CHAPTER (1)

INTRODUCTION AND LITERATURE SURVEY

1.1 Definition and Classification of Ferrite.

Ferrite always results from the calcinations of metal oxides and iron oxide, which generally involve reaction at high temperature for long period of time [1]. The term ferrite denotes a group of iron oxides, which has the general formula;

$$\{ MeO. Fe_2O_3\}$$

Where Me is a divalent metal ion such as, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+},....,...., .it is also possible to start from mixture of compounds as the carbonates of the metal ions or a combination with other ions . By replacing the divalent iron ion Fe_2O_3 by another divalent ion, ferrite can be produced with different coercivity and intrinsic magnetization. For example: Magnetite is a type of ferrite and it is known as a magnetic oxide since ancient times [2]. Its formula can be written as;

$$Fe_3O_4 = \{FeO.Fe_2O_3\},$$

Also barium ferrite $BaFe_{12}O_{19}$, can be represented by the formula;

$$\{BaO.6Fe_2O_3\}$$

There are four main headings under which ferromagnetic materials or ceramic ferrites can be grouped for applications according to their hysteresis loop shape [1,3].

1-Soft Ferrite:

These types have a slender, S- shape hysteresis loop and tend to lose their magnetization very easily after the magnetizing field is removed, figure (1.1a). Magnesium-Zinc and Nickel -Zinc ferrites with spinel structure exhibit such properties. These types of ferrites are used in general as cores for radio, television, carrier telephone coil, and transformers.

2-Square-Loop Ferrite:

These types exhibit rectangular hysteresis loop and return to one of the two distinct states of magnetization when the magnetizing field is removed figure (1.1b) . The Mg-Mn-Zn ferrites are used in the computers memories and in the application required stability and fast switching over a wide range of temperature.

3-*Microwave Ferrites*:

These types of ferrites have garnet, spinel and hexagonal crystal structure with low electric and magnetic loss factors. The Mg-Mn-Al. and Mg-Mn ferrites are used at the lower part of the microwave spectrum.

4- *Hard Ferrites*:

These types of ferrites are characterized by a hysteresis loop enclosing a large area and by their ability to be used as a permanent magnet figure(1.1c). Hard ferrites exhibit a hexagonal crystal structure such as $BaFe_{12}O_{19}$. They have important applications as permanent magnet cores of the small motors, generators and measuring instruments. They find extensive use in the portable

Fig.(1.1a). *Hysteresis loop for soft ferrites*

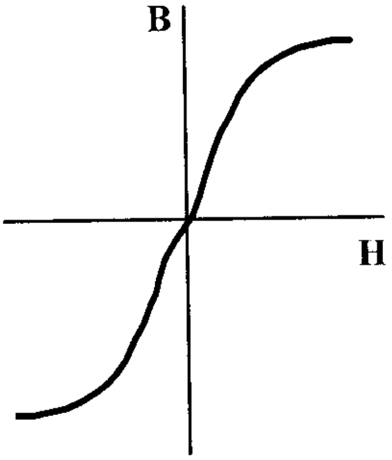


Fig.(1.1b) *Hysteresis loop for square-loop ferrites*

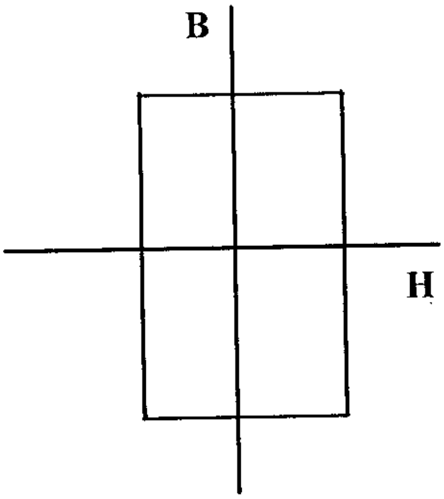
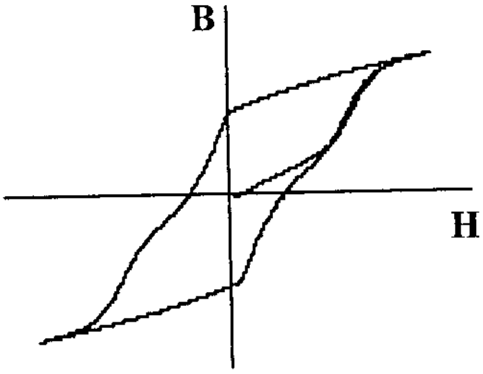


