CHAPTER-V

ELECTRON MICROSCOPY OF FERRITES

INTRODUCTION

The ferrimagnetic oxides (Ferrites) have advanced to a position of technological prominance in the time period from the past several years to the present. Their development has demonstrated the needs and led to entirely new applications. For each material application intrinsic parameters as well as microstructure play an important role. Though the intrinsic properties like saturation magnetization and anisotropy depend on chemical composition, electronic structure of magnetic ions and crystal symmetry about the lattice, the properties like permeability, coercivity etc are strongly dependent on grain size, porosity and inclusions i.e. on their microstructure, which in turn is governed by the method of preparation. Thus, the intrinsic parameters decide the particular application of ferrites, the combined efforts of scientific and technical disciplines are required to realise the improvements in the ceramic products. Present attempts are directed to improve the ferrite properties through the chemical additions and use of different sintering techniques to achieve the desired microstructure.

5.1 STRUCTURE-PROPERTY CORRELATION

The most apparent features of microstructure are grain size, grain orientation, grain boundries, pores, inclusions, regions of inhomogeneity and crystal defects. Therefore the relation between microstructure and property assumes a variety of forms in magnetic oxides. The crystallites in these oxides split up into small regions of spontaneous magnetization (domains) at particular temperature. The mobility of domains is largely influenced by microstructure of ferrites. The structure with large and fault free crystallites favours domain wall mobility giving rise to high permeability and low coercivity. On the other hand domain wall motion is not possible in a fine grained structure resulting in a large retentivity and coercivity which is desirable for permanent magnets and high frequency ferrites. The structure with small grains and low porosity is also required for microwave ferrites to suppress the unwanted excitation of spin waves.

Grain boundries act as current barries to ensure the required behaviour. They are very much pronounced in Mn-Zn ferrites operating at about 1000 Hz frequency range. These current barriers act as internal lamellae to reduce the eddy current losses. The grain orientation favours maximum BH which is an essential requirement of permanent magnets.

Another aspect of microstructure is viz porosity which pins the domain wall motion. However pores are unwanted because they impede domain wall motion and make internal field inhomogeneous by creating internal depolarization regions.

Peloschek and Kooy[1] have commented that the improvement in any one of the properties most likely deteriorates the other properties. Ross and Hanke[2] established the correlation between magnetic properties, pores and boundries. The influence of inclusions on magnetic properties via grain growth was discussed by Heister[3]. The micrograph of Ni-Zi ferrite obtained by Paulus[4] indicated the systematic relation between magnetic properties and inclusions at grain boundries.

The effect of sintering temperature on microstructure is demonstrated in the electron micrographs of nickel-zinc ferrites[5]. Mishra and Thomas[6] analysed the crystallography, defect structure and phase transformation in relation to magnetic properties via coercivity and hysteresis characteristics.

5.2 MICROSTRUCTURE AND FERRITES

In addition to mechanical strength, the electrical and magnetic properties of ferrites depend to a large extent on ceramic structure.

5.2.a Electrical Properties

The phenomenon of electrical conductivity in ferrites poses number of problems. In polycrystalline ferrites, the nature of grain boundries acts as sources of resistance. It has been well established that the mobility of charge carriers by a.c. measurement is much more greater than that obtained by d.c. measurement for the same sample[7]. Guillaud[8] found that the measured resistivity of Mn-Zn ferrite completely dominated by relatively high resistance of grain boundries. Though, the structure and general properties of grain boundries are not well understood, they represent lattice strain and disorder and act as sinks for impurities and preferred sites for nucleation of inclusions. The firing temperature greatly changes the percentage of porosity that in turn affect the properties of grain boundries. Pores on the grain boundries have an obvious effect on the resistance. Heister[3] found that Mn-Zn ferrites sintered at 1200°C fractured at grain boundries. He emphasized the importance of uniform grain size in minimizing the eddy current losses.

The effect of grain boundary and structure distortion on the resistivity of ferrites has been studied by Long Kla and others[9]. They observed maximum resistance in spinel ferrites fired at 1300°C by impurity doping. Thus conductivity decreases by adding impurities. The same behaviour is noticed by Uitert[10] by substituting few mole of Mn for divalent ions in nickel and cobalt ferrites.

The increase in grain size causes for the decrease in density of porosity. As pores are providing insulating medium, the decrease in their concentration increases the conductivity. Such a phenomenon has been reported in case of Ni-Zn ferrites[11].

5.2.b Magnetic Properties

Many of the magnetic properties are closely related to their microstructures[12]. Initial permeability and intrinsic magnetic properties of polycrystalline ferrites are influenced very much by pinned wall domains due to porosity at the grain boundries[13].

