ACHIEVING PROCESS CONTROL THROUGH IMPROVED GRINDING TECHNIQUES FOR FERRITE MATERIALS

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ABSTRACT

In manufacturing soft ferrite materials the particle size of the raw material has a significant impact on the reactivity at calcination. The control of particle size distribution and final formulation at wet milling after calcining impacts the reactivity during sintering and the magnetic properties of the final product. This paper will deal with steps taken to improve process control during the grinding operations of raw material and calcine in soft ferrite production. Equipment modifications as well as changes to the grinding and material handling techniques will be included. All examples of process control and improvements will be supported by data.

INTRODUCTION

Ferrite markets including power line filters, local area network transformers, switch-mode power supplies, and electromagnetic interference suppressors are challenging the ferrite industry to produce high quality ferrite cores capable of meeting increasing demands. High efficiency switch mode power supplies have pushed the application range of manganese zinc power ferrites to well above one megahertz with minimal power loss. Filter and pulse transformer applications push toroidal cores to exhibit the highest possible permeabilities while maintaining low loss factors. EMI suppression ferrites are "lossy" by design. Escalating computer clock oscillator frequencies are pushing requirements for ferrite materials to exhibit good EMI attenuation properties up to one gigahertz. In order to meet these requirements and to provide customers with a quality product with short lead times and accurate delivery dates, today's ferrite manufacturer must practice stringent methods of process control.

MATERIAL REQUIREMENTS

Depending on the intended application, the magnetic properties that must be controlled include permeability, saturation flux density, power loss, loss factor, temperature coefficient, etc. Achieving target composition and density and establishing the proper crystal structure (spinel) with the proper ion distribution on the various lattice sites is necessary to obtain these magnetic properties.

A low porosity dense structure is generally preferred with any existing pores occurring in the grain boundaries since intragranular pores will impede domain wall movement. Grain size should be uniform rather than random or duplex. Large grains and thin grain boundaries are advantages for high permeability because they minimize interference with domain wall movement. For high frequency application materials a finer grain size is preferred with highly resistive grain boundaries to minimize core losses. Core losses can be significantly reduced by minimizing eddy currents within a core material. Eddy current loss is due to electrical resistance losses and can be reduced by increasing the overall resistivity of the material. Additives can be used to increase the resistivity of the grain boundary without significantly affecting the magnetic performance of the core. Other types of additives can be used to alter magnetic properties by affecting microstructure development or dissolving into the spinel structure. Small amounts of additives can greatly affect the properties of ferrites. These additives are not the focus of this paper, but they are mentioned because in many cases they are introduced and controlled at the milling stage of the process.

PROCESS DESIGN

There are at least as many different methods to manufacture a ferrite as there are ferrite manufacturers. A ferrite producer must be able to design a manufacturing process that conforms to the available equipment and raw materials. The four major steps of the production process are powder preparation, forming powder into a core, sintering, and finishing. Repeatability and consistency must be the top criteria when designing the manufacturing process. Each process step must complement preceding and subsequent steps to achieve reproducibility. Better reproducibility increases the uniformity of finished product characteristics and therefore increases process yield. The main factor governing reproducibility is control of process variables. To achieve the desired magnetic properties, the process engineer must establish control of chemical composition, crystal structure and density through identification and management of critical process variables.

Figure 1 represents what is likely the most conventional processing sequence used by ferrite manufacturers today and the one on which this paper will focus.