Fig.(1.1c) *Hysteresis loop for hard ferrites*



appliance, audio speakers and microwave devices. In the fine form ,it is also a suitable material for high density perpendicular recording medium where a reduction in particle size and a narrow size distribution are desirable to achieve an increase in the number of particles per bit of information stored as well as medium noise reductions [4-6].

1.2 Preparation of Ferrite.

The first attempt to prepare ferrite was made in 1715, which were obtained by a reaction of powdered iron and potassium nitrate to give potassium orthoferrate (K_2FeO_4). In 1909 barium ferrite have been prepared by heating barium and iron hydroxide in solid phases at 400°C in a current of oxygen, and in more recent times, 1955, ferrites containing all of the alkali and alkaline earth elements were synthesized [7,8]. Barium ferrite is more stable among the alkali ferrites, and the conventional method for preparing barium ferrite (ordinary powdered method), consists of firing mixture of iron oxide and barium carbonate at a high temperature for long period of time [9]. The ferrite must then be ground to reduce the particle size. These procedures lead to large agglomerates with inhomogeneous composition, besides impurities and lattice strain are introduced by milling. Consequently, an independent effect on the permanent magnet properties will occur [10]. The magnetic properties are strongly affected by the preparation methods and conditions. To avoid the milling process and overcome the limitations of ceramic preparation method. Recently many methods (freeze-drying, spray-drying, mechanical alloying, glass ceramic, and chemical co-precipitation methods) have been proposed for preparing ferrites. The most important feature of these methods is the intimate mixing of the starting materials on an ionic level, so that subsequent crystallization can occur at relatively low temperatures, leading to small particle size and high magnetic properties [11].

In fact, all these methods intersect at one point, they depend on the precipitation treatment during preparation to reduce particle size and increase the homogeneity before any heat treatment owing to improve the magnetic properties of the final product.

I- ***Freeze-drying method,*** consists of drying the precursor after precipitation at low temperatures by fragmentation of the powder's particles due to the water expansion by freezing , leading to small particle size in the nanometer range [12,13].

II- Spray-drying, is a method capable of producing truly spherical and homogeneous particles with average size smaller than ~2μm in few seconds by feeding directly into a spray –drying apparatus [14].

III- ***Mechanical alloying,*** is a powerful and conventional method for the production of nano- crystalline materials .Recently, it has been introduced to the preparation of magnetic ferrite materials by mechanical milling and mixing of the powders prior to annealing [15], or mechanical milling for the precursor after precipitation [13]. This method is suitable for the preparation doped ferrites [16].

IV- ***Glass ceramic method*** can be used successfully to prepare ferrites at a relatively low temperatures to prevent the large scale-grain growth which accompanies the formation of ceramic by solid state reaction at high temperatures [17].

There are other many methods used for mass production of ferrites such as, *self- propagation, sol-gel, and aerosol pyrolysis* [18].