To have high permeability the material must contain highly mobile domain walls. This implies that the crystallites must be large without pores or imperfections and crystalline anisotropy must be small.

As grain size increases domain walls increase in extent[14] and oscillate more easily while remaining are pinned at the grain boundries. The pinning effect is due to the magnetostatic effect associated with intragranular pores or discontinuity in the direction of magnetization.

It has been reported that the domain wall relaxation frequency and maximum losses shift to lower values with increasing grain size[15]. The parameters controlling the permeability have been discussed by Perduijn and Peloschek[16]. They obtained large crystallites by choosing the suitable sintering procedure and noticed the linear variation of permeability with the diameter of the crystallites. The linear relationship between initial permeability and grain diameter is demonstrated by Globus and Duplex[17] in Yttrium-iron garnet. It is noted that there is no region of constant permeability at low grain diameter.

The effect of porosity and grain size on the magnetic properties of Ni-Zn ferrite is reported by Igarashi and Okazaki[18]. On the basis of permeability porosity relation, the demagnetizing factor is found to be proportional to porosity. The experimental results on B-H loop indicate that magnetic flux density and coercive force are independent of grain size and porosity respectively.

The influence of grain size and porosity on radio-frequency field dependence of magnetic permeability and loss factor is discussed by Kubo, T, Ido and Yokoyama[19] in Ni-Zn-Co ferrites. It is observed that the dynamic 'tan δm' increases significantly with increasing grain size.

Besenicar et al[20] studied the microstructural properties on a local scale by Mössbauer spectra of Fe at room temperature. The hyperfine parameters were correlated with magnetic properties. They observed the close similarity in the behaviour of hot pressed Co-Ni-Zn ferrites and those produced by usual ceramic techniques.

It can be concluded that single crystal would be ideal for constant or slow varying field, polycrystalline structure is preferred at high frequencies due to the losses arising at such frequency fields.

5.3. ASPECTS OF FERRITE MICROSTRUCTURE

It is of importance to have the knowledge of the characteristic elements of microstructure in order to obtain optimal properties. It is equally important to know how the microstructure is controlled by ceramic process. Porosity, inclusions, grain size, their orientation and distribution with respect to other phases are the dominent elements in giving a particular structure. As most of the ferrites are single phase ceramics, porosity and grain boundries are considered as an essential elements of ferrite microstructure.

In a ceramic process the starting material is in the powder form which is densified by compacting it into the desired shape and then sintering at elevated temperature. The final microstructure develops during the sintering process.

5.3.a Sintering

Sintering consists of heating the powder compact to a temperature at which the mobility is sufficiently high to decrease the free energy associated with the grain boundries. Initially there is a formation of neck between the pairs of particles and atomic diffusion governs the rate of neck growth. At a density of about 60%, the grains begin to grow in volume. The density then increases logarithmically with time. Pores are swept away by the moving grain boundries.

The pores occluded within the grains are latter on removed by the diffusion of vacancies to the grain boundries.

The driving force for sintering process is obtained from surface energy of particles. To achieve self-sustained sintering process, the available energy must be sufficiently high. This means that the size of the particles must be small. The surface energy per unit volume of a spherical particle is given by

$$E_s = \frac{6\gamma}{D} \qquad ------ \qquad (5.1)$$

where γ = surface tension/energy

D = diameter of the particle

The volume of the void determines the amount of material to be transported. This requires high density powder compact to have good contact between the particles. Sintering and densification involves the diffusion of vacancies from pores to grain boundries, where they can be annihilated consequent This results in the material transport by migration of individual ions by grain boundries to the pores producing shrinkage. Thus volume diffusion is the most transport mechanism in ionic solids such as spinels. Nabarro[21] and Herring[22] theory for diffusional microcreep is considered to be the principal mechanism for densification.

The migration of vacancies occurs as a result of concentration gradient between the curved surface of the pore and equilibrium vacancy concentration under the flat surface. The concentration of vacancy under a surface of radius (r) is represented by Kelvin equation

$$Cr = Co \exp\left(\frac{2\gamma a^3}{rKT}\right) \qquad ------ (5.2)$$

where Co = vacancy concentration under flat surface

a^3 = vacancy volume

γ = surface energy/surface tension

At grain boundries, the concentration is equal to Co and is constant. Therefore vacancies migrate from the pore surface into grain boundries, at temperatures where the mobility is sufficiently high.

Due attention must also be paid to the partial pressure of oxygen during sintering. The firing at high temperatures may fuse aggregates of the oxide particles to give large crystallites with high porosity. When pores cease to interconnect oxygen balance cannot be adjusted and ultimately inhomogeneity results.

