

Manufacturing of Manganese-Zinc Soft Ferrite by Powder Metallurgy

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Abstract: Objective of this paper is, improvement of quality of Mn-Zn soft ferrites manufactured by powder metallurgy and overall output yield of it's plant. The efforts have been made to synthesize the crucial parameters which are responsible for better material preparation, pressing and sintering. By adopting these recommendations, the rejection rate is substantially reduced and the variation in magnetic properties is less. Data, which give more uniformity in bigger lots and are responsible for more uniform magnetic properties, have been discussed. Simple, quality-control instruments and their measurement methods which can be incorporated for stage inspection have been explained. The additives for better ferrite powder preparation, granules making and to obtain better magnetic have been discussed. Improved pressing, sintering, porosity, density and permeability relationship have been drawn. A sintering method to obtain better sintered density and high permeability in ferrites is also explained.

Keywords: Mn Zn ferrites manufacturing, powder metallurgy, process conditions, sintering.

1. INTRODUCTION

In ceramic industries, powder metallurgy method of manufacturing is extensively, in use. Soft ferrites are also manufactured by this method. Soft ferrites are magnetically soft materials, being used as core of electronic transformers and other electromagnetic applications, where the frequency ranges from 100 KHz to a few GHz. Soft ferrites means magnetically soft materials. Few important magnetic properties of soft ferrites are explained below, which are discussed in this paper.

Magnetic flux density(B)- This is defined as the number of magnetic lines if force passing through a unit area of cross-section.

Resistivity-This is electrical resistance of a ferrite core, having constant cross-sectional area and it's unit is ohm-cm.

Saturation magnetization- This is saturation magnetic flux density of a magnetic core at a given magnetic field strength. The unit is Gauss.

Coercive force(Hc)- This is magnetizing field strength(H) required to bring the magnetic flux density(B) of a magnetizes material to zero. It's unit is oersted.

The other useful properties like **initial permeability**, which is the ratio of flux density (kept at less than 10 Gauss), to the field strength and **Al value**, which is inductance of the ferrite core divided by square of number of turns, have been selected for analyses.

There are three types of soft ferrites commonly in use, Manganese- Zinc, Nickel-Zinc and Lithium-Titanium (microwave) Ferrites. The study made in this paper is mainly related to Manganese- Zinc ferrites. Since the method of

manufacturing of other two types of ferrites is similar, the process techniques discussed in this paper, are useful to other ferrites also.

The methods for improving overall yield in each manufacturing steps are very important. In this research work, operations of a soft ferrite manufacturing plant were closely observed. It was found that the overall rejection-rate was of the order of 50%. Most of the ferrite products were found to be rejected in magnetic quality, dimensional deviations, cracks and chipping-off. The remaining rejection was appearing at various stages like-mixing, calcination, grinding, compacting, sintering, lapping and machining etc. This accumulates the huge financial losses and makes difficult for an industry to survive.

The stage inspection methods including measurement of slurry-viscosity, flux density of calcined powder, green density with go/no-go gages, etc. have been discussed. Relationship curves, between density- porosity, density-initial permeability and density-Al value have been drawn. These curves are very useful in manufacturing high permeability soft ferrites.

If the quality measures discussed in this article are adopted, the huge process loss/ rejection may be reduced, processing cost may be saved and the quality of the products will improve.

2. EXPERIMENTS

Several lots of 200 Kg. each, mixed material of specified composition, to manufacture Mn-Zn soft ferrite, were monitored from the first stage of raw material weighting & mixing, to the recovery of end products.

Details of preparation of the samples- First of all weighting of raw materials is done on electronic balance. Production Batch size is 200 Kg. These raw materials are now dry mixed in a conical drum mixer with axial blades rotating for an hour. After that, dry mixed powder is passed

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through a rotary kiln made by Reidhammer-Germay by screw feeding. The rate of passing is around 20 Kg./hr. The temperature of rotary kiln is maintained at 940°C. Thus the powder is calcined. Further this calcined powder is milled in an attritor with water (forming slurry) and additives like PVA (Poly vinyl alcohol), PEG (Poly ethylene glycol) and CaCO₃. This ferrite slurry is passed through spray drier (make-DORST, Germany) to form granules. These granules are now pressed to prepare Torroidal shape (T-20) samples and sintered in Tunnel Kiln made by Reidhammer-Germay at different temperatures and by changing the ambient atmosphere inside the tunnel kiln.

