CHAPTER - V

F E R R I T E M I C R O S T R U C T U R E

5.1 INTRODUCTION

The term microstructure as the name itself suggests, means the structure that can be seen through the microscope. But now a days the term has out grown it's meaning in scientific and engineering usage. The elements of micro structure concerned are [1] :

i) The phases present, their number and identification,

ii) The volume fraction of the phases present,

iii) Characteristic elements of each phase, such as grains, their size, shape, orientation, distribution and texture [3] with respect to other phases present.

Microstructure affects structure sensitive properties like magnetic properties, electrical properties and 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. Thus, these days, it is possible for us to produce ceramic materials with desired properties, for specific applications, by controlling their microstructure.

SHIVAJI UNIVERSITY LIBRARY KOLHAPUR

It is therefore of great importance to have a complete knowledge of the physical relation between the physical properties and the characteristic elements of microstructure in order to obtain optimal properties. It is equally important to know how the microstructure is controlled by the ceramic process.

5.2 MICROSTRUCTURE AND FERRITES

Microstructure plays a role in determining high power handling ability as well as low power loss in saturated microwave devices. Fine grained ferrites are used for this purpose. At the lower frequencies ferrites are almost invariably employed as an unstaturated material. The operation of device depends on a change in the relative size of the domains or in the orientation of the magnetic moment within the domains, under the in fluence of an externally applied field. Therefore in devices at lower frequencies large grained, less porous ferrites are used to give large domains and high μ values. The good performance of devices operating at RF and AF depends upon high initial μ values of the material used in them. Therefore these devices use ferrites with large grains free from intragranular pores. The high resistivity requirement of the components is achieved by chemical composition and process control. In computers and magnetic systems where storage of information is of prime

importance, ferrites with square loop characteristics ie. with large remanence and small porosity are used.

5.3 DEVELOPMENT OF MICROSTRUCTURE DURING SINTERING [4,5,6].

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

In the first place the 'sinter 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

$$E_S = \frac{6\gamma_S}{D} \qquad \ldots(5.1)$$

where γ_S = surface tension of material,

D = diameter of spherical particle.

the particle size of the starting powder must be small for sintering to proceed. As sintering proceeds, the particles of the powder compact grow together and the pores in the compact are filled up with material leading to densification of the compact [6].

Sintering and densification require material to be transported. The principal mechanism for densification in ionic solids such as spinels and garnets, is considered to be described by the Nabarro – Herring [7,8] theory for diffusional microcreep. 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

$$C(r) = C_o \exp\left[\frac{2\gamma_s a^3}{rKT} \right] \qquad \ldots(5.2)$$

where C_o = equillibrium vacancy concentration of almost flat surface of grain boundary,

γ_s = surface tension of material,

a^3 = vacancy volume.

Since C(r) is always greater than C(o) migration of vacancies from pore surface to grain boundaries occurs as a result of vacancy concentration gradient between curued surface of pore and almost flat surface of grain, at temperatures where mobility of ions is sufficiently high. Thus grain boundaries play a role in the elimination of porosity [9].

The grain boundaries represent a certain amount of interfacial energy which forms the driving force for grain growth on heating. Since large grains, usually, have more sides than those of small grains, according to the topological requirement, former grow at the expense of latter. The rate of grain growth is given by [9,10]

$$D - D_o = Kt^{1/2} \qquad \ldots(5.3)$$

where D_o = original size of the particle,

D = size of particle at time t ,

K = temperature dependent factor.

In practice low rate of grain growth is observed due to the presence of impurities in the grain boundaries which hinder the movement of grain boundaries.

The impediment of grain growth can even be stronger when inclusions are present. One of the main influencing factors is the change in size, amount and distribution of the inclusions during heating. During sintering the disapperance of pores or inclusions caused the formation of a large grain in a matrix of fine grains. Then the driving force for the further growth of this large grain suddenly becomes very large because of the increasing curvatures of the grain boundaries. This leads to discontinuous [9] grain growth forming a 'duplex structure'. This is an intermediate structure which upon

further heating to a high sintering temperature leads to normal or continuous grain growth.

According to Zener [11] grain growth occurs until the condition

$$D_{crit} = \frac{d_i}{f_i} \qquad \ldots(5.4)$$

is fulfilled, where

d_i = diameter of the inclusion,

and f_i = volume fraction of the inclusion.

