Chapter - II

PREPARATION OF FERRITES

2.0 Introduction

Ferrites were first prepared by nature. The ferrous ferrite (Fe_3O_4) called magnetite is the naturally occurring ferrite. The solid state reaction in which, a transformation of crystal configuration takes place instead of a change in chemical comopsition. First of all the solid state reaction in metals, scientifically introduced by Faraday [1]. The poineering work on solid sate reactions has been carried out by J. Hedvall [2], G. Tammann [3] and W. Jander [4]. Forestier[5] in 1928 prepared ferrites by basic precipitation from chloride solutions and subsequent heat treatment. Wold [6] prepared the number of ferrites by solid state double decomposition of transition metal chloride with alkali.

$$MCl_2 + Na_2Fe_2O_4 \longrightarrow MFe_2O_4 + 2NaCl$$

The physical and chemical properties of ferrites depend on the method of preparation [7]. The preparation of ferrite under different sintering atmosphere affects the electrical resistivity, apparent density, initial permeability and size of unit cell [8]. Toshio Takada et al [9] showed that cation distribution of manganese ferrite prepared by wet method is different from that of manganese ferrite prepared by ceramic method. Synthesis of high permeability Cu-Mg-Zn ferrites using oxalate precursor is studied by Bhosale et al [10]. They observed considerable improvement in permeability and saturation magnetization as compared to samples prepared by ceramic method [11].

Verma et al [12] have prepared high resistivity Ni-Zn ferrites by the citrate precursor method and observed imporvment in the the electrical and magnetic properties of these ferrites.

K. Suresh and K.C. Patil [13] reported the preparation of high density Mn-Zn ferrites by the solid state recation of ultrafine Mn Fe_2O_4 and $ZnFe_2O_4$ obtained by the thermal decomposition of solid state solution precursor. They observed that, the ferrites prepared in nitrogen atmosphere show less pores as compared to ferrites prepared in air.

For present investigation samples have been prepared by oxalate precipitation method .

2.1 Preparation of polycrystalline ferrites

K.J. Standley [14] describes the four steps in the preparation

i. Preparation of materials to form an intimate mixture with the metal ions

ii. Presintering or calcination

iii. Milling after calcination and pressing the powder into the required shape

iv. Sintering to form final product.

On account of preparation of materials Standley K.J. [14] describes four methods for the preparation of ferrite materials.

a) Oxide or ceramic method.

b) Decomposition method.

c) Precipitation technique

i. Hydroxide precipitation

ii. Oxalate precipitation

a) Oxide or ceramic method

Ceramic method is the most widely accepted commercial method for the preparation of ferrite powders. In this method, appropriate metal oxides are accurately weighed in desired proportion and mixed thoroughly. The mixture is wet milled with steel balls for a long period. After milling, the mixture is dried and presintered at suitable temperature for a few hours. The presintered material is again milled to have fine powder. This powder is pressed into desired shape with the help of hydrolic pressure gauge and subjected to final sintering at suitable high temperature.This method requires high sintering temperature. The heating at high temperature results in evaporation of elements like zinc, lithium giving chemical inhomogenity. Additionally because of this method, the particle size gets increased. Also the oxygen evolution and reabsorption increases the porosity of the ferrite. These are disadvantage of ceramic method [15]. Ferrites have been prepared by this method by many authors [16-19].

b) Decomposition method

In this method required proportion of starting materials such as carbonate, nitrates and oxalates are thermally decomposed in order to obtain oxides. Other details of this method are similar to that of oxide or ceramic method.

c) Precipitation technique

i. Hydroxide precipitation

In this method, the required hydroxide solutions are precipitated simultaneously, so that the precipitate contain required metal ions in correct proportion.

The disadvantage of this method of preparing ferrites from co-precipitated hydroxides is that the hydroxides are gelatinous and voluminous precipitates are difficult to handle, filter and wash. In addition, precipitation of metal ions as hydroxides using ammonia causes loss of some ions like Cu^{2+} and Ni^{2+} by complexing [15].