It was found that weight wise loss of material from raw material mixing to the recovery of sintered components, was of the order of 50%. Of course overall process loss up to 20% is inevitable. Sintered density of the samples was measured. The densities were compared with an assumed value of ideal density (5.1 gm/cc) which would give the measure of porosity. These values are shown in Table 1.

Table 1. Calculation of Porosity from Actual Sintered Density

Ideal Density(A) gm/cc	Actual Density(B) gm/cc	C=A-B	D=C/A	C+D	Porosity % =[(C+D)*100]
5.1	4.6	0.5	0.10	0.60	60
5.1	4.7	0.4	0.08	0.48	48
5.1	4.8	0.3	0.06	0.36	36
5.1	4.9	0.2	0.04	0.24	24
5.1	5.0	0.1	0.02	0.12	12

A graph has been plotted between the values of sintered density and porosity as shown in Fig. (1), which shows a linear trend.

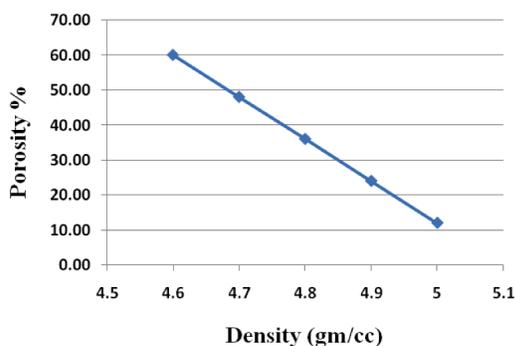


Fig. (1). Sintered density vs porosity.

Measurement of initial permeability and corresponding sintered density was done on the samples having round torroidal shape with 10 no. of turns on LCR meter. These values are shown in Table 2.

A graph has been plotted based on above data and a curve has been fitted to find out the function. The curve equation obtained is,

$$y = -5341.x^2 + 57507x - 14682$$

Table 2. Sintered Density and Corresponding Initial Permeability

Sr. No.	Material Code	Sintered Density (gm/cc)	Initial Permeability
1	A7	4.41	2857
2	A7	4.46	3540
3	A7	4.66	5000
4	A7	4.89	6890
5	A7	5.0	7071

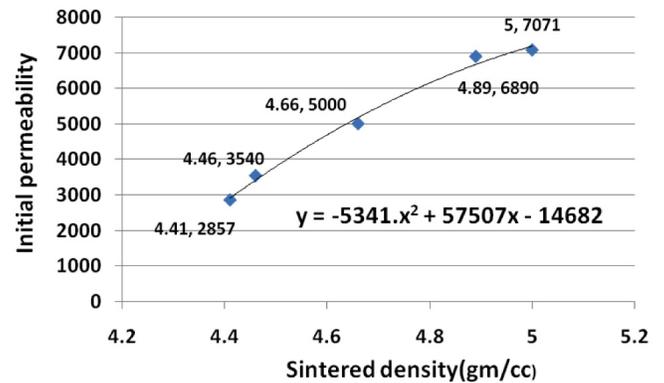


Fig. (2). Values of Sintered density and initial permeability.

Similarly AI value and corresponding density of sintered samples were measured. The values are shown in Table 3 and a graph has been plotted as shown in Fig. (3).

