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CHAPTER V

MICROSTRUCTURE AND FERRITES

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INTRODUCTION

The term "microstructure" has outgrown its earlier meaning, namely, the structure that is seen through a microscope. Recently the increasingly broadening use of the term "microstructure" includes the nature of grain boundaries, chemical composition of phases and the shape and size of the individual crystallites. It is highly important to have a knowledge of the inter relationship between the properties and the characteristic element of microstructure in order to obtain optimal properties.

The important quantities of ferrites for technical applications such as permeability, coercive force depend to a great extent on grain size,porosity and inclusions i.e. on microstructure of the product. For this reason combined efforts of various scientific and technical disciplines are being directed towards improvements in product performance through microstructure control (1). More essential improvements are obtained by advances in technology, such as the use of very pure raw materials or of wet chemical preparation methods. Microwave materials with unique properties have been obtained by new fabrication techniques such as hot pressing. The studies regarding sintering process and grain growth phenomena can lead to control of microstructure. Of late, attempts are being directed towards improvement ferrite properties through the chemical additions and use of different

sintering techniques to achieve the desired microstructure. The present section deals with the physical background required to understand the relation between microstructural aspects and physical properties, the advanced ceramic technology and improvement of properties through microstructure control.

5.1 MICROSTRUCTURE AND PROPERTIES

At the beginning optical microscope was used for the study of microstructure. Recently, high resolution electron microscopic studies of Manganese Zinc ferrites have been carried out by Mishra (2). The mechanical strength as well as other physical properties i.e. electrical and magnetic properties depend to a great extent on the ceramic microstructure. Small grain size influences the conduction because the grains are closely packed. The ferrites which are sintered at higher temperatures have smaller activation energy for electrical conduction because at higher sintering temperatures small grains are destroyed. The electrical properties of polycrystalline specimens like conductivity, permeability, eddy current losses etc. depend upon the heat treatment during the preparation .

The loss factor, dielectric constant, the ac/dc conductivity depend upon extrinsic parameters such as purity of the starting compound stoichiometry,sintering temperature, porosity, density, physico chemical history, surface conditions, grain size etc. Electrical conductivity also depends upon the cation distribution.

Peloschek and Kooy (3) have commented that the improvement in any one of the properties most likely deteriorates the other properties. The correlation between magnetic properties, pores and boundaries have been established by Ross and Hanke(4). Heister (5) has discussed the influence of inclusions on magnetic properties via grain growth. The micrograph of Ni-Zn ferrite obtained by Paulus (6) indicates the systematic relation between magnetic properties and inclusions at grain boundaries. Mishra and Thomas (2) analyzed the crystallography, defect structure and phase transformation in relation to magnetic properties via coercivity and hysteresis characteristics.

Grain boundaries act as current barriers to ensure the required behavior. 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 magnet materials.

5.2 MICROSTRUCTURE AND FERRITES

Not only the mechanical strength but also the electrical and magnetic properties of ferrites depend on ceramic structure.

5.2.1 ELECTRICAL PROPERTIES

As grain size increases the density of pores decreases. Since, the pores are providing insulating medium, the decrease in concentration of pores increases the conductivity. This phenomenon has been reported in case of Ni-Zn ferrites (7). It has been well established that the mobility of charge carriers by a.c.measurement is much greater than that obtained by d.c.measurement for the same sample (8). Guillaud (9) found that the measured resistivity of Mn-Zn ferrites is completely dominated be relatively high resistence of grain boundaries. In polycrystalline samples, the nature of grain boundaries acts as source of resistance.

The grain boundaries act as sinks for impurities and preferred sites for nucleation of inclusions. Percentage of porosity in ferrites can be changed by changing firing temperature which in turn, affects the properties of grain boundaries. Pores on grain boundaries have an obvious effect on the resistance. Heister (5) found that Mn-Zn ferrites sintered at 1200°C fractured at grain boundaries. 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 (10). They observed maximum resistance in spinel ferrites fired at 1300 °C by impurity doping. Thus conductivity decreases by adding impurities. The same behavior is noticed by Uitert (11) by substituting few mole of Mn for divalent ions in nickel and cobalt ferrites.

5.2.2 MAGNETIC PROPERTIES

Magnetic properties of ferrites are also related with their microstructure. The effect of porosity and grain size on magnetic properties of Ni-Zn ferrites is

reported by Igarashi and Okazaki (12). On the basis of permeability-porosity relation, the demagnetizing factor is found to be proportional to porosity. The effect of grain size and porosity on radio frequency field dependence of magnetic permeability and loss factor is discussed by Kubo et al (13) in Ni-Zn-Co ferrites. They observed that the dynamic, tan m increases significantly with increasing grain size.

Initial permeability and magnetic properties of polycrystalline ferrites are influenced by pinned wall domains because pores are at the grain boundaries (14). If ferrite possesses highly mobile domain walls, it has high permeability. As the grain size increase the domain wall relaxation frequency and maximum losses shift to lower values (15). It has been also reported that as grain size increases domain walls increase and oscillate more easily while remaining are pinned at the grain boundaries (16).