The formation of ferrite is due to the counter-diffusion mechanism of cations through the relatively rigid oxygen lattice[23,24]. Lattice vacancies affect the rate of diffusion and reaction and experiments have indicated the diffusion of Fe^{2+} ions instead of Fe^{3+} ions. Then oxygen is evolved where the iron goes into solution of spinel phase and reabsorbed at the divalent metal oxide-spinel interface.

5.3.b Normal Grain Growth

The grain boundries are associated with certain amount of interfacial energy which forms the driving force for grain growth on heating. In grain growth the grain boundary energy is decreased when boundries move towards their centre of curvature. The empirical rate of grain growth is given by[25]

$$D - D_o = Kt^n \qquad - - - - - \qquad (5.3)$$

where D_o = original particle size

K = temperature dependence factor

t = time

n = grain growth exponent = $\frac{1}{2}$ or $\frac{1}{3}$

The presence of impurities in the grain boundries hinders the grain growth because impurities have to diffuse with boundries. When pores or inclusions disappear during heating, a somewhat large grain is formed in a matrix of finer grains. Grain growth during sintering is therefore almost impossible to describe in general terms and difficult to control in practice. The grain growth occurs until the following condition is satisfied.

$$D_{cr} = \frac{d_i}{f_i} \qquad \text{-------} \qquad (5.4)$$

D_{cr} = critical diameter of the grain

where d_i = diameter of inclusion

f_i = volume fraction of inclusion

When the grain size reaches this dimension, further grain growth is inhibited. During sintering D_{cr} decreases as smallest pores disappear and f_i decreases. If the whole compact is homogeneous an uniform grain size would be expected and eventually full density may be approached. The goal of ceramic technique is to obtain lowest possible porosity and full densification. This is achieved by promoting sintering rate and by using powders with large surface area. Reijnen[26] showed that the microstructure with large pores is related to compounds having intrinsically a low sintering rate.

5.3.c Exaggerated Grain Growth

The exaggerated grain growth occurs when the average grain size reaches the critical size. In this situation few grains grow rapidly at the expense of others due to lack of homogeneity. This discontinuous grain growth leads to a duplex structure of gaint grains in a matrix of small grains. This appears to be quite common in technical ferrites leading to a characteristically porous structure. The rapid growth of grains entraps pores within the matrix, and it is almost impossible to eliminate such pores due to their great distance from the grain boundries.

Lack of chemical homogeneity as well as variations in density and the presence of impurities favour exaggerated grain growth[27].

The observations on growing of large grains show that their diameters increase linearly with time until impingement on other grains occurs. It was showaby Beck et al[28] that the exaggerated growth can be associated with the disappearance of inclusions by solution.

In conclusion it can be stated that grain size cannot be well controoled in the normal sintering process unless very pure raw-materials are used.

5.3.d Porosity

Porosity is the phase that is always present in ceramics prepared by powder compaction and heat treatment. In order to obtain low porosity, it is useful to promote the sintering rate by using powders with large surface area. Large pores will grow at the expense of small pores in its direct vicinity by volume or grain boundary diffusion of vacancies. However very small pores move along with moving grain boundary[29] due to vacancy gradient over the two pore surfaces. Under special conditions, quite large pores will move along - with the grain boundary in some ferric oxides[30] having cation deficiency with different valency state and sintered in oxygen atmosphere.

The pores grow in size during sintering means, no grain growth impediment occurs unless the material is overheated. The grains remain free from pores and this microstructure therefore leads to very high permeabilities. It has been well established that the microstructure with large pores is related to compounds having intrinsically low sintering rate. The optimum sintering rate is achieved when the condition

$$D_cC_c = D_oC_o \qquad ----- \qquad (5.5)$$

is satisfied. Where D_c is diffusion constant of cation vacancies, D_o is diffusion constant of oxygen vacancies, C_c is bulk concentration of the cation vacancies and C_o is bulk concentration of the oxygen vacancies. At low sintering pore growth becomes predominent and if no pore growth occurs, discontinuous grain growth is observed.

From the above considerations it is evident that the combination of low porosity and small grain size is extremely difficult to realise with normal ceramic process. The application of external pressure promotes sintering process but not grain growth. By the method of continuous hot pressing it is possible to conserve the original particle size of the starting powder with a very low porosity.

5.3.e Hot Pressing

Hot pressing or sintering under pressure, has been used increasingly on an experimental scale during recent years and continuous process has been developed in the Philips laboratories. It seems apparent that pressure leads to a high degree of densification and enhances contact between the grains during sintering. This method yields ferrites of extremely small grain size and high density. Grain diameters of 0.5μ are reported, with densities of more than 99.5% of theoretical values. Hence hot pressing technique permits densification without the normal accompanying grain growth.