Table 3. Sintered Density and Corresponding AI Value

Sr. No.	Sintered Density (gm/cc)	AI Value
1	4.87	9100
2	4.81	9100
3	4.82	8400
4	4.81	8400
5	4.7	6800
6	4.58	6800

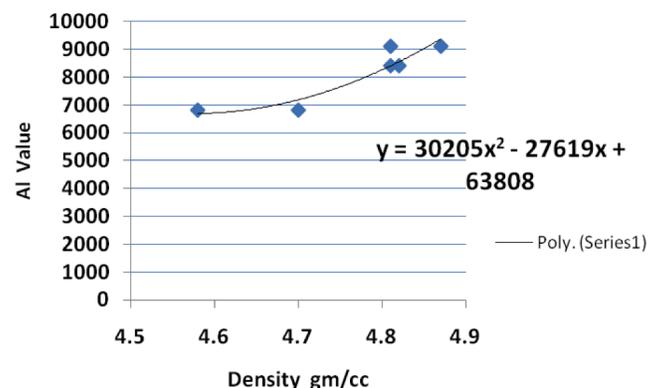


Fig. (3). Sintered density and corresponding AI value.

The curve fitting equation describes the relation as polynomial, shown below.

$$y = 30205x^2 - 27619x + 63808.$$

3. RESULTS AND DISCUSSION

Overall yield improvement is possible by adopting the following recommendations.

3.1. General

To reduce the rejection from 50% to the acceptable limit, it was recommended to create "In-process quality control team", which will have the members from the same manufacturing stage. Quality standards for each of these stages are defined. Go/No Go gages must establish the limit of tolerances.

This "In-process quality control team", must report to the General Manager of the plant directly. The manufacturing, shop floor, testing or quality control employees should not interfere in decisions of "In-Process Quality Control Team". Only the General Manager can permit the deviations after looking at the overall situation.

With the help of these standards the rejected components are identified at early stage and the further processing cost is avoided. Again, most of these rejected components are suitable for reprocessing, thus the cost is saved drastically.

Since the acceptable tolerance on weight % is $\pm 0.06\%$ an electronic balance of $\pm 0.5\%$ tolerance with print out facility is recommended. This balance must be calibrated, time to time.

Chemical analyses of the composition should be done after blending of raw materials, calcinations, grinding and spray drying.

The density of calcined material, granulated material, green pressed components and sintered components must be monitored within the specified limits.

3.2. Raw Material

The rejection in magnetic quality of ferrite components is caused due to the larger deviation of composition from the standard value. The permitted variation in the mol % is ± 0.1 and wt.% is $\pm 0.06\%$.

Once standardized for the accepted quality, the source/make of raw material should not preferably be changed, because unknown impurities play a vital role in preparing some critical ferrite compositions, particularly high permeability and Lithium-Titanium ferrites for phase shifter applications. The impurities and silica content should not exceed the limits specified by the supplier in their specifications. For high permeability material, silica content should remain within 0.015-0.20%. The chemical analyses/X-ray fluorescent of raw material is very important to measure the purity of the material.

Relationship between chemical composition, microstructure and core losses of Mn-Zn Ferrites were studied by Lebourgeois R. [1], who explained dense microstructure or high density leads to improved initial permeability. Silica-calcia addition and Ti-substitution, influence the power optimization for the operating frequencies from 25 KHz to 2MHz. Optimization of losses also

depend upon the specific conditions of temperature, frequency and induction.

By adding 0.02 to 0.03% of Calcium, the resistivity of Mn-Zn ferrite powder is increased. Silica addition also increases the resistivity. Titanium may also be added in place of Ca to increase resistivity. Calcium and silica increase the resistivity in grain boundaries while Titanium increases the resistivity of crystal. Maximum recommended % of Calcium is 0.6%.

Effect of composition (adding titanium) plays a great role in influencing the initial permeability of the material [2].

Silica increase resistivity reduces permeability and does not have any effect on loss.

3.3. Mixing

Weighting of raw materials is very important and should be done with great care. For Weighting, electronic balance with print out facility has been suggested to eliminate the weighting error. A small error in weighting may change mol% of raw material and finally the properties. A change in 0.5 mol % of Fe_2O_3 in composition shifts the location of the secondary maxima of μ_i by 50°C . After mixing, the composition of mixed batch must be checked by using X-ray fluorescence and deviation must be corrected by adding the deficit raw material. Additives (like CaO-0.01%), remain in the grain boundaries hence need not be taken into mol %age.