5.3 TECHNOLOGY OF SINTERING AND MICROSTRUCTURE IN FERRITES

The microstructure is controlled by ceramic process. The porosity, inclusions, grain size, their orientation and distribution with respect to other phases are the

dominant elements in giving a particular structure. However, grain boundaries and porosity are considered as essential elements of ferrite microstructure.

5.3.1 SINTERING

In ceramic process, initially, the material is in the form of powder. It can be made into a dense solid by first compacting it into desired shape and then sintering this compact at a high temperature. The final microstructure develops during the sintering process (17). The surface energy of the particles gives the driving force for sintering process by which the particles in powder compact grow together and the pores in the compact are filled up with materials. The interface between crystallites represents an amount of energy, which can be reduced by grain growth. Sintering, densification and grain growth, all occur at the same time and give rise to a variety of microstructures (18).

According to the definition of the sintering reactivity, the particle size of the powder must be small. Spherical powder particles with diameter D have

a total surface energy/unit volume.

$$E = 6\gamma / D \qquad \text{----------(5.1)}$$

Where γ surface energy, and D = diameter of powder particle.

The amount of material to be transported is determined by the void volume. At the start, the powder compact is made in such a way that the density is sufficiently high to have good contact between the particles (19). The principal mechanism for densification is considered to be described by Nabarro and Herring for diffusional microcreep (20, 21). The surface of the pore acts as a source of vacancies. These vacancies diffuse through the bulk of the particles to the grain boundaries where they can be discharged. The resulting effect is the material transport by the migration of individual ions from the grain boundaries to the pores, producing shrinkage.

The formation of ferrite is due to the counter diffusion mechanism of cations through the rigid oxygen lattice (22,23). Lattice vacancies affect the rate of diffusion and reaction. Experiments have indicated the diffusion of Fe^{2+} ions instead of Fe^{3+} ions. The oxygen is evolved where the iron goes into solution of spinel phase and reabsorbed at the divalent metal oxide spinel interface.

5.3.2 NORMAL GRAIN GROWTH

Grain growth in ceramic compacts occurs as a result of decreasing grain boundary energy. The rules applied for grain growth in ceramics include (a) Grain boundary moves towards the centre of curvature, (b) Grain growth takes place by grain boundary migration, (c) Grains with more than six numbers of sides grow and their counterparts having less than six - number of sides shrink, the grains with six number of sides being most stable.

An attempt to reduce the grain boundary velocity is sometimes made by adding certain impurities. The presence of impurities lower the rate of grain growth.

The general grain growth law is given by (24)

$$D - Do = Kt^n \quad \text{----------(5.2)}$$

where

Do = Original particle size.

K = is constant which depends upon temperature.

t = is time.

n = grain growth exponent.

The values between 0.3 to 0.5 have been assigned to grain growth exponent depending on the primary situation. Grain growth in sintering is almost impossible to describe in single term due to the

simultaneous activation of several factors and therefore it is almost difficult to have control over grain size.

When pores or inclusions disappear during heating a somewhat larger grain is formed in a matrix of finer grains. The grain growth occurs until the following condition is satisfied.

$$D_{cr} = di/fi \qquad \text{----------(5.3)}$$

where

D_{cr} = critical diameter of the grain.
di = diameter of inclusion.
fi = volume fraction of inclusion.

When the grain size reaches this dimension further grain growth is inhibited. If the whole compact is homogeneous an uniform grain size would be expected and 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.

5.3.3 POROSITY

The extra phase which is present in ferrites is porosity. It is formed in ceramics during powder compaction and heat treatment. Porosity can be characterized by the volume fraction of pores present and their size, shape and distribution compared to other phases. The amount of porosity can be varied in order to increase the density. Kingery and Francois (25) have argued that pore growth presents problem in interpretation because most pores are interconnected by grain boundaries. Which provide sites of lower chemical potential for the vacancies than to either of the connected pore surfaces.

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

$$D_v C_v = Do\ Co \qquad \text{----------(5.4)}$$

is satisfied. Where D_v is diffusion constant of cation vacancies, Do is diffusion constant of oxygen vacancies, C_v is bulk concentration of the cation vacancies and Co is bulk concentration of the oxygen vacancies. At low sintering,pore growth becomes predominant and if no pore growth occurs, discontinuous grain growth is observed. The total porosity in ferrite sample can be measured by determining the bulk

density of a sample and comparing it with its X - ray density.

5.3.4 HOT PRESSING

This is the technique which involves simultaneous application of high pressure and temperature (26). In the conventional process, the pressing is done at room temperature and the firing at atmospheric pressure. In this technique, the application of pressure makes possible the use of lower sintering temperatures. The main factors affecting the hot pressing process are time, temperature, pressure, particle characteristics and environment. Hot pressing is the obvious process for eliminating porosity.