When the grain reaches this dimension further grain growth is inhibited. If in this situation for some or the other reason a large grain is formed it can grow very rapidly to a much larger size than fine grains in the matrix.

5.3.1 *CONTROL OF GRAIN SIZE*

For producing technical ferrites the art developed has been the control of raw materials and processing in order to obtain reproductible microstructures. Subtle changes in the impurity content, the packing density and processing parameters can have a very marked effect on grain growth.

A better control of grain size will be obtained with pure materials. If no special measures are taken, undesirable grain growth occurs during sintering. However, a relatively high chemical reactivity of ferrites makes it difficult to find

suitable grain growth inhibitors. A second phase can be included in the matrix to control grain growth [12,13,14]. The addition of CaO to MnZn ferrites is an example of an impurity segregated in grain boundaries which decreases the grain growth rate [15] and also that of sintering. In all these cases discontinuous grain growth remains possible by the dissolution of the addition in the crystal lattice.

In pure materials the occurance of discontinuous grain growth during sintering is inevitable. According to equation $D_{crit} = \frac{d_i}{f_i}$, a decreasing pore volume (f_i) during sintering will increase D_{crit} , for constant d_i , and there by the possibility for discontinuous grain growth. The actual behaviour will be strongly dependent on the relative velocities of the sintering and grain growth processes, and more over d_i need not be constant during sintering. If the sintering rate is sufficiently high it has proved to be readily possible to control discontinuous grain growth in a ferrite [16] by optimizing the ceramic procedure. Apparently grain size and pore size distributions are important parameters which make it possible to avoid duplex structures in pure materials. Fully dense NiZn ferrites have been made in this way. Paulus [15] has made a number of studies of