3.4. Calcination

After mixing, the powder should be transformed into pallets, using pelletizer to prevent light weight oxides, (zinc Oxide), loss in calcinations. However in some plants, mixed powder is directly calcined in rotary kiln.

The reactivity of the ferrite powder is proportional to the grinding time and thereby reduction in particle size. Finer the particle size more is the reactivity. Similarly reactivity of the ferrite powder depends upon the calcination temperature also. Because higher the calcination temperature, harder are the powder particles which are difficult to ground and reduction in its size. More over harder particles are difficult to be pressed.

Therefore this is recommended to keep the calcination temperature low. For Mn-Zn ferrites, calcination temperature of mixed material is suggested at 950°C , because particles do not become hard at low temperature and are easy to grind and press.

After calcination chemical analyses of the ferrite powder is very essential.

Measurement of flux density of calcined material should be done, to ensure electromagnetic compatibility of the material and the deviations must be corrected. In Fig. (4), a test jig is shown to measure the flux density of calcined material. Sudden insertion of test tube into the magnetic poles shall give the deflection in flux meter which in turn shall give the flux density.

3.5. Grinding

The particle size during grinding must be controlled. It should be in the range of 1-2 μm . The viscosity of slurry is checked by using a simple viscosity/ flow meter. Time taken

to empty the measured volume of slurry through a hole as shown in Fig. (5), will give the subsequent viscosity.

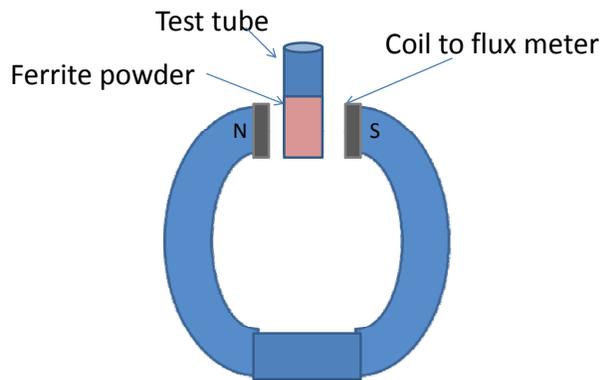


Fig. (4). Test jig for measurement of flux density of calcined material.

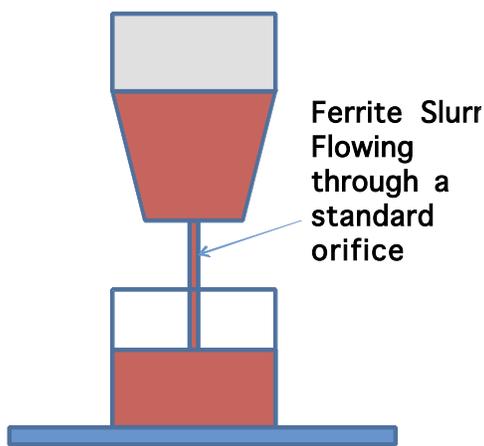


Fig. (5). Measurement of viscosity of ferrite slurry.

Small amount of ammonium citrate (0.05 %) may be used as dispersant during grinding.

3.6. Granulation

The bulk density and moisture content of granules must be monitored. The more granule density results more density of green pressed components and leads to more sintered density. Also, it results in better compaction. The moisture content should be in the range of 0.3 to 0.6%.

PVA (poly vinyl alcohol) and water are used as binder. It has been seen that by replacing water by PEG (poly ethylene glycol), the strength of the green samples is improved. Moreover the fabrication of these ferrites is simpler [3].

To obtain better quality of granules the following tips are essential-

- (i) The size of granules should lie between 70 μm to 120 μm .
- (ii) After spray drier granules, some additional water and solid lubricant should be added before pressing. Zinc stearate is (0.05%) recommended to be added in the

granules as solid lubricant. Mixing time may be 15 minutes.

