CHAPTER - IV

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*** MICROSTRUCTURE ***

4.1 INTRODUCTION :

Most of the structure sensitive properties are depend upon microstructure. Such as magnetic properties electrical properties & mechanical properties of the materials. Therefore physical properties of the materials can be controlled by controlling their microstructures, which can be done by following the appropriate sintering process during their manufacturing.[1] Thus, it is possible for us to produce ceramic materials with desired properties, fcr specific applications, by controlling their microstructure the scanning Electron Microscopy is one such powerful technique which is of immense importance in determining the intrinsic properties, based on grain size, porosity & inclusions.

4.2 MICROSTRUCTURE AND FERRITES :

The relation between microstructure & property assumes a variety of forms in ferrites. The structure with large crystallites favour domain wall motion , high permeability & low coercivity. Fine grained structure inhibits the wall motion and results in large retentivily & large coercivity . The proper grain orientation favours maximum B_H value. Improvement in any one relation most likely affects the other relations. Many investigatores have tried such improvements in specitic relations.Heister [2] & Paulus [3] have studied the magnetic properties via. grain growth with SEM

technique

The large crystallites without pores or-imperfection & with small anisotropy posseses high permeability. This is due to the highly mobile domain wall. The domain walls increases in size & oscillate more freely as the grain size increases & domain wall relaxation frequency & maximum lossses, shiff to lower values with increasing grain size [4] .Igarashi [5] studied the effect of grain size on μi & showed it is proportional to $Dm^{1/3}$,Dm is average grain diameter. Inui[6] compiled a number of references & obtained a linear relationship between μi & average grain size Dm.

4.3 ASPECTS OF MICROSTRUCTURE :

The Knowledge of characterstic elements of microstructure & its controll is necessary in order to extract optimal properties from a specimen. These characterstic elements in ferrite are grain size, their orientation, porosity etc. The final microstructure of the ferrite is due to the sintering process.

a) Sintering :

The starting material is the powder which is made into a dense solid by first compacting it in to the desired shape & then sintered at high temperature. The final microstructure develops during the sintering process. It is therefore necessary to know the microstructural changes that occur during sintering & the reactions which determine the structures, to be able to controll the final properties of material. Sintering

reactivity which is defined as the amount of energy available for sintering, must be sufficiently high for the process to proceed. As surface energy per unit volume of spherical particles is given by

$$Es = 6 \gamma_s / D \qquad \ldots.1$$

Where γ_s - Surface tension of material

D - Diameter of spherical particle.

As sintering proceeds, the particles of the powder compact grow together & the pores in the compact are filled up with material leading to densification of the compact (7)

Sintering & densification require material to be transported. The surface of pore acts as a source of vacancies. These vacancies diffuse through the bulk of the grain to the grain boundaries where they can be discharged. The resulting effect is material transport by the migration of individual ion from the grain boundaries to the pores producing shrinkage.

The vacancy concentration C(r) under a surface of radius of curvature r is given by Kelvin's equation as

$$C(r) = Co \exp \left| \frac{2 \gamma_s a^3}{rKT} \right| \qquad 2$$

Where Co - equillibrium vacancy concentration of almost flat surface of grain boundary.

a^3 - Vacancy volume, s - surface tension.

For good quality of ferrite, introduction of atmosphere having controlled amount of oxygen during sintering is essential. The atmosphere is either air or oxygen while soaking, but oxygen partial pressure has to

be changed during cooling, so that ferrite is in equilibrium with atmosphere and no oxidation reduction of Fe^{2+} ions takes place. This controls the amount of Fe^{2+} ions & does not allow to form the gradient of Fe^{2+} from surface to the interior.

b) Grain Growth :

The source of driving force for grain growth is grain boundary. As grain size increases, the energy of boundary decreases & boundaries move towards the centre of curvature. The rate of grain growth is given by (8,9)

$$D-D_o = Kt^n \qquad 3$$

where Do - original particle size, t - time

K - temperature dependent factor

n - grain growth exponent = 1/2 or 1/3

The presence of impurities in the grain boundaries hinders the grain growth. The grain growth occurs untill the ratio of diameter of inclusion to the volume fraction is equal to the critical diameter of grain. Further growth is inhibited. The lowest possible porosity & full densification can be obtained by promoting rate of sintering & by using fine particles. Reijnen (10), Herring (11) are the main research workers in the field of microstructure of ferrites.

c) Controll of Grain Size :

The grain size cannot be controlled completely in the sintering process, unless very pure raw materials are used. After reaching a critical grain size, few grains grow rapidly at the cost of others, constituting

known as discontinuous growth. It leads to duplex structure. This is favoured if impurities & inhomogeneity exist (12) & it can be related to inclusions (13).

d) Controll of Porosity :