Economos [8] has prepared $MgFe_2O_4$ ferrite by hydroxide precipitation method. Nickel ferrite [20] and cobalt ferrites [21] have prepared by hydroxide precipitation technique.

ii. Oxalate precipitation

In this method precipitation of metallic oxalates carried out by using ammonium oxalate, which does not leave any residue after ignition. The principle advantage of this method is the mixning of the metal ions on a molecular scale, so that greater reactivity and more homogenous product results. By this method, high density ferrites can be prepared at relatively low sintering temperature and smaller duration.

Economos [8] has prepared magnesium ferrite by oxalate precipitation technique. Stuijts [22] reported the formation of nickel ferrite at 300 °C from co- precipitated oxalate precursor. Schuele and Deetscreek [23] have reported the preparation of fine particle nickel ferrite and cobalt ferrite using oxalate solid solutions.

2.2 Presintering or calcination

The purpose of presintering is to decompose the oxalates into metal oxides, resulting into end product as ferrite. This process also helps to homogenize the material and control the shrinkage that occurs in the final sintering. During presintering, the amount of reaction depends on the reactivity of the components and on the presintering temperature [24].

2.3 Milling

In this step reactivity of powder is improved. The smaller particle is achieved , so that the secondary grain growth is avoided during final sintering. After milling, powder is dried and used for preparing the final product of required shape.

2.4 Sintering

Sintering is the most important heat treatment process by which a mass of compacted powder is transformed into a dense form. For good quality ferrites, the grain size should be uniform. The final sintering process achieves inetrgranular pores, continuous grain growth and develops microstructure. The sintering temperature [19], sintering time [25] and sintering atmosphere [13] plays important role in the development of microstrure.

The factors like particle size, particle shape, particle size distribution, intreparticle porosity, homogeneity in chemical composition, pore size distribution, temperature gradients are affected by sintering process [26].

2.5 Mechanism of solid state reaction

To initiate the mechanism of solid state reaction, homogenous mixture of metal oxide (MO) and ferric oxide (Fe_2O_3) is heated to an elevated temperature. The mechanism is based on diffusion between the divalent metal oxide (MO) and the trivalent iron oxide (Fe_2O_3).

In the initial stage of reaction, there is only one phase boundary between the divalent metal oxide (MO) and ferric oxide (Fe_2O_3). After the nucleation of the ferrite, the boundary changes to two phases, one between Fe_2O_3 an MFe_2O_4 and other between MO and MFe_2O_4 as shown in Figure 2.1. Further in the reaction, the divalent metal oxide (MO) and ferric oxide (Fe_2O_3) are transported through the ferrite phase. The transfer mechanism can be explained in the three different modes, which leads to the formation of ferrite.

In the first mode of transfer mechanism, only the cations migrate in the opposite directions, whereas the oxygen ions essentially remains stationary [27].

In the second mode of transfer mechanism, diffusion of cations is compensated by an associated flux of anions instead of counter current of another cations.