- (iii) Blending of three, spray dried lots (200 Kg each), in the drum blender, brings compositional uniformity more closer and therefore the batch to batch variation in the products is eliminated. But each lot must pass the QC standards, before blending.
- (iv) During grinding solid contents of slurry must be controlled. Recommended solid percentage in spray drier slurry is 65 to 70%.

It was further investigated that at this stage if 0.3% of water is added and the material is kept overnight before pressing for better distribution of moisture, the pressure (tonnage) required for compacting is reduced and pressing density is also improved. Although moisture content in granules should be 0.3 to 0.6%, depending upon the environmental or whether condition, but if another 0.2% of moisture is added the granules become softer. If the granules are dry (less moisture content) the water may be sprayed in the blender and slight drying is recommended in the oven. If oven drying is to be avoided then the material should be kept for 7-8 hours or overnight before pressing. However, if the granules are not pressed within 24 hours of adding 0.2% moisture, these granules must be covered and sealed perfectly.

Less moisture will need higher compacting pressure which is not desired. Low compacting pressure yields to good resistivity and better results.

Standard normal green density should be 3.2 gm/cc. This value may slightly vary (± 0.2) with respect to specific composition.

3.7. Pressing

The compressibility study shows that the higher compression ratio is required if PEG is used as plasticizer in comparison if only PVA is used [4].

The following factors while pressing must be monitored, for consistency of green components.

- (i) Pressing ratio (die-fill/green height of the component)
- (ii) Bulk density of green component
- (iii) Pressure (in tonnage) applied on per cm^2 of cross sectional area of the component.

The homogeneity of the density profile along the compact, is related to the chance of crack development and product deformation during sintering [5] this obviously means deterioration in its density and permeability.

Since measurement of green density is very essential in production shop, a convenient Go/No Go gauge is shown in the Fig. (6) to measure green height of pressed components. For a fixed component coming out of same die will have the same density, if bulk density of the granules is same and the green height of the component is same. This means for the same lot of material and for the same die and pressure we can observe the variation in green density of the component merely by measuring its green height. The acceptable limits of variation in heights will have to be fixed.

Green density may be measured by coating the pieces with hot wax, cooling down and then using water dipping method. Alternatively the glycerin may be used in place of water. In this case the measurement of weight has to be done very quickly or the green pieces may break.

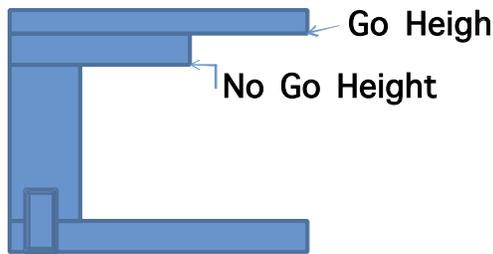


Fig. (6). Schematic diagram of Go/ No Go gage.

3.8. Sintering

The mechanical and electromagnetic properties are greatly influenced by the sintering process. Lot of material is likely to be rejected at this stage. Therefore this process is very critical.

The atmosphere in sintering also plays a vital role. The sintered density must be in the range of 4.80 to 4.95 gm/cc.

For 10,000 permeability minimum sintered density should be 4.85 gm/cc.

For 2,000 permeability minimum sintered density should be 4.7 gm/cc.

Dawson [6], studied and established that for Mn-Zn ferrites sintered in air, strength is critically dependant upon the formation of Fe^{2+} ions. These Fe^{2+} ions give rise to residual compressive stresses which increase strength and decrease permeability. Electrical resistivity decreases, whilst saturation magnetization increases. For a given composition, μ_i and strength both increase with increasing sinter temperature (i.e. increasing grain size). Cooling in N_2 results in a further improvement in permeability without a significant decrease in strength.

For manufacturing high permeability ferrites ($\mu_i > 7500$) firing in a closed chamber is recommended. This means the sintering material should be covered by a ceramic plate. However a little gap for ventilation is required. The loading plates (of alumina) may be coated with the ferrite slurry because zinc is volatile at high temperature and by coating it is not absorbed by the alumina plates. The coating thickness of ferrite slurry is approximately 1mm.

