Chapter II
Preparation of ferrites

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PREPARATION OF FERRITES

2.1. Introduction

Ferrites can be classified based on their properties in two categories - intrinsic and extrinsic. Saturation magnetization, anisotropy, magnetostriction and Curie temperature are considered to be intrinsic properties. Hysteresis, resistivity, dielectric constant are supposed to be extrinsic properties. Extrinsic properties depend on structural - aspects like grain size, porosity and impurities.

Polycrystalline ferrites are generally formed by a certain type of solid state reaction. Commercially the ferrite material will be required in solid form. The material produced by the reaction will then be powdered, formed into the desired shape and size and again heated to high temperature to form the homogeneous solid again by the sintering process.

It is also very important to be able to make material of known composition and properties. For this initial and final firing conditions must be correctly maintained otherwise with a given starting material the final chemical composition may not be the same. This is because the valence state of the metal ions present and the amount of oxygen present in lattice may change.

These variation can affect the physical properties of the solid which in turn, change the electrical and resistivity and saturation magnetization.

A signeted material is not truly solid but contains a large number of pores. The quantity, size, shape and distribution of crystal grains and pores in the solid will vary according to the forming techniques and with firing temperature, atmosphere and time. Pore distribution affects physical properties like density considerably.

The oxygen content is important for the magnetic properties. Apart from the firing temperature, the oxygen content of the atmosphere in which the material is signeted influences magnetic parameters to a large extent. To achieve a suitable microstructure together with the proper oxygen content and distribution of the cations, time and temperature of sintering, the partial pressure of oxygen in the sintering atmosphere and the cooling rate are considered to be the most important factors.

The various factors required to be kept under control in the preparation of ferrites are chemical homogeneity of the final product, purity, stoichiometry, porosity and pore distribution, grain size, density etc.

2.2 Solid State Reaction

The production of the ferrite structure occur due to the counter diffusion of cations through the oxygen lattice. This process is called as the solid state reaction mechanism.

The oxides to be used must be fine powders in order to be highly reactive. It is also recommended to have particles of the same size. The solid state reaction takes place very slowly at higher temperature between 800° C to 1500° C. The rate of forming ferrite depends on the temperature. For this, high temperature must be maintained for several hours.

The homogeneous mixture of metal oxide and ferric oxide (Fe_2O_3) is heated to a high temperature. The mechanism of diffusion takes place at this high temperature between MO and Fe_2O_3. In the primary stage of the reaction, there exists only one phase boundary between the reactants. After the nucleation of the ferrite this initial phase boundary is replaced by two different phase boundaries, one between MO and ferrite MFe_2O_3 and other between Fe_2O_3 and MFe_2O_4.

In this reaction stage, further - process takes place by the transport of reactants through the ferrite phase. The transfer mechanism to form MFe_2O_4 can be explained by three different modes. According to the