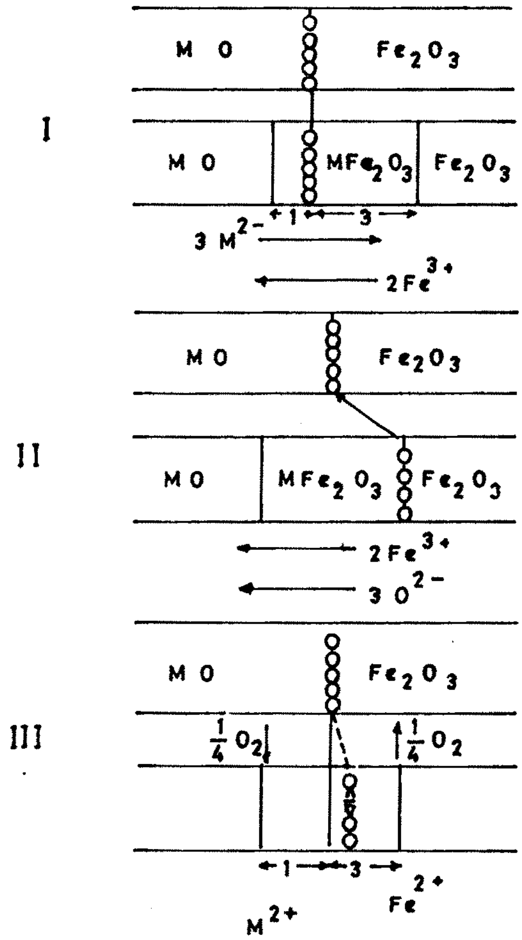

FIG.2·1 - REACTION MECHANISM INVOLVED IN FER
FORMATION.

Third mode of transfer mechanism involves the diffusion of iron through ferrite layer in a reduced state of Fe^{2+}. During this, the oxygen is transported through the gas phase, being given off at the MFe_2O_4/Fe_2O_3 interface and taken up again at MO/MFe_2O_4 interface.

2.6 Hot pressing

The sintering with simultaneous applications of an external pressure is called hot pressing. Hot pressing is the way of achieving a dense ferrite material at sufficiently low temperature. A loose or compacted powder is placed in a suitable chamber and hot pressed by applying the pressure from one or more direction at elevated temperature, after cooling the finished form is removed by releasing the pressure. Several new techniques have been developed to obtain high density and hard ferrites by using uniaxial hot pressing technique in a very short time. To obtain high density materials, it is important to sinter a powder under isostatic pressure. The preparation of Mn-Zn dense ferrites by isosttic hot pressing have been studied by Buthker and Berben [28]. Hardtl [29] described a novel "moldless" technique for hot pressing.

2.7 Preparation of ferrites under investigation

The ferrite samples in the present study were prepared by oxalate precipitation method using nickel zinc and ferrous sulphates as a starting materials.

The general formula of ferrite system is $Ni_{1-x}Zn_xFe_2O_4$, where x=0, 0.20, 0.40, 0.60, 0.80 and 1.00.

The nickel sulphate, zinc sulphate and ferrous sulphate were taken in required proportion using the single pan semi-microbalance and dissolved in the distilled water. The pH of the solution was maintained at 4.7. The solution of ammonium oxalate was then added into the mixture excessively in order to complete the process of precipitation. This can be explained by chemical reactions as follows

$$NiSO_4 + 2H_2O + C_2O_4^{-} \longrightarrow NiC_2O_4, 2H_2O + SO_4^{--}$$

$$ZnSO_4 + 2H_2O + C_2O_4^{-} \longrightarrow ZnC_2O_4\ 2H2O + SO_4^{--}$$

$$FeSO_4 + 2H_2O + C_2O_4^{-} \longrightarrow FeC_2O_4\ 2H_2O + SO_4^{--}$$

The precipitate was the solid solution of nickel, zinc and ferrous oxalates. To obtain a sample in powder form, precipitates of oxalates were filtered by using Buckner funnel and washed four to five times with the distilled water in order to remove sulphate ions. The removal of sulphate ions was confirmed by barium chloride test. The precipitate was finally dried. The careful presintering of co- precipitated oxalate were carried out in air at 600 °C for 1 h. The presintered powder was milled using acetone base in agate morter and sintered at 1000 °C for 4 h in air. The sintered powder was again milled to have fine powder. For preparation of pellets a small quantity of powder was subjected to the pressure of 7 tons for 5 minutes by keeping it in a die of diameter 1 cm and was finally sintered at 1000 °C for 4 h in air. The cooling to the room temperature was carried out at rate of 80 °C h^{-1}[30].

The presintering and sintering processes were carried out by using glowbar furnace. The temperature of furnace was measured with the help of well calibrated chromel-alumel thermocouple.

Figure 2.2 shows flowchart of the precipitation of ferrites under investigation.

2.8 Measurement of density

Generally density measurement of ferrite pellets is carried out by using physical dimension method.