This method is particularly very useful to those materials for which high density and very small particle size are of distinct advantage. Grain size influences both low frequency permeability and power handling ability in microwave devices.

The main factor affecting the hot pressing process are time, temperature, pressure, particle characteristics and environment. In contrast to conventional sintering, the added variables of pressure and pressure-temperature interactions lead to process mechanism that are different from pressureless sintering. When carried out as a function of starting particle size, all other factors being same, it is found that the material of fine particle size undergoes densification more easily than that of coarser sized particles of same material.

More recently, gas isostatic hot pressing has been described to achieve maximum possible density. Härdtl[31] has reported the density more than 99.6% in garnets and spinel ferrites by this technique. The success of technique depends on convential firing to get about 95% of theoretical density, so that subsequent firing under the pressure about $10^6 Kg/m^2$ can be done on a sample without connected pores.

5.4 EXPERIMENTAL TECHNIQUE

SEM is the most exciting instrument that has been added in the study of metallography in the past several years. Compared to optical microscopy, it possesses high resolving power and magnification along with the formation of three dimensional image. Hence in the present case SEM is selected to take the micrographs of all samples to characterise their microstructure. The electron microscopy work is carried out at the Minerological Institute, University of Mysore, Mysore using JEOL scanning electron microscope.

5.5 RESULTS AND DISCUSSION

The SEM micrographs of the samples in the present case are presented in Figs. 5.1 to 5.6 along with the conditions of sintering for each sample. These micrographs reveal the following important features. The porosity of the samples varies from 20 to 30%, as they have been prepared by ceramic technique. Depending upon heat treatment the grain size varies upto 10μ. The maximum grain size is

