% ZnO. The firing schedule and

**Table 1.** Densification rates of hot pressed Mn–Zn ferrites

| Sintering time (hr) | Observed density ($kgm^{-3}$) | % of theoretical density | Calculated strain rates for: Nabarro Herring $10^{-3} sec^{-1}$ | Coble $10^{3} sec^{-1}$ | Bird *et al* $10^{4} sec^{-1}$ | Total densification rate $10^{4} kg m^{-3} sec^{-1}$ | Calculated % density |
|---|---|---|---|---|---|---|---|
| 0·5 | 4990 | 97·27 | 5·68 | 4·27 | 2·36 | 72·0 | 98·21 |
| 1·0 | 5090 | 99·22 | 5·68 | 4·27 | 2·36 | 61·7 | 98·98 |
| 2·0 | 5093 | 99·28 | 3·20 | 1·80 | 2·36 | 11·9 | 99·46 |
| 3·0 | 5108 | 99·57 | 1·80 | 7·60 | 2·36 | 10·3 | 99·66 |
| 4·0 | 5119 | 99·79 | 1·50 | 3·89 | 2·36 | 4·7 | 99·79 |

ambient were adjusted to yield good density and single phase. The sintering schedule finally adopted was as follows: 1275°C in $N_2 + 1\% O_2$ for 3 hr followed by 1350°C in $N_2 + 1\% O_2$ for 4 hours and cooled in pure $N_2$ to room temperature. Atomic absorption spectroscopy and wet chemical analysis on several samples showed the final composition to be Zn deficient up to 6 wt % ZnO. Hence different samples were prepared with varying ZnO excess, progressively increasing from 0 to 10 %, keeping the same sintering schedule as above. The results are discussed in § 3.2.

## 3. Discussion

In this investigation the aim was to study the rate of densification using the hot pressing method by varying the duration of the final sintering. The change in microstructure was also studied. Normal sintering was used to study the effect of zinc loss on microstructure and permeability.

### 3.1 *Densification mechanism in hot pressing*

There are three significant processes which have been reported to occur during the final stages of hot pressing (Wilkinson and Ashby 1975; Notis *et al* 1975). These are (i) vacancy motion through the bulk lattice along a stress-induced gradient (Nabarro-Herring model) (ii) stress directed diffusional flow along the grain boundaries (Coble model) and (iii) deformation accompanied by climb and glide of dislocations (Bird *et al* model). These mechanisms have been used to compute the strain rate ($\dot{\varepsilon}$) using the equations given in Notis *et al* (1975). These in turn were used to calculate the total densification rate using

$$\dot{\rho} = \dot{\varepsilon}(3/2)^{n+1} (g/n)^n \frac{(1-\rho)}{[1-(1-\rho)^{1/n}]^n}, \tag{1}$$

where $n$ is the effective stress exponent obtained from our data, $g$ the stress correction ($\sim 1$) when $\rho$, the relative density is close to 1. The results of this calculation are given in table 1. In figure 1 we plot the density as a function of sintering time at the final temperature. The observed and calculated values show good agreement.

From table 1 it is clear that the Nabarro-Herring type strain rate is the predominant densification mechanism. This process also leads to higher grain boundary mobilities resulting in enhanced grain growth. It has also been observed that the soak at 1100°C

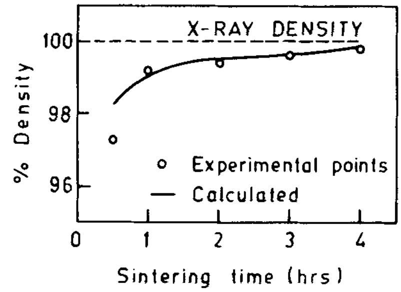
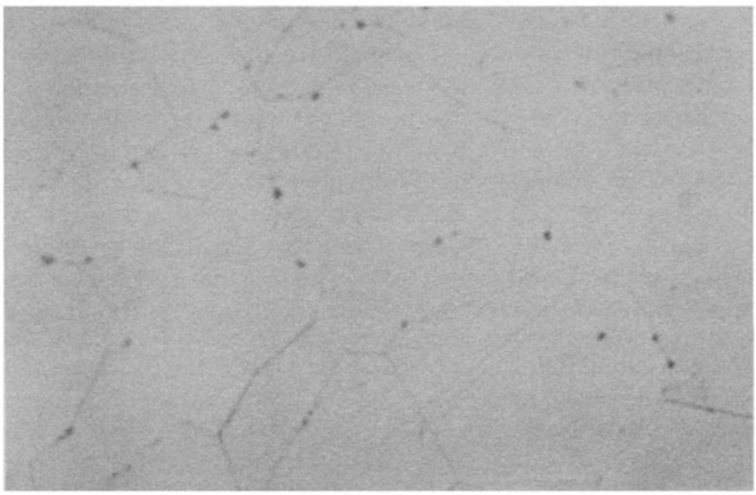
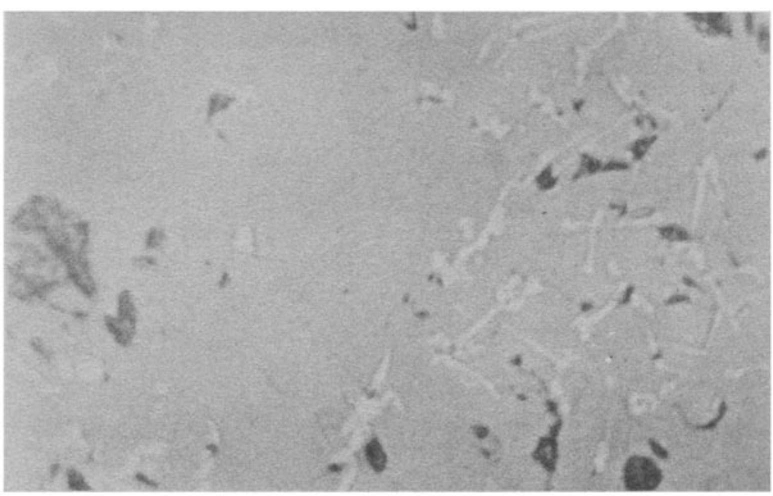