The density of pellet is calculated by the relation

$$\rho_s = \frac{M}{\pi r^2 h} \qquad \text{.... 2.1}$$

where M - mass of the pellet

r - radius of the pellet

h - thickness of the pellet

S.R. Murthy and T.S. Rao [31} measured the bulk density of Ni-Zn and Co-Zn ferrites from volume and weight measurement in air at room temperature. They found the values within 85% to 95 % of the corresponding x-ray densities.

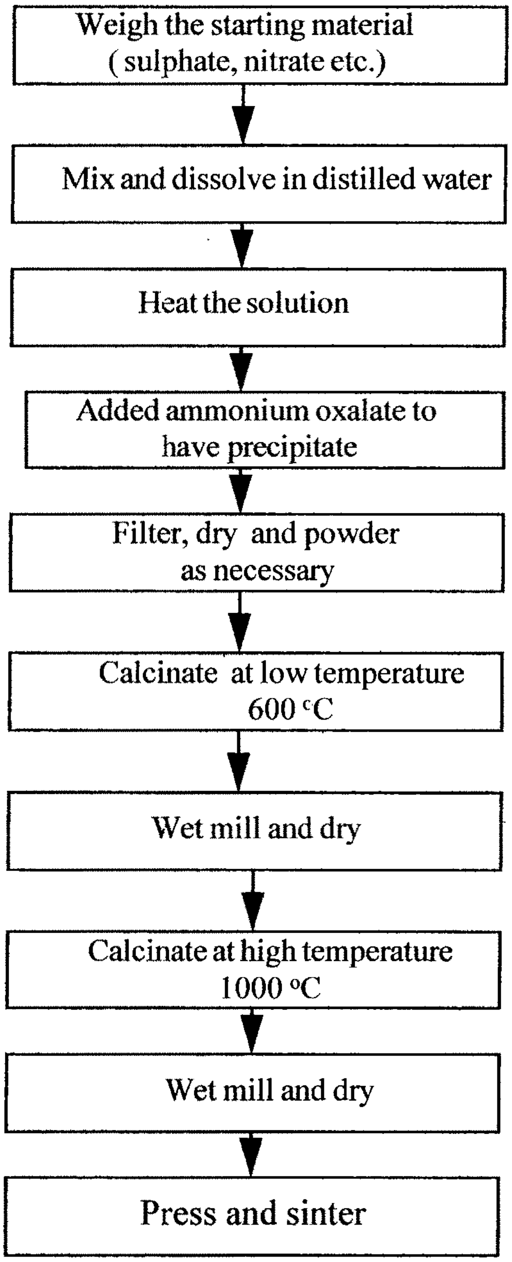

Fig. 2.2 Flow chart of oxalate precipitation method

Physical densities of all the samples under investigation were determined by Archimedies principle [32, 33].

Initially weight of the sintered pellet was measured by a single pan digital balance in air. The pellet was then immersed in A.R grade xylene for 12 h. Then weight of the pellet in xylene was measured. The density of pellet was calculated by using the formula.

$$\rho_s = \frac{W_1}{W_1 - W_2} \rho_L \qquad \ldots 2.2$$

where W_1 = weight of the pellet in air

W_2 = weight of the pellet in xylene

ρ_L - density of xylene

The values of physical densities and porosities are presented in table 2.1. From this table it can be noticed that the densities are greater than 5.0 gm/cm^3 which is more than the samples prepared by ceramic method. The percentage porosity lies in the range 1.18 % to 2.97 %. Y. Xu et al [34] also observed ~ 98 % of the therotically density in Ni-Zn ferrite core prepared by oxalates.

Table 2.1

X-ray density, physical density and porosity data of $Zn_xNi_{1-x}Fe_2O_4$ system

Zinc content x	X- ray density ρ_x gm/cm^3	Physical density ρ_s gm/cm^3	Porosity %
0	5.4059	5.3418	1.185
0.2	5.4292	5.2675	2.97
0.4	5.4090	5.2691	2.5
0.6	5.3832	5.2935	1.6
0.8	5.3801	5.2998	1.51
1.0	5.3550	5.2884	1.248

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