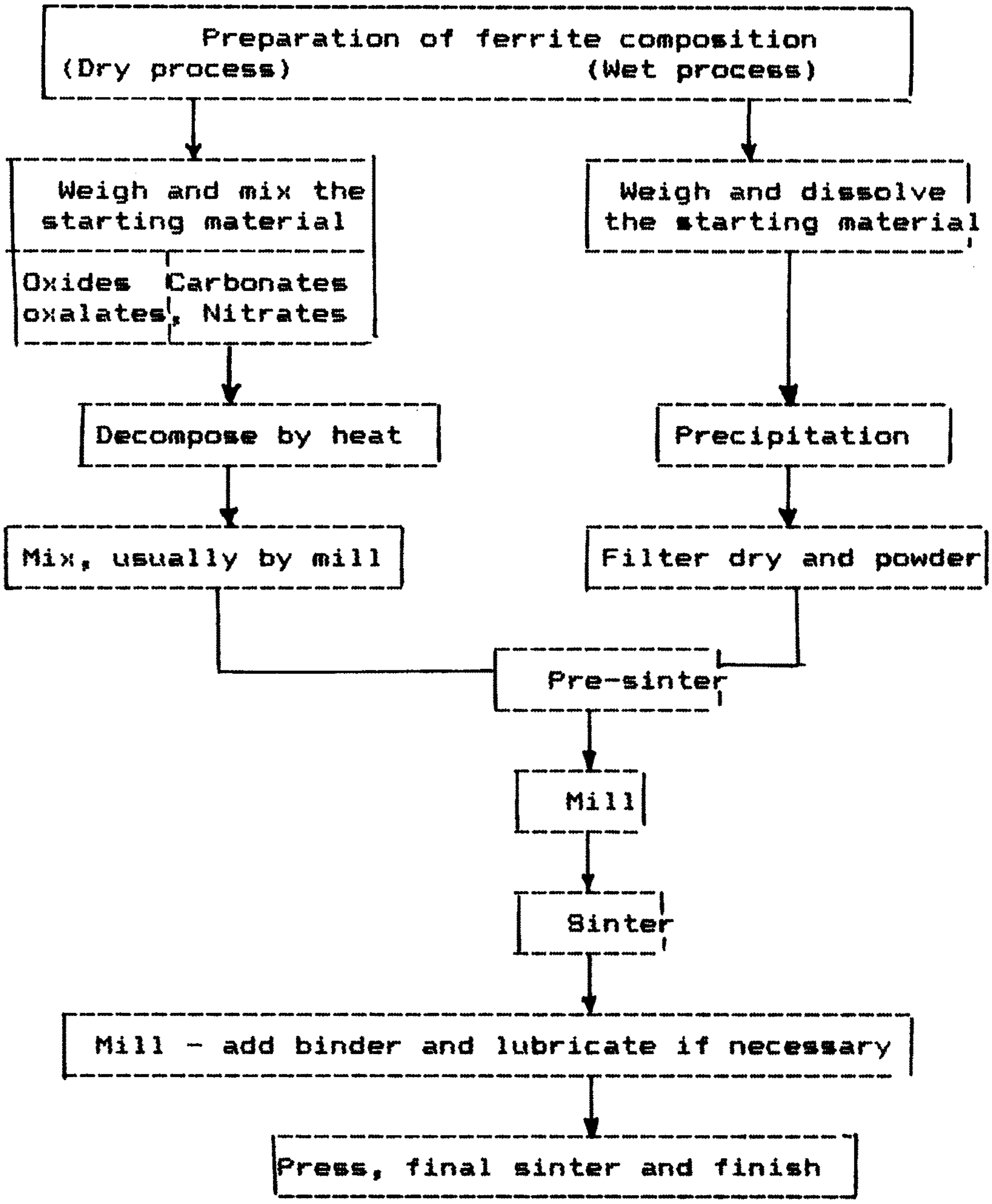
Wagner during the counter diffusion mechanism, only cations migrate in the opposite directions, the oxygen ions are being considered stationary.

According to the second mode of transfer mechanism, the anions take part in the diffusion process in which diffusion of single cation is compensated by an associated flux of anions instead of counter current of another cation. In third mechanism iron diffuses through the ferrite layer in the reduced state 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 the MO / MFe_2O_4 interface.

2.3 Methods of Preparation

In order to prepare ferrites by any method care must be taken which includes the suppression of porosity, control of grain size and production of grain orientation.

Flow chart of the stages in the Ferrite preparation



2.3.1 Oxide Method

This is considered to be the simplest method of ferrite preparation to be used for bulk production. High purity oxide materials are mixed together in the required proportions. The mixing is generally done by wet milling for a long period in ball mill. After the milling, the mixture is dried and then pressed into the desired shape and densified before presintering. After this final sintering is carried out.

2.3.2 Decomposition method

This is a method in which the starting materials used are salts, such as, carbonates, nitrates and oxalates instead of usual oxides. These salts are mixed in the required proportions and subjected to wet grinding using ball mill to get homogeneous mixture constituent compounds. This charge is pre-heated in air so as to produce the oxides by thermal decomposition. The other details are exactly similar to those of oxide method.

2.3.3 Oxalate precipitation

If the salts of the different cations have the same crystal structure form, the precipitate may consist of mixed crystals. This mixing on the molecular scale will lead to the formation of the ferrite at much lower temperatures than those for usual oxide mixtures. Oxalates of Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} give mixed crystals rather than crystal mixtures. X-ray diffraction studies have revealed that the precipitates are single phase.