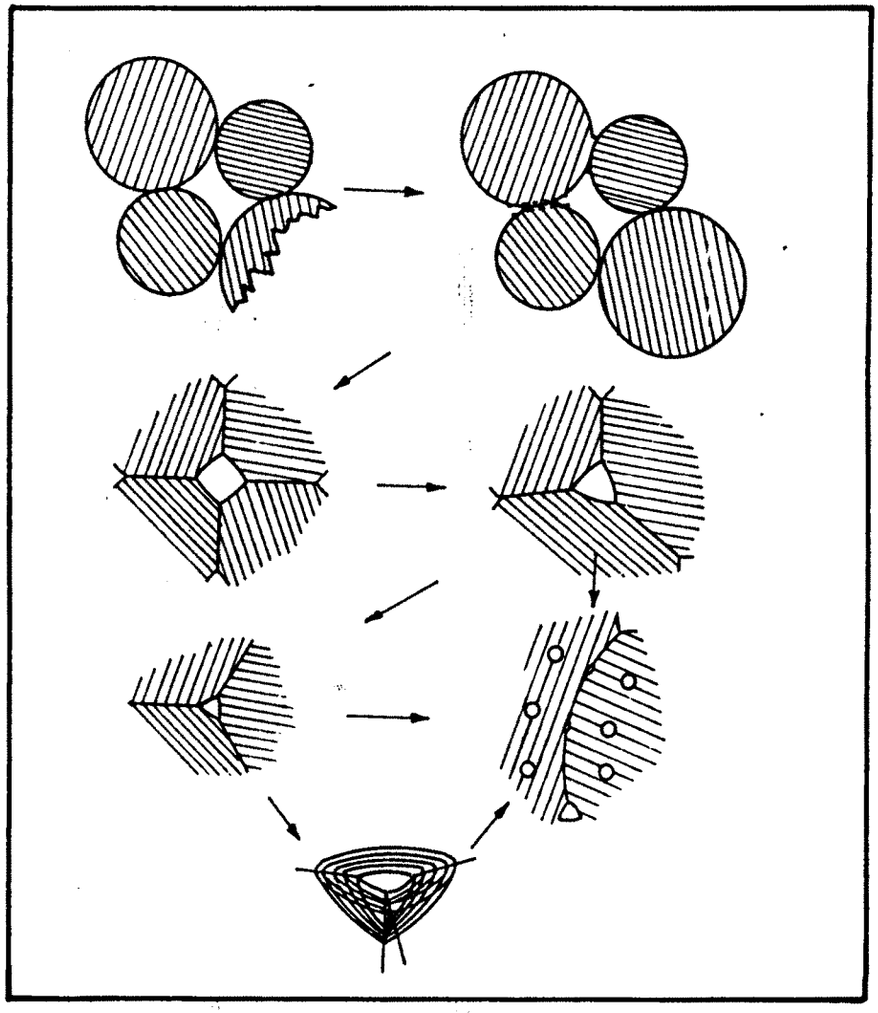

Fig. 5·1 Schematic representation of typical structures observed during sintering. All views are two-diamensional except bottom center which is a perspective view of a closed pore at a corner where four grains meet. After Coble and Burke.

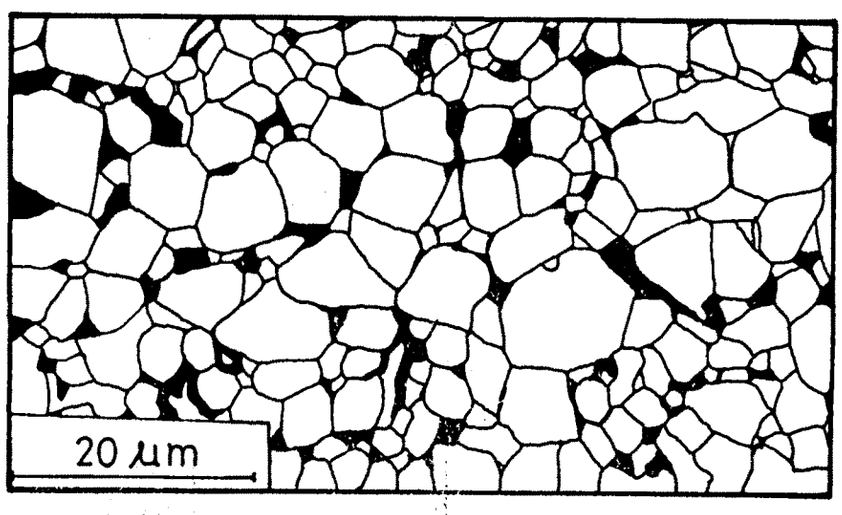

Fig. 5·2 Homogeneous grain structure (MgMn spinel ferrite).

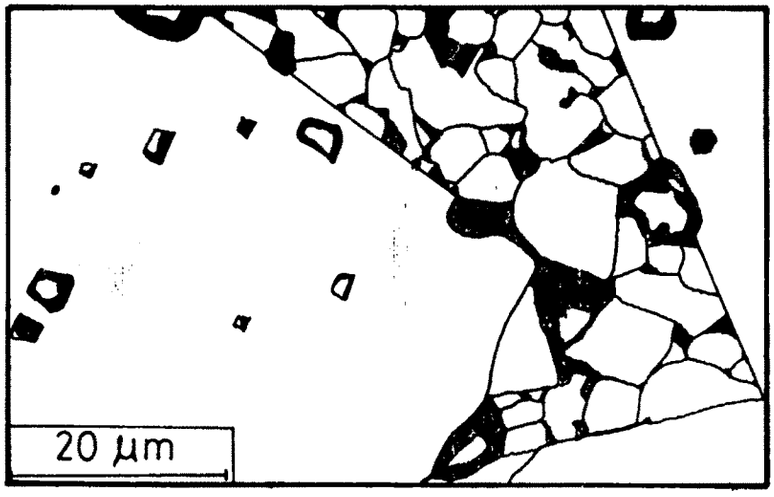

Fig. 5·3 Discontinuous grain growth (MgMnZn spinel ferrite). Very large grains embedded in matrix of small grains, the duplex structure.