**Figure 1.** Densification characteristics of hot pressed Mn–Zn ferrites.



(a)



(b)

**Figure 2.** Microstructure photographs of Mn–Zn ferrites (**a**) hot pressed at 1100°C for 2 hr, 1250°C for 3 hr, hot ejected and cooled in $N_2$ (**b**) hot pressed at 1275°C for 2·5 hr and cooled within the die. (1 cm = 15 $\mu$m)

gives higher densities without appreciable grain growth. The energy supplied at 1200°C after the soak period leads to only grain growth since the separation of the densification process and grain growth is seen in this sintering schedule.

Using such an approach we have prepared a large grain Mn–Zn ferrite ($\sim$ 30–40 $\mu$m) with useful properties for recording head applications. The permeability is between 4000 and 5000. In contrast a sample sintered at 1275°C without soaking at 1100°C and without hot ejection resulted in a grain size of 10 $\mu$m and a density of 5050 kg $m^{-3}$. These differences are evident from figure 2 which shows the microstructure photographs of these two samples. The second phase precipitation in figure 2(b) is due to cooling within the die.

### 3.2 *Normal sintered ferrites*

We have observed that as the excess ZnO concentration increases from 0 to 4·5% the initial permeability increases and the microstructure gets refined, becoming more homogeneous. Thereafter the microstructure worsens again leading to discontinuous grain growth which also lowers the permeability. Figure 3 shows the variation of $\mu_i$ with excess ZnO concentration and figure 4 shows the microstructures of 2 wt%, 4 wt% and 5 wt% excess, ZnO compositions. From these results we see that the optimum composition is close to 4% excess ZnO. This composition has a density of 4850 kg $m^{-3}$ and an average grain size of 12 $\mu$m. On varying the composition in smaller steps in this range the best composition was found to be 4·2 wt% excess ZnO. This composition was prepared and found to have a homogeneous microstructure with minimal pores (figure 5) and an initial permeability $\sim$4000.

## 4. Conclusions

In hot-pressed manganese zinc ferrites control of grain size with good density can be obtained by soaking at a lower temperature, a suitable choice of the final sintering temperature and hot ejection. To achieve high permeability in normal sintered ferrites