Thus the precipitation of the metallic oxalates preferable for two reasons. The first reason is that precipitation can be carried out using ammonium oxalate which will not leave any residue after heating. Secondly most of the metal oxalates have very similar crystal structure so that the precipitation tends to produce mixed crystals which contain the metallic cations in exactly the same proportion in which they were present in the solution.

2.3.4 Hydroxide precipitation

In order to avoid the lengthy milling process involved in dry mixing, a large number of attempts have been made so as to precipitate simultaneously the required hydroxides from a solution so that the precipitate contains the required metals in the exact proportions already intimately mixed. For this purpose it is essential to have the knowledge regarding the solubility product of the substances so that one can determine the pH value for the complete precipitation.

2.3.5 Chelate precipitation

The organometallic compounds are known as chelates. Some organometallic compounds are found crystalline which are insoluble in water and are unstable. They can be coprecipitated and reduced to ferrite materials after calcination. At present this method is developing fast and a large number of organometallic compounds are being put to test.

2.4 Sintering process

The final microstructure develops during the final sintering process. We assume that the cations are present in correct proportions. The object then remains to achieve suitable microstructure together with correct oxygen content and the distribution of cations which are affected by the time, temperature of sintering, the partial pressure of oxygen or any other sintering atmosphere and cooling rate.

Sintering consists of heating the compact to a temperature at which the mobility is sufficient to permit the decrease of free energy associated with grain boundaries. During sintering densification and grain growth occur simultaneously giving rise to a variety of microstructure.

Sintering reactivity is important for densification. This reactivity is defined as the amount of energy available for sintering mostly sufficiently for the process to proceed.

Surface energy is defined by the equation

$$E = \frac{6T}{D}$$

where T = surface tension

D = diameter of the spherical powder particle

It is important that the material possesses good sinterability.

Volume diffusion is the main transport mechanism in ionic solids such as spinels. Surface diffusion may play a part in the beginning of the process in the formation of contact areas between particles. Before the start, the powder is compacted in such a way that the density is high to have good contact between particles. 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 material transport by the migration of individual ions from the grain boundaries to the pores producing shrinkage. Migration of vacancies occurs as a result of concentration gradient between the curved surface of the pores and equilibrium vacancy concentration under the flat surface. In grain growth, the grain boundary energy is decreased and boundaries move to their centre of curvature. The rate of grain growth is given by

$$D - Do = kt^{n}$$

where Do = original particle size

k = temperature dependent factor

t = time

The expected grain growth is proportional to $t^{1/2}$. However in practice the lower rate of grain growth is observed which is proportional to $t^{1/3}$ due to the presence of impurities. Grain growth during sintering is almost impossible to describe in general terms and also difficult to control in practice.

A discontinuous grain growth is also possible sometimes leading to doplex structure of the giant grain in a matrix of small grains. Lack of chemical homogeneity as well as variation in density and the presence of impurities can influence discontinuous grain growth. If the initial powder is incompletely reacted there is a volume change, as the ferrite is formed at sintering temperature leading to porosity and stresses that may result possibly in cracking.

One of the aims of ceramic technique is to achieve the lowest possible porosity in the product. This is possibly done by promoting the sintering rate by using powder with large surface area. For this purpose wet chemical preparation methods such as coprecipitation are more preferred. Reijnen showed that the microstructure with large pores is related to compounds having intrinsically a low sintering rate. The low concentration oxygen vacancies, which reduce strongly the sintering rate and the pore growth becomes predominant. In these materials very long sintering times are needed to achieve densification. If no pore growth occurs discontinuous grain growth is found. Thus the combination of the low porosity and small grain size is extremely difficult to obtain by the normal ceramic process. For this achievement an external force by pressing the sample during the sintering is necessary. This may promote the sintering process but not grain growth. Hence hot pressing and continuous hot methods are highly appreciated.

With every additional calcination step followed by grinding results in a large bulk density in the sintered product giving improved electrical properties.

2.5 Actual method used for ferrite preparation

In this section the actual method of preparation of the ferrite system under investigation has been presented. The method of preparation employed is standard ceramic technique. All the steps followed in this method are given together with explanation for the stoichiometric ferrites.

1. General formula

The ferrite systems prepared have the general formula $NiAl_xFe_{12-x}O_{19}$ with varying x from 2 to 10.