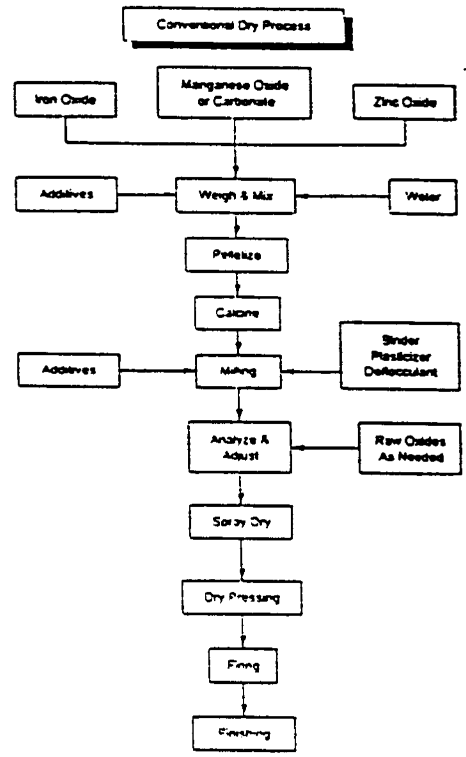

Figure 1 Conventional Dry Process For Soft Ferrites

RAW MATERIALS

As with other advanced electronic ceramics, the quality of the raw materials will have a marked effect on the final properties of a ferrite product. Raw material selection must include characterization of purity, particle size, distribution, surface area, consistency, and cost. Carefully planning the initial processing step to complement the chosen raw materials is the first key to controlling microstructure and making a consistent product. For manganese zinc ferrites, the source of manganese can be in either carbonate or oxide form. French process zinc oxide of high purity is readily available. For nickel and copper zinc ferrites, sources vary in purity, oxidation state, and particle size. The largest number of options for any of the raw materials is in the selection of iron oxide. Cost is a major consideration in consumer driven applications. Depending on the targeted market for which the ferrite is being produced, the iron oxide can be from natural ore, steel mill pickle liquors, or other synthetic processes. Table 1 shows assays of commercial iron oxides with major impurity levels and typical surface area.

Iron Oxide Assays

Source	% Fe_2O_3	% SiO_2	% CaO	% Cl	SA
Natural Ore	95-98	0.7-2.0	0.2-0.5	-	Coarse
Purified Ore	99.6	0.2	0.02-0.05	-	2.7
Lurgi	99.4	0.1	0.15	-	-
Ruthner	99.3	0.15	0.04	0.15	2.8
Ruthner	99.3	0.007	0.01	0.1	5.0
Fe Sulfate	99.5	0.15	0.02	-	8.3
Carbonyl	99	0.002	0.001	0.001	10-160

Table 1 Typical Iron OxideAssays

IRON GRINDING

For products where iron from a natural ore, Lurgi, or one of the lower cost Ruthner types is applicable, grinding may be necessary to improve and control reactivity during calcining. Spray roasted iron oxide particles are hollow spheres with an apparent density of .25-.40 g/cc. Grinding and high intensity mixing will destroy the spheres and increase the apparent density 3-4 times. This effective narrowing of particle size distribution will serve to avoid formation of non-uniform grain sizes. Types of equipment to be considered include attrittor, jet, vibratory, and ball mills. Since the flow chart chosen for focus includes a dry, batch-type mixing, a dry grinding method is selected. These iron oxide types typically include 5 to 10 micron particles or agglomerates. If we consider a 1-2 micron target particle size after grinding, a dry continuous attrittor emerges as a logical selection of grinding equipment.

Dry grinding offers several advantages over wet grinding. Dry processing greatly simplifies material transfers and eliminates the need for an energy consuming drying step. Continuous dry grinding is well suited for satisfying large capacity requirements.

Generally, grinding media selection must be made based on numerous factors. For iron or ferrite grinding the selection process is simplified greatly and limited to a choice of low carbon or chrome steels. Ninety percent of contamination from milling operations is the result of media wear. Iron pick-up from media can be expected at approximately 1%. Media diameter should be greater than the largest in-feed particles to achieve effective breakdown. Generally, smaller media are more efficient when grinding to extremely fine particle sizes. For dry attrittor grinding, media size ranges from 3mm to 10mm. The dry attrittor can be continuously charged from the top and discharged through the bottom grid to provide a constant flow of finely ground processed material (see Figure 2). Continuous grinding requires that a stable condition be maintained inside the mill at all times. A proper proportion of material to media must be established. If the ratio of media to material is too high, the velocity and impact force of the media will be reduced and inefficient particle size reduction will result. If the ratio is too low, the media will impact against itself, causing excessive media wear. The most efficient particle size