Among these methods, the ***co-precipitation*** method is one of the most suitable for the low cost production of barium ferrite powders because it does not require sophisticated production equipments and the particle size morphology and the formed phases can be controlled by the co-precipitation conditions[19]. In addition ferrites formed by the co-precipitation method exhibits good magnetic properties than any other methods [20-23]. This method is recommended in the present work and will be discussed as follows;-

Many of the preparation parameters such as, *1- Fe/Ba molar ratio* (n) [11,19], *2- PH of solution* [10,19], *3- the sequence of reagent addition* [23], *4 - the presence of NaCl* [18,22,24], *5- grinding level (particle size)* [25,26], *6- treatment temperature* [11,12,25], 7- *annealing time* [27], *8- atmosphere [oxygen or air]*, and *9-addition of protective agent* [28], which can be controlled during the synthesis of the powder by a co-precipitation method, are taken into account by many investigators since the discovery of barium ferrite, owing to the improvement in the magnetic characteristics specially coercive force, which is defined *as the field strength required to reverse intrinsic induction or the field* *strength at zero magnetization.* It strongly depends on the particle size, morphology, and microstructure; the latter depends on the preparation method [25]. At the same time, barium ferrite particles are required to be single domain, chemically homogeneous, and exhibit a high saturation magnetization, large coercive force, narrow size distribution and good dispersiability (, especially in the case of magnetic recording application. Narrow size distribution is desirable to achieve an increase of the number of particles per bit of information stored as well as medium noise reduction [6].

1.3 Definition of Polymers and Rubber

The constitution of a polymeric substance is described by its structural units. The structural units are connected to one another in the polymer molecule or polymeric structure by covalent bonds. Although the structures of polymers vary widely, nearly those of interest may be of expressed as combinations of a limited number of different structural units; in many cases a single type of structural unit suffices for the representation of the entire polymer molecule. This feature, namely, the generation of the entire structure through a repetition of one or few elementary units, is a basic characteristic of a polymeric substance. The structural units may be connected together in any conceivable pattern. In the simplest of all polymers, the *linear polymer,* the structural units are connected one to in other linear sequences. Such a polymer may be represented by the formula [29];

$$A' - A - A - - - - - A'' \quad \text{or} \quad A\,(-A-)_{x-2} - A''$$

Where the principle structural units is represented by A, and X is the degree of polymerization ,or number of structural units in the molecule .Alternatively, the structural units of the polymer may be connected together in such a manner as to form nonlinear, or branched, structural of one sort or another. Accordingly, some of the structural units must then possess valences greater than two.

Rubber and rubberlike materials are distinguished from other substances by a remarkable combination of two characteristics. In the first, they are capable of sustaining large deformations without rupture; a maximum elongation of five to ten times the unstretched length is commonplace among typical rubbers. Secondly, the deformed rubber possesses the capacity to recover spontaneously very nearly to its initial dimensions, no appreciable fraction of the deformation remains permanently after removal of the stress. Rubberlike bodies resemble liquids in respect to their deformability without rupture; they resemble solids in their capacity to recover. This combination of properties, aptly described by the term *long-range elasticity* [30].

The unique structural feature common to all rubberlike substances is the presence of long polymer chains. These chains ordinarily are connected to one another by cross-linkages, but the preponderance of the structure consists of the intervening polymer chains each comprising a hundred or more single bonds between points of cross-linkage. That long polymer chains should be required for the fulfillment of high extensibility is immediately apparent. In the unstrained state the chains normally occur in randomly coiled arrangements, but they are able to rearrange to other configurations, and in particular to more highly extended ones. Thus, when the rubber is subjected to an externally applied stress, a large deformation can be accommodated merely through rearrangement of the configurations of the chains.

1.4 Definition and Classification of polymer bonded magnets (PBMs)

Polymer bonded magnets (include plastic magnets and rubber magnets) are compounds of plastics or rubbers with magnetic powders. They are light in specific weight, soft, elastic, stable, easy to be processed, energy-saving, etc. In addition to the polymer binder coats the magnetic particles acts as an isolators suppressing eddy current loss [31] . These advantages offered by (PBMs) make them useful materials than the metallic and ceramic magnets for special application ,where the impregnation of magnetic fillers in the matrix imparts magnetic properties to the matrix and modifies the dielectric and magnetic properties[32].