In ceramics, prepared by powder compaction & sintering, porosity is always present. High rate of sintering with small particle size reduces the porosity. Permeability will decreases because of pores pin domain walls. The grains free from pores lead to very high permeability. Because of poor rate of sintering is the cause of microstructure with large pore concentrations. The optimum rate of sintering is achieved when the condition

$$D_c C_c = D_o C_o \qquad \text{- - - -} \quad 4$$

where Dc - diffusion constant of cation vacancies

Do - diffusion constant of oxygen vacancies

Cc - bulk concentration of cation vacancies

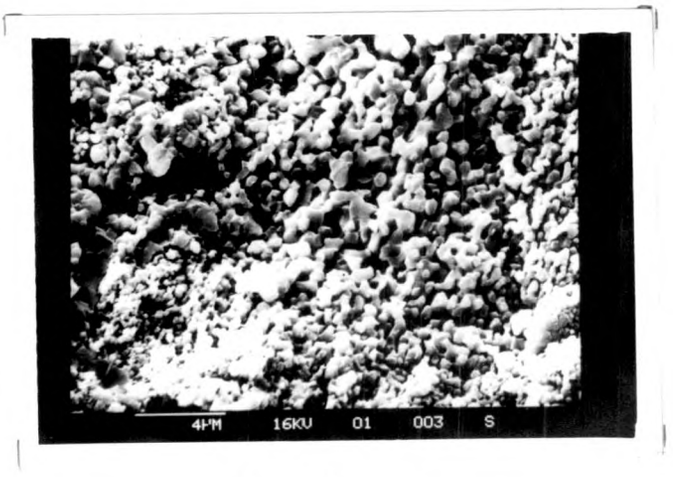
Co - bulk concentration of oxygen vacancies

Discontinuous grain growth is favoured for no pore growth. The low poresity & small grain size combination is very difficult to realise in practice. However, such combinations are achieved by using hot pressing technique.

4.4 EXPERIMENTAL TECHNIQUE :

Scanning Electron Microscope (SEM) is the most advanced instrument used in the study of microstructure It possesses high magnification & high depth of focussing with the ability to form three dimensional

Micrographs Of $Ni_{0.6-x}Co_xZn_{0.4}Fe_2O_4$



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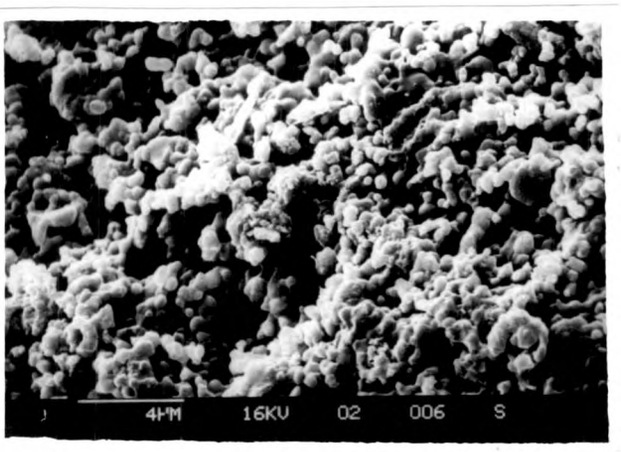

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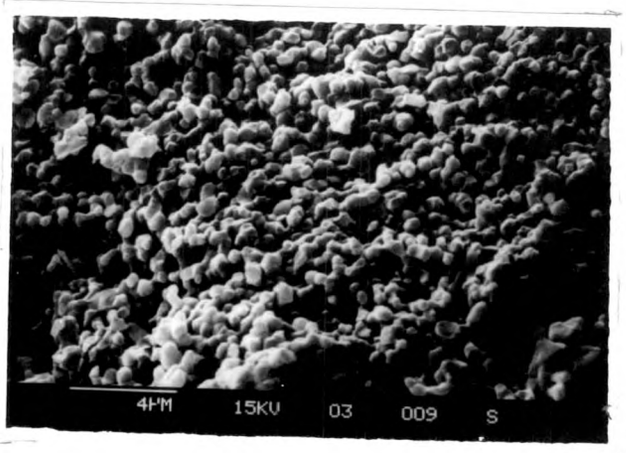

X = 0·02

image.

We have used SEM to obtain micrographs of three of our samples by Cambridge steroscan 5.250 MK.II. This facility is made available to us, by R.S.I.C. Nagapur University, Nagapur.

4.5 RESULT & DISCUSSION :

From the SEM photographs the grain size D has been calculated as follow (14)

1. Drawing a diagonal on the photgraph
2. Measuring the maximum unidirectional particle size in the verticle direction against the diagonal
3. Averaging the maximum unidirectional particle size.

Most of the magnetic properties of polycrystaline magnetic materials are micro-structure dependent. Johnson et al (15) have developed a model to describe grain size dependance of the rotational permeability in polycrystaline ferrites. There is almost a liner dependance of permeability with grain size for the fine grained polycrystals under the condition that the grain size $D_m << \mu_i d$

$$\mu_c = \frac{\mu_i D_m}{\mu_i d + D_m} = \frac{D_m}{d}$$

where d is non-magnetic grain boundary thickness for large grains where $D_m >> \mu_i$ this model predicts a constant rotational permeability μ_{rk} equivalent to that in a single crystal of the same material.

The SEM photographs of the summary presentative ferrite compostions have been shown in Fig (4.1 a,b,c) which clearly indicate the fine grain nature of the

ferrites formed - a characterstic of chemical method of ferrite preparation. The grains stained tobe larger when the ferrite is formed by ceramic method. It is clearly seen that on an average the grain size is less than 0.5μM (micrometer). The fine grains lead to the improvement of density & hence the bulk magnetic properties, this type of grain structure has been reported by some others (16,17). Carefull observation of every micrograph reveals that the porosity within the material is very low and the chances of pores being present within the grains are also negligible. There is no change of either microstructure or the grain size & topology with the addition of Co^{2+} in the material.

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