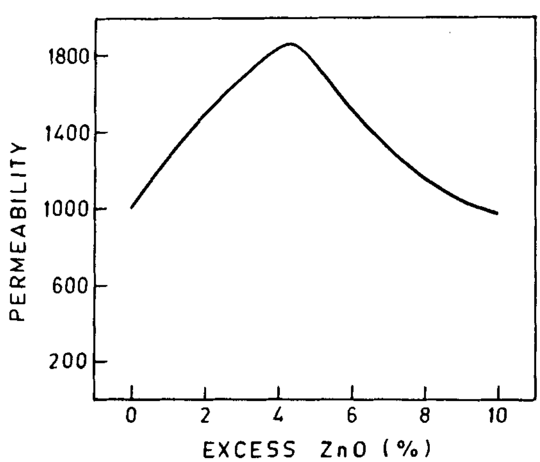
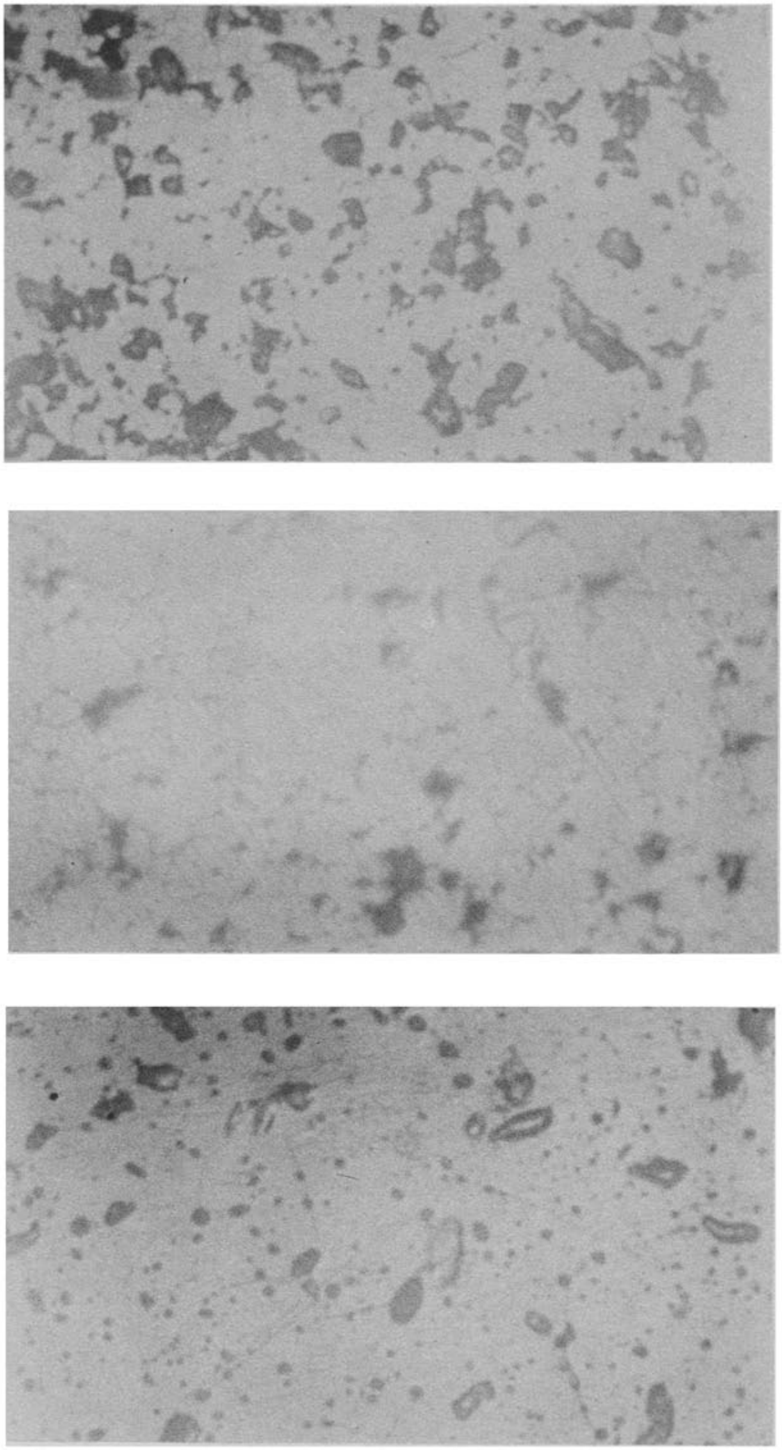



**Figure 3.** Permeability as a function of excess ZnO in normal sintered Mn–Zn ferrites.



(a)

(b)

(c)

**Figure 4.** Microstructure photographs of (**a**) 2 wt% (**b**) 4 wt% and (**c**) 5 wt% excess ZnO compositions. (1 cm = 30 $\mu$m)

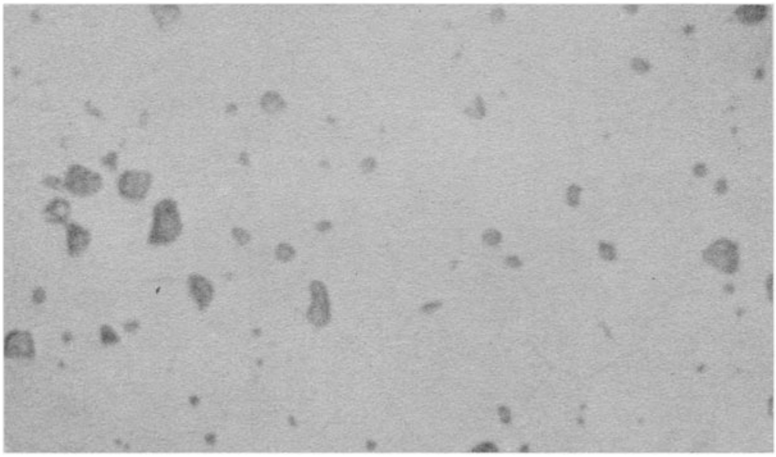


**Figure 5.** Microstructure photograph of 4·2 wt % excess composition. (1 cm = 15 $\mu$m)

using the sintering schedule discussed here an optimum excess of 4·2 wt % ZnO over the stoichiometry is necessary.

## Acknowledgement

The authors are grateful to the Department of Science and Technology for financing this study.

## References

Notis M R, Smoak R M and Krishnamachari V 1975 *Materials science research* (ed.) G C Kuczynski (New York: Plenum) **Vol. 10**, p. 493

Roess E 1970 *Ferrites*, Proc. Int. Conf. (eds.) Y Hoshino and S Iida (Tokyo: University of Tokyo Press) p. 203

Venkataramani N, Aiyar R, Sekar P S and Srivastava C M 1982 *Ceramics*, Proc. Int. Symposium (Bangalore: BHEL) p. 6.12

Wilkinson D S and Ashby M F 1975 *Materials science research* (ed.) G C Kuzynski (New York: Plenum) **Vol. 10**, p. 473