Mauczok R. and Zaspalis V.T. [7], investigated the binder burnout process step for MnZn-ferrite materials, in order to explain the origin of the binder burnout cracks that occur during the sintering of Mn-Zn ferrites.

Efficiency of tunnel kiln is improved by loading components in double or multi layer. This gives more uniformity in atmosphere and partial pressure of Zinc is better maintained. If interruption is there in material loading of tunnel kiln the loading should be resumed only after pushing around 50 plates of sintered reject material so that the kiln atmosphere and temperature is stabilized.

The optimum soaking time is that at which the desired sintered density, mechanical properties and magnetic properties are achieved. More soaking time may lead to loss of oxygen from the micro structure.

For getting 10,000 permeability oxygen is required at maximum temperature-soaking zone. To allow more oxygen absorption by grains at maximum temperature, a dip of $50^\circ C$ in temperature is recommended, after four hours of soaking. This dip is allowed for one hour and again the temperature is raised to the maximum for another one hour as shown in Fig. (7).

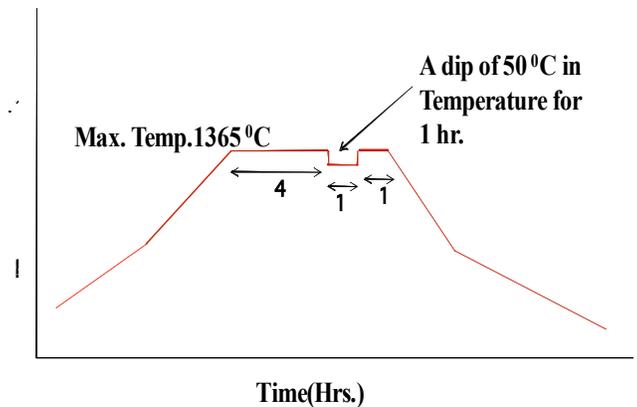


Fig. (7). Temperature profile of high permeability ferrite showing typical dip during maximum temperature zone.

3.9. Microstructure

The crystal size (grain size) of ferrites should be monitored on the mating surface of the cores. This mating surface should be polished and etched for obtaining a good microscopic view and size evaluation. Average crystal size must be less than $10 \mu m$ for power ferrites and more than $20 \mu m$ for initial permeability of 10,000.

The microstructure of ferrite should be more uniform and large. Large and more uniform crystals indicate uniform composition.

The small crystals are indicative of variation in composition. There is linear relationship between grain size and initial permeability. More grain size leads to more permeability.

The properties of Mn-Zn ferrites are strongly dependant on their microstructure. The formation of microstructure is influenced by several processing steps. One of the most important is the powder preparation route which influences the sintering behavior. One important goal is the achievement of very homogeneous microstructure at low sintering temperatures. The most reactive the used powder the lower the temperature necessary for getting the same microstructure [8].

For initial permeability, value of 1000, the grain size required is $2 \mu m$ and for initial permeability, value of 10,000, the grain size required is $20 \mu m$.

4. CONCLUSION

In Powder Metallurgy process higher rejection rate and inherent process loss may be of the order of 50%. To reduce the rejection rate and to improve overall output yield, it is

recommended to create “In-process quality control team”, which will have the members from the same manufacturing stage. This team is separate from Quality Control team. Quality standards for each of these stages have been defined. A Comparative, green density measurement method, for pressed components, has been suggested with the help of simple go/no go gages. Measuring tools for slurry-viscosity, and flux density of calcined powder have been described. The green density of pressed components could be increased from 2.9-3.0 gm/cc to 3.2 gm/cc and sintered density obtained is 5.0 gm/cc.

By adopting above recommendations the rejection rate could be reduced from 50% to 30%. Also, the rejected components were identified at early stage and further processing cost was avoided. The rejected components and material are suitable for reuse and there is a considerable saving in cost. Relationship curves which have been drawn are of immense use in manufacturing of soft ferrites by powder metallurgy.

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