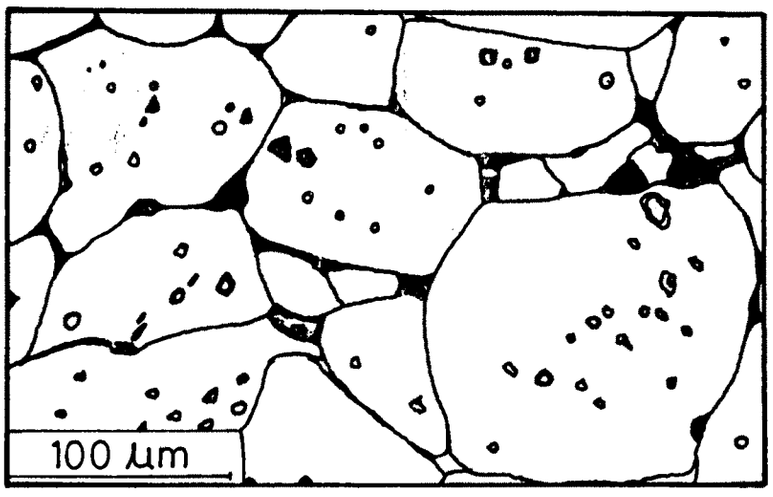

Fig. 5·4 Discontinuous grains growth (MgMnZn spinel ferrite). High nucleation rate; Large grains of nearly equal size with pores trapped inside the grain boundaries.

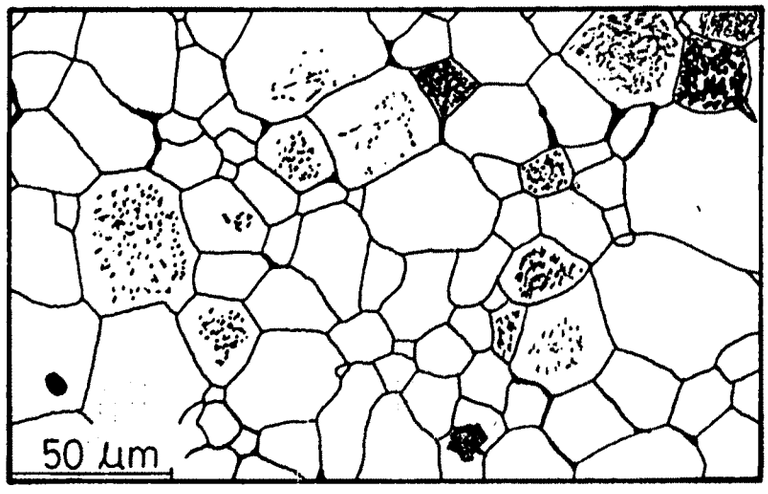

Fig. 5·5 Dense sintered NiZn ferrite prepared from very pure raw materials A. L. Stuijts, private communication.

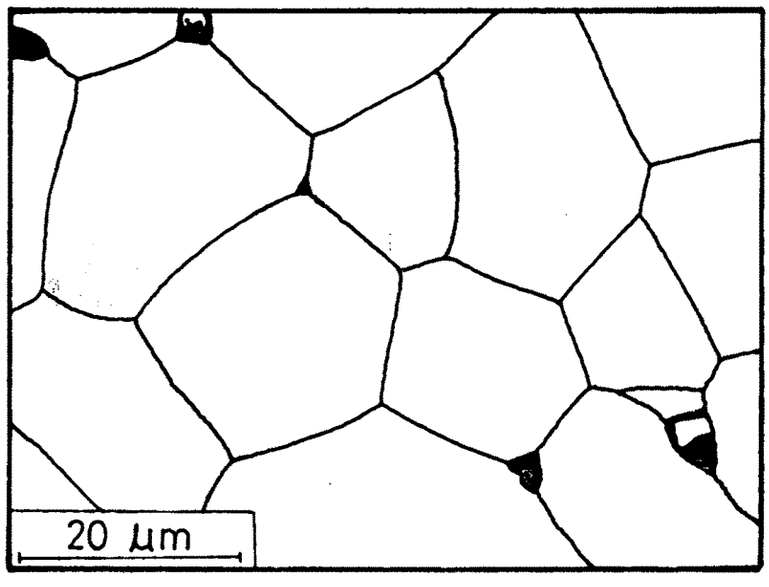

Fig. 5·6 Continuous grain growth to large grains. Some single pores remain at corners where grain boundaries meet (YIG, porosity 0·5 %).

growth kinetics in NiZn and MnZn ferrites. (different types of grain structures are shown in Figs. 5.1 – 5.6).