1.4.1 Applications of polymer-bonded magnets

The magnetic polymeric composites represent a commercially important system due to their wide applications such as line printers and memories in computer, centering magnets for television, magnetic rolls of copying machines, timing motor rotors, refrigerator door latches, clamps, speedometers, tachographs, video tape recorders, etc. These composite materials contain barium or strontium ferrite or rare earth cobalt at up to 60 to 70 vol % or 87 to 92 wt % in appropriate polymer matrices [33—35].

In the case of high energy products the application takes the advantage in numerous medical applications, motor arcs and cylinders which have been use in hand held tools, especially portable drills and screwdrivers. Another example is short axial length , thin wall cylinders which are used in high volume to make spindle motors in floppy and hard drivers for computer equipments. Cylindrical magnets can be from two poles to more than 40 [36-37] .

Common applications for Flexible Magnets are used in a variety of applications from labeling, holding, door gaskets, and signs, CRT focusing, crafts, toys, games, magnetic signs, displays, warehouse shelf labeling, door gaskets, small tool and instrument holders, movable markers, advertising premiums, magnetic business cards, architectural planning layouts, etc. The size, shape and magnetization pattern can be manufactured according to user's need.

Today, four permanent magnet materials are predominant in use; Ferrite, Alnico (aluminum-nickel-cobalt), samarium-cobalt, and neodymium-iron-boron. Although bonded magnets are manufactured within each of these families, only bonded ferrite and isotropic bonded neodymium are manufactured to any great extent. In 1995, industry sources estimated that approximately 74% were bonded ferrite and 22% were bonded neodymium [38].

1.4.2 Classification of polymer-bonded magnets

Polymer bonded magnet is mixture of permanent magnetic powder and polymer as a binder. The binder that holds the magnetic particles in a place may produce either *flexible* or *rigid* magnet. Typical polymer binders for flexible magnets are rubber and vinyl, binders for rigid magnets include nylon, polyphenylen sulfide, polyester, Teflon, and thermoset epoxies. Figure (1.2) schematically describes these classifications. From this figure, we can notice that, rubber by calendaring process produces flexible magnets by mixing with ferrite.

Each material has unique properties that make it more suitable for selected applications than other magnet options. Selection criteria include: magnetic strength, cost, constancy of magnetic output over temperature extremes, corrosion resistance, resistance to demagnetization, and mechanical properties such as density, physical strength or flexibility. Ferrite magnets, while providing less magnetic strength than rare earth magnets, cost far less. Therefore, they are still widely used wherever product cost is a major consideration over magnetic performance [36].