2. Raw materials

The pure oxides such as Al_2O_3, NiO, Fe_2O_3 all with AR grade were used as starting materials.

Using atomic weights of the constituent elements of ferrite were noted down as shown below using standard chart.

Element	**Atomic Wt.**
Al	26.971 gms.
Fe	55.8470 gms.
Ni	58.69 gms.
O	15.9994 gms.

Then molecular weights of Al_2O_3, NiO and Fe_2O_3 were obtained.

Table : Molecular weights

Sr. No.	Substance	Molecular Wt.(Gms)
1.	Al_2O_3	101.96
2.	NiO	74.71
3.	Fe_2O_3	159.694

It is desired to have around 9 gms of the starting materials for preparation of ferrite divide by same number of molecular weights.

Now considering 1st member of series $NiAl_xFe_{12-x}O_{19}$ i.e x = 2

Therefore $NiAl_2Fe_{10}O_{19}$ with x = 2

For this we get NiO is 0.7471 gms, Al_2O_3 is 1.0196 and Fe_2O_3 is 7.984. Total amount of starting material of sample number 1 is 9.4826 gms.

Using single pan balance available in the laboratory 0.74 grams of Nio, 1.0196 gms of Al_2O_3 and 7.984 grams of Fe_2O_3 were weighed separately. The formation of $NiAl_2Fe_{10}O_{19}$ takes place according to the following reaction

$$NiO + Al_2O_3 + 5(Fe_2O_3) = NiAl_2Fe_{10}O_{19}$$

The same procedure is followed in case of the remaining samples listed below.

S_1	x = 2	$NiAl_2Fe_{10}O_{19}$
S_2	x = 3	$NiAl_3Fe_9O_{19}$
S_3	x = 4	$NiAl_4Fe_8O_{19}$
S_4	x = 5	$NiAl_5Fe_7O_{19}$
S_5	x = 6	$NiAl_6Fe_6O_{19}$
S_6	x = 7	$NiAl_7Fe_5O_{19}$
S_7	x = 8	$NiAl_8Fe_4O_{19}$
S_8	x = 9	$NiAl_9Fe_3O_{19}$
S_9	x = 10	$NiAl_{10}Fe_2O_{19}$

2.5.1 Stoichiometry

Due to the weights taken in proportions as given above the charges in the prepared ferrites get balanced and thus the desired stoichiometry in the prepared systems is achieved.

2.5.2 Mixing of Oxides

Single pan balance available in the laboratory was used to weigh the oxides very accurately. The fine powders of oxides, in proper molecular proportions, were dry mixed. Each dry mixture of oxides was mixed thoroughly and a paste was prepared in an agate motor with acetone media. The mixtures were dried in the atmosphere and were transferred into Alumina crucibles.

2.5.3 Presintering

The mixtures were taken in Alumina crucibles and were heated in a glow - bar furnace by increasing the temperature of the furnace slowly up to 1000 C and maintained steadily, continuously for about 10 hours. The samples were cooled by switching off the furnace current. The calibrated Al - Cr thermocouple and a digital voltmeter were used for measurement of temperature of furnace. The pellets of each composition were thus collected in required number.

2.5.4 Milling

The presintered samples taken out of the crucibles were ball milled in acetone medium for 6 hours. The samples were again transferred to Alumina crucibles.

2.5.5 Calcination to final product

The samples were calcinated to achieve their final products. The temperature of the furnace was increased slowly up to 1200 C and were maintained steadily for about 12 hours. During this period the solid state reaction is completed. Then samples were cooled slowly by decreasing the current.

2.5.6 Remilling

The final products thus obtained were milled and ground in a ball mill with acetone medium for six hours. The material in a powder form was collected by specified dry bottle.

2.5.7 Pressing to shape

The one gram of the sample was taken in agate motor and mixed thoroughly. The dry powder was completely transferred to a clean die of 1.5 centimeter diameter. The cold pressing in a hydraulic press was done by applying 7 tonnes per sq. inch for about 10 minutes.

2.5.8 Final Sintering

All series samples were sintered at a steady temperature of 1200°C for about 12 hours. Then they were furnace cooled. The slow cooled samples were collected after 24 hours from the time of switching off of the furnace when room temperature was reached.

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