5.3.2 *CONTROL OF POROSITY*

Porosity is considered as a phase that is always present in ceramics, prepared by powder compaction and heat treatment. In order to obtain a low porosity it is useful to promote the sintering rate by using powders with large surface area. The exhaggarated pore growth occurs when the pores do not impede grain growth but move along the moving grain boundary. Mechanism described by Reijnen has shown that it is possible for this phenomenon to occur in all oxidic materials where cation vacancies are present, and which contain ions with different valency states.

From theoretical and experimental studies on the sintering process in oxidic materials Reijnen [17] showed that the microstructure with large pores is related to compounds which have intrinsically a low sintering rate. It appears that the sintering theories, as developed originally for metals [18] have to be modified for ionic solids.

Sintering rate is optimum when

$$D_c\ C_c = D_o\ C_o \qquad \ldots(5.5)$$

where D_c = diffusion constant of cation vacancies;

C_c = bulk conentration of cation vacancies;

D_o = diffusion constant of oxygen vacancies;

and C_o = bulk concentration of oxygen vacancies.

At low sintering rate pore growth becomes predominant. If no pore growth occurs, discontinuous grain growth is found.

From the consideration given above it is clear that the combination of a low porosity and small grain size is extremely difficult to realise with normal ceramic process. It is found that the application of pressure promotes the sintering process but not grain growth. This investigation is being used in hot pressing techinque to achieve low porosity and to control grain growth. By the method of continuous hot pressing [19] it is possible to conserve the original particle size of the starting material [20] and to combine this with a very low porosity.

5.4 QUANTITATIVE MICROSCOPY OR STERIOLOGY

Quantitative steriology[21] or metallography is concerned with the quantitative characterization of microstructures in terms of their point, lineal, areal, and volume elements. By

means of suitable two-dimensional measurements on the plane of polish, statistically exact information can be obtained about the microstructural features in the three dimensional space occupied by the alloy (material).

Symbols—Table 6.1 shows the principal symbols used and gives examples of the combined notation in common usage. The term N_V, for example, refers to the number of objects per unit volume, and represents a fraction (N/V_T), where N is the total number of objects in the arbitrarily selected test volume V_T. On the other hand, P_L (or P/L_T) stands for a measurement in which a test line of total length L_T is laid down repeatedly on the microstructure, giving P number of point intersections with lineal features, perimeters etc. Each symbol represents both a geometrical element as well as a specific dimension.

Table I : Principal symbols [21] and combined notation

P	points of intersections	mm^0	$P_L = P/L_T$
L	lines	mm	$L_A = L/A_T$
A	flat surfaces	mm^2	$A_A = A/A_T$
S	curved surfaces	mm^2	$S_V = S/V_T$
V	volumes	mm^3	$N_V = N/V_T$
N	number of objects	mm^0	

Basic Equations:

Table given below reveals in compact form the interrelationships between microstructural features that can be measured and those that cannot. Arrows indicate those quantities that yield the normally inaccessible three dimensional quantities V_V, S_V, L_V, and P_V. In the triangular mtrix given below, the corresponding basic equations are written.

Table II : Relationships[21] of measured (⬡) and Calculated (□) quantities.

(Dimensions arbitrarily expressed)

Microstructural feature	Dimensions of symbols mm^0	mm^{-1}	mm^{-2}	mm^{-3}
Points	P_P	P_L	P_A	P_V
lines	L_L	L_A	$\lvert \overline{L_V} \rvert$	
Surfaces	A_A	$\lvert \overline{S_V} \rvert$		
Volumes	$\lvert \overline{V_V} \rvert$			

Basic Equations

$$V_V = A_A = L_L = P_P \quad mm^0$$

$$S_V = (4/\pi)L_A = 2P_L \quad mm^{-1}$$

$$L_V = 2\ P_A \quad mm^{-2}$$

$$P_V \quad mm^{-3}$$

Two dimensional features of microstructures can be measured on SEM micrographs of plane polish of sample. Using these and above equations quantitative microstructures can be determined. Physical properties of sample are studied experimentally, and correlation between microstructure and properties can be established.

Average grain size [22] $\bar{D}$ is given by the relation $\bar{D} = K\ \bar{L}$, where $\bar{L}$ is the average concept size of the grain and K is proportionality constant = 1.5 for spherical grain geometry with uniform size distribution (in case of optical microscopy).