Mikharskil et al (27) reported that changing the pressure in the hot pressing of Manganese-Zinc ferrites affects both the composition and state of the solid phase system and the structural characteristics of specimens. The Fe^{2+} ion concentration, density, Curie temperature and degree of inversion also increases. There is also a tendency for the initial magnetic permeability to fall and for the crystallites size to grow. An interrelationship is shown to exist between

the Fe^{2+} ion content of Manganese-Zinc ferrospinel and the degree of nonstoichiometry and inversion. Hot pressing technique looks particularly promising for electroceramics.

5.4 EXPERIMENTAL TECHNIQUES

Electron microscope is the most versatile instrument compared to optical microscope. Now-a-days SEM is being used in the study of metallography. It possesses high resolving power and magnification along with the formation of three dimensional image. The electron microscopy work reported here is carried out at the Mineralogical Institute, University of Mysore, Mysore, using JEOL scanning electron microscope.

5.5 RESULTS AND DISCUSSION

New developments in techniques and the understanding of factors affecting microstructure development have provided a more complete picture of what the structure is actually like and better interpretation of it's origin. The scanning electron microscopy has developed a much deeper understanding into the complexity of ceramic materials.

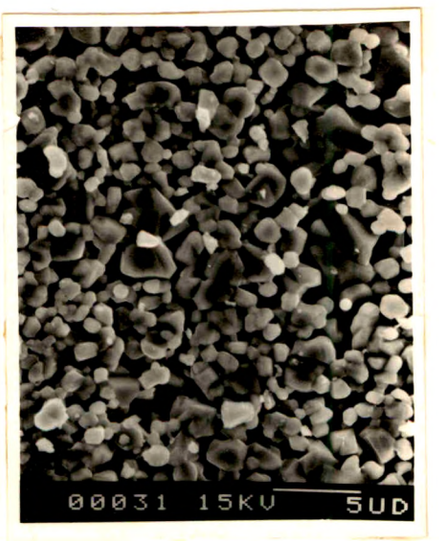
The SEM micrographs of the samples in the present case are presented in figs. 5.1 and 5.2 along with the conditions of sintering for each sample. These micrographs give us following important information. Porosity of samples varies from 20 to 30 % as they have been prepared by ceramic technique. Depending upon heat treatment the grain size varies. The large grain size is found in a sample sintered at 1100 °C for 30 hours than the sample sintered at 1100 °C for 15 hours. From the micrograph of the samples it is observed that both closed and open pores along with few exaggerated grains characterize the microstructure. The sample sintered for 15 hours exhibits almost open pores along with relatively small grains. Thus concentration of porosity is found to decrease with increase in sintering time.

The mechanism of pore growth combined with grain growth results in characteristic microstructure of ferrites in which residual porosity appears in intragrannular space. This is indicated in figs.5.1 and 5.2 . The

survey of the micrographs reveals that the samples sintered for 15 hours contain large number of small grains with more porosity than the samples of same composition sintered for 30 hours.

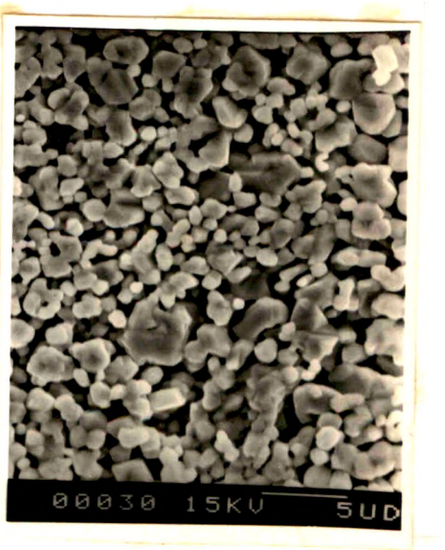
Greskovich and Lay's (28) observation of increase in average particle size during the initial stage of sintering holds good in our samples also. This indicates that densification mechanism through solid state diffusion is more effective at higher sintering temperatures. When two particles are placed in contact with each other and heated to an appropriate temperature they bond together and with continued heating a measurable neck forms between them. The further growth in this region may occurs by transport of matter from the neighboring particles towards the neck. 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 (29).

The effect of sintering time and temperature on the microstructure and magnetic properties of ferrites $Ni_{0.32}Zn_{0.68}Fe_2O_4$ were studied by Lin et al (18) and have reported that the control of sintering time is also equally important.



$Mg_{0.6}\ Zn_{0.4}\ Fe_2O_4$
SINTERED AT 1100 °C FOR
30 HOURS.

FIG.- 5·1



$Mg_{0.6}\ Zn_{0.4}\ Fe_2O_4$
SINTERED AT 1100 °C FOR
15 HOURS.

FIG.- 5·2

FIG.5 - SCANNING ELECTRON MICROGRAPHS.

It can be concluded that diameter of the grains increases with decreases in porosity as sintering time increases and under specific conditions exaggerated grain growth also occurs. The densification via necks is more pronounced at higher sintering timings.

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