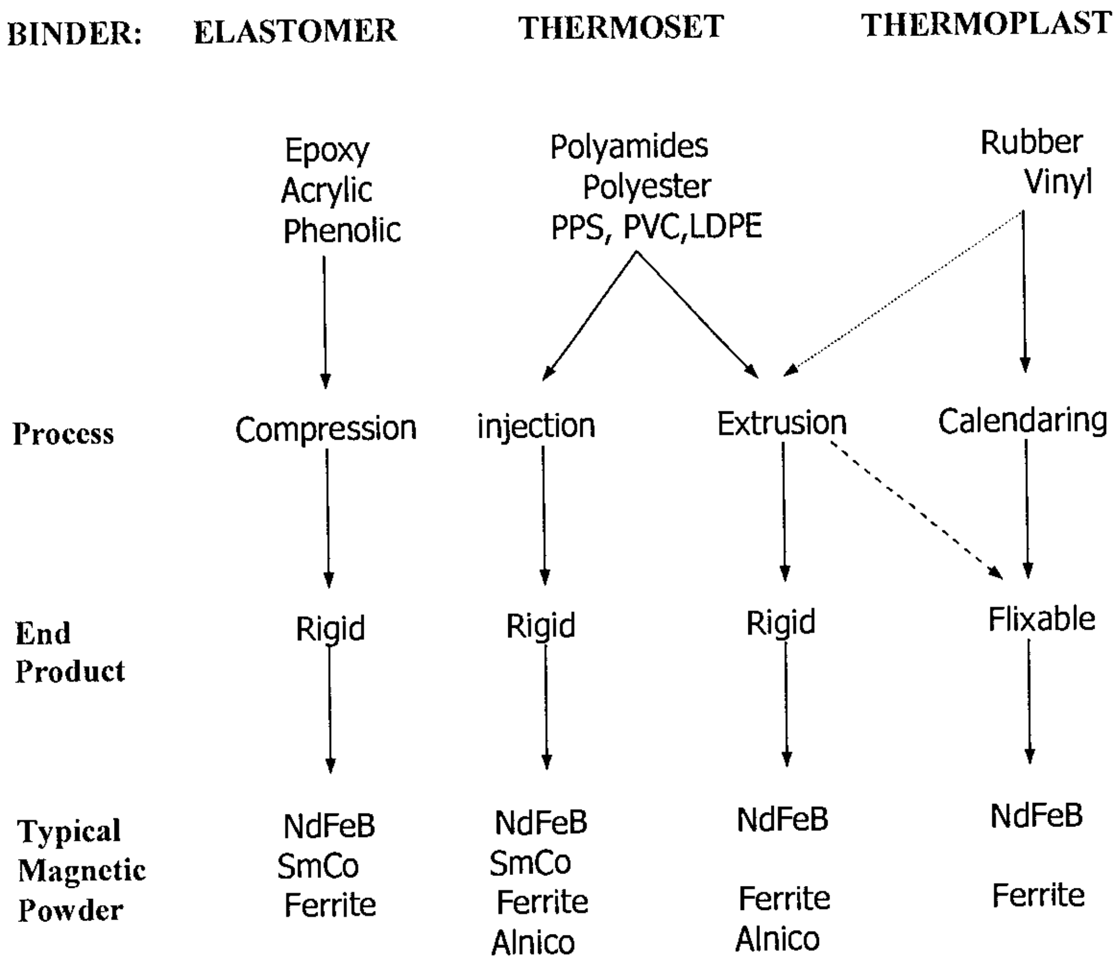


Fig. (1.2). Bonded-magnets types

1.5 Preparation of polymer bonded magnets

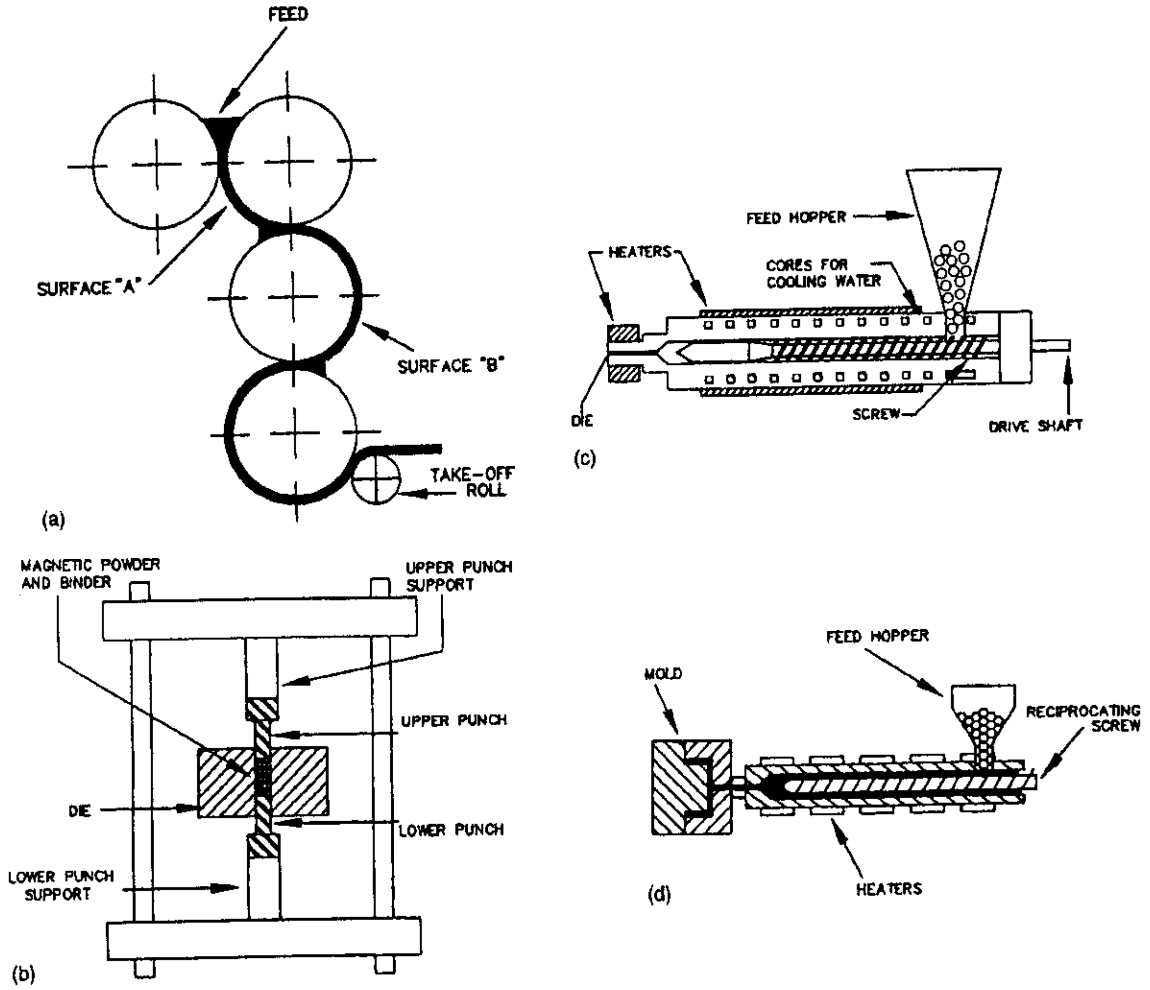
There are four processes for manufacturing bonded magnets as described in figure (1.3). These processes are; Calendaring, *Injection*, *Extrusion*, and C*ompression* [36].

I-Calendaring, is forming of a continuous strip by processing of the materials between rollers. The stripe may be up to several hundred feet long. Magnet powders are mostly ferrites.

II- Injection, molding is the process of forcing the heated compounded through channels and into mold cavities where it is allowed to cool and harden. Then the mold is opened and the parts removed. Both calendaring and injection molding use magnetic powders up to 70 volume percent.

III- Extrusion, is the squeezing of compound through an orifice while heating and controlling the profile as the compound cools and becomes either firm (flexible end product) or rigid. Magnetic particles loaded in a rigid product can be used in the range of about 75 volume percent. Ferrites and rare earth magnetic alloys are very abrasive. One of the challenges for manufacturers of these magnets need to develop tooling resistant to wear. Inexpensive ferrite extrusions are used for gasketing around doors and signs seen on vehicles.

IV- Compression, Magnetic powder is mixed with the binder, usually a thermoset epoxy, flowed into a press cavity and be compacted under pressures of about 10^9 N/m^2. The compacted magnet is cured at a temperature in the range 150—175 °C. One advantage is that the magnetic loading can be as high



(a) Calendaring,

(b) Compression

(c) Extrusion

(d) Injection

Fig. (1.3). Bonded-magnets manufacturing processes as high as 80% by volume, resulting in higher output than calendared, injection molded process, and most extruded magnets. Dimensional tolerances are almost as tight as for injection-molded products, making secondary operations generally unnecessary.