5.5 EXPERIMENTAL

SEM is the most important and exciting technique used in microstructure analysis of materials. It is preferred to optical microscopy because of it's high resolution, high magnification and high depth of focussing. In the present

work we have used SEM to obtain micrographs of two of our samples. The electron microscopy work was carried out at the Minerological Institute, University of Mysore, Mysore using JEOL scanning election microscope.

Mesurement of the average grain size of the samples was done by counting the number of grain boundaries intersected by a measured length of a random straight line drawn on the micrograph [23].

5.6 RESULTS AND DISCUSSION

In Fig. 5.7 and 5.8 SEM micrographs of samples $CoFe_2O_4$ and $Co_{0.6}Zn_{0.4}Fe_2O_4$ sintered at 900°C for 15 hrs and 30 hrs are presented along with measured grain size. The porosity of the samples varies from 20% to 30% as they have been prepared by ceramic technique.

Each set of our micrographs reveals small grains with more open pores along grain boundaries and hence large porosity at lower sintering time (15 hrs), and large grains with less open pores along grain boundaries and hence small porosity at higher sintering time (30 hrs). Similar type of findings have been reported by earlier workers [25]. Our findings are in accordance with grain growth rate equation [11,12], $D - D_0 = K\ t^{1/n}$.

Greskovich and Lay's [24] observation of increase in average grain size during initial stage of sintering holds good in our samples also. This indicates that the densification mechanism through solid state diffusion is more effective at higher sintering time as it is so at higher sintering temperatures.

In our micrographs [NO.36 & 38] the on set of the exagerated grain growth can also be seen in Figs. 5.7 and 5.8. This indicates that a few grains have grown to the size beyond the critical size expressed by equation [6.4].

STRUCTURE - PROPERTY CORRELATION

In Table 5.1 sintering conditions, grain size and physical properties determined experimentally for the two samples mentioned above are presented to make the microstructure property correlation self-evident.

The observed changes in electrical and magnetic properties can be explained on the basis of the microstructural changes brought in by sintering conditions. The pores invariably introduce the insulating or impending paths to the electrons. In otherwords pores offer extrinsic contribution to the activation energy. At higher sintering time/temperature it is obvious that there is more densification or less porosity. The reduction in activation energy may be attributed to the

reduction in number of pores due to densification. Due to reduced number of pores, the individual grains become larger and come closer, thus increasing the effective area of grain to grain contact. The resistivity is inversely proportional to the cross sectional area of the conductor and so that total resistance of the matrix decreases. Reduction in resistivity or increase in conductivity is the consequence of reduction in activation energy.

Each grain possesses certain resultant magnetic moment. Since the rate of grain growth depends upon the sintering time/temperature [9], the porosity is high for specimen sintered for lower sintering time or at low temperature. A pore is a sort of void or the gap and this will break up the magnetic circuit between grains. If the number of pores is large this may lead to the net reduction of magnetization in the bulk. The grain boundary acts as an impediment to the domain wall motion or rotation. Due to large number of grains per cc, the net area of grain boundary increases and thus there is more resistance for the process of magnetization. When the material is sintered for higher sintering time or at high temperature the net area decreases due to densification of grains and the magnetization gets increased. M_s and μ_B values for our samples sintered for 30 hrs are higher than those values for samples sintered for 15 hrs.

Even though much progress is made in controlling ferrite properties through microstructure advanced work is yet to be done in reducing porosity, in eliminating pores within grains, in controlling grain size in the investigation of high curie temperature material and grain oriented cubic ferrites.

$CoFe_2O_4$

Sintered at 900°C for 15 hrs.

$CoFe_2O_4$

Sintered at 900°C for 30 hrs.

Fig. 5·7 – SEM micrographs of $CoFe_2O_4$ samples.

$Co_{0.6}Zn_{0.4}Fe_2O_4$

Sintered at 900°C for 15 hrs.

$Co_{0.6}Zn_{0.4}Fe_2O_4$

Sintered at 900°C for 30 hrs.

Fig. 5·8 – SEM micrographs of $Co_{0.6}Zn_{0.4}Fe_2O_4$ samples.