$CuFe_2O_4$

SINTERED AT 800°C FOR 20 HOURS

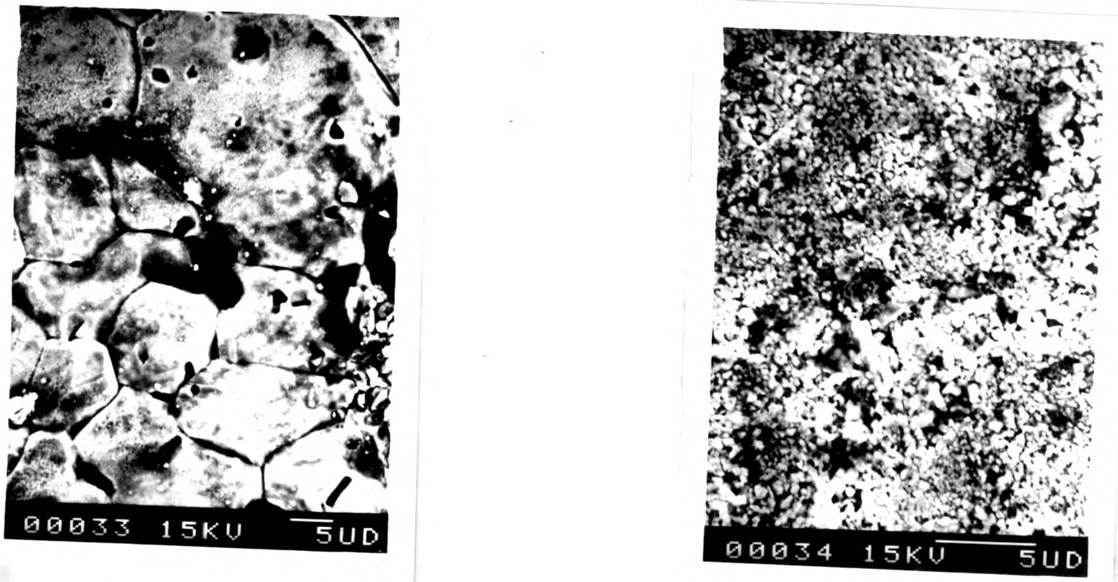
5.1

$CuFe_2O_4$

SINTERED AT 900°C FOR 20 HOURS

5.2

Fig.5 SCANNING ELECTRON MICROGRAPHS



$CuFe_2O_4$
SINTERED AT 900°C FOR 30 HOURS
5.3

$CoFe_2O_4$
SINTERED AT 800°C FOR 20 HOURS
5.4

Fig.5· SCANNING ELECTRON MICROGRAPHS

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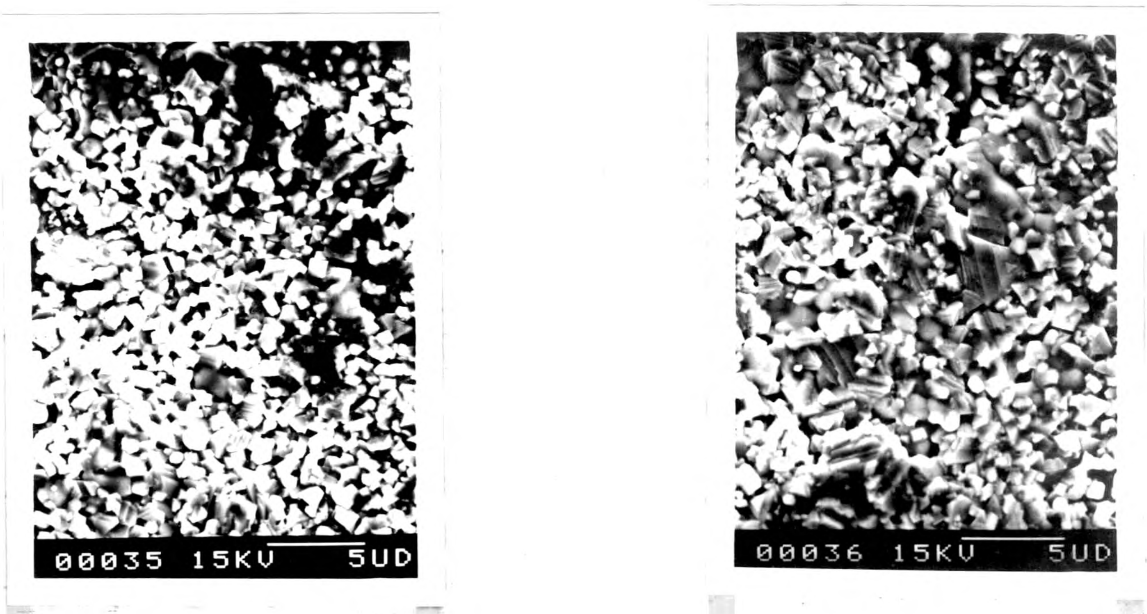

$CoFe_2O_4$
SINTERED AT 900°C FOR 20 HOURS.
5.5

$CoFe_2O_4$
SINTERED AT 900°C FOR 30 HOURS
5.6

Fig.5 SCANNING ELECTRON MICROGRAPHS

found in a sample sintered at 900°C for 30 hours (Fig.5.3). From the micrograph of this sample it is observed that both closed and open pores along with few exaggerated grains characterise the microstructure. The samples sintered at low temperature (800°C) for comparatively less time exhibit almost open pores along with relatively small grains. Thus concentration of porosity is found to decrease with increase in sintering temperature and time. In case of exaggerated grain growth (Fig.5.3), closed pores are trapped inside the grains. They are isolated from the grain boundries and hence cannot shrink any more. Under such condition sintering is practically inhibited[32]. A similar behaviour has been reported in case of Mg-Mn-Zn ferrites[33].

The mechanism of neck growth as a consequence of migration of vacancies from pore or neck to grain boundary is clearly indicated in the micrographs. Due to unequal diffusion rates, porosity develops at the base of the neck[34].

The mechanism of pore growth combined with grain growth results in the characteristic microstructure of ferrites in which residual porosity appears in intragranular space. This is clearly indicated in the present samples (Fig. 5.1, 5.2, 5.4, 5.5).

The close survey of the micrographs reveals that the samples sintered at 800°C for 20 hours contain large number of small grains with more porosity than the samples of same composition sintered at 900°C for 20 and 30 hours.

GresKovich and Lay's[35] observation of increase in average particle size during the initial stage of sintering holds good in our samples also. This indicates that densification mechanism through solid-state diffusion is more effective at higher sintering temperatures.

The micrographs also represent two typical microstructures that cover entire field of magnetoceramics. One type has a high density containing large grains (5.3) more than 10 μ and remaining porosity is present as clouds of fine spherical pores inside the crystallites. Such microstructure may be due to oxygen vacancies as a result of reduction during firing or certain dopes. Another type consists of smaller and pore free crystallites (Fig.5.1, 5.4, 5.5, 5.6). The large pores are present at the boundries of the crystallites. Such structure is due to the certain amount of metal ion vacancies caused by oxidation or suitable doping. These results are in good agreement with those reported for Ni-Zn ferrites[33].

It can be concluded that diameter of the grains increases with decrease in porosity as sintering temperature/time increases and under specific conditions exaggerated grain growth also occurs (Fig.5.3). The densification via necks is more pronounced at higher sintering temperature.

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