TABLE - 5.1

Microstructure property correlation data of $CoFe_2O_4$ and $Co_{0.6}Zn_{0.4}Fe_2O_4$ Samples Sintered at 900°C for 15 hrs and 30 hrs.

S.No.	Composition	Sintering temparature °C	Sintering time hrs	Average grain size D in microns	Porosity P	Resistivity at 100°C $\rho_{100} \times 10^5$ ohms cms.	Activation energy (eV)	Sat,Moment m_H in Bhor Magneton	sat Magnetization $4\pi M_s$ in gauss
1	$CoFe_2O_4$	900	15	1.25	0.230	4.1	E_p= 0.55 E_F= 0.31	3.41	4122
		900	30	1.64	0.210	1.2	E_p= 0.51 E_F= 0.29	3.51	4298
2	$Co_{0.6}Zn_{0.4}Fe_2O_4$	900	15	0.68	0.270	6.6	E_p= 0.34 E_F= 0.26	4.90	5580
		900	30	1.11	0.259	2.6	E_p= 0.31 E_F= 0.25	5.19	6033

REFERENCES

[1] Broese Van Groenou A., Bonger P.F., and Stuijts A.L., "Magnetism, Microstructure and Crystal Chemistry of spinel ferrites", Mater. Sci. Eng. 3, 373 (1968/69).

[2] Rodrigue G.P., in "Treatise on Materials Science and Tech", Vol. II, Academic Press, NY, P. 383 - 449 (1977).

[3] Jonker G.H., Stuijts A.L., "Controlling the properties of electromagnetic materials through their microstructure", Philips. Tech. Rev. 32, No-3/4, P. 83, (1971).

[4] Fisch meister and Exner E., Metall, 18, 932 (1964) ; 19, 113 (1965); 19, 941 (1965).

[5] Thummher F., Thomma W., Met. Rev. 115, 69 (1967).

[6] Stuijts A.L., and Kooy C., Sci. Ceram. 2, 231 (1965).

[7] Herring C., J. Appl. Phys. 21, 437 (1950).

[8] Nabarrow F.R.N., Rept. Conf. strength of solids, Phys. Soc. London, P. 75 (1948).

[9] Burke J.E., in Kingery W.D. Ed. "Kinetics of high temp. processes, NY, 109 (1959).

[10] Burke J.E. and Turnbull., Progr. Metal Phys. 3, 220 (1952).

[11] Zener C., in Smith C.S., Trans. AIME, 175, (1948), 15.

[12] Baba P.D., J. Am. Ceram. Soc. 48, 305 (1965).

[13] Paulus M., and Guillaud C.M., J. Phys. Soc. Japan, 17, 632, suppl. B-1 (1962).

BARR. BALASAHEB KHARDEKAR LIBRARY
SHIVAJI UNIVERSITY, KOLHAPUR

[14] Krijtenburg G.,
Europ Tagung Uber Magnetismus,
Wien, 21 - 24 (Sept, 1965).

[15] Paulus M.,
Phys. Status. Solidi, 2, 1181 and 1325 (1962).

[16] Stuijts A.L.,
Proc. Brit. Ceram. Soc. 2, 73 (1964).

[17] Reijnen P.J.L.,
Sci. Ceram. 4, 169 (1968).

[18] Kuczynski G.C.,
J. Metals Trans Met. Soc. AIME 185, P, 169 (1949).

[19] Oudemans G.J.,
Philips Tech. Rev. 29, P. 45 (1948).

[20] DE Lau. J.G.M.,
Proc. Brit. Ceram. Soc. 10, P. 275 (1968).

[21] Underwood E.E.,
in "Microstructural Analysis, Tools and Tech",
Plenum Press, NY, London, P. 35 - 40 (1973).

[22] Narayan R., Tripathi R.B., Das B.K., and Jain G.C.,
"Microstructure and Grain growth Kinetics".
J. Mat. Sci. 18, P. 1583 - 89 (1983).

[23] Goel N.C.,
Ph.D. Thesis. Univ. of Delhi, (1977).

[24] Greskovich C., and Lay K.,
J. Am. Ceram. Soc. 35, 142 - 146 (1972).

[25] Pujar R.B.,
M Phil Thesis (1987), Shivaji University, Kolhapur.

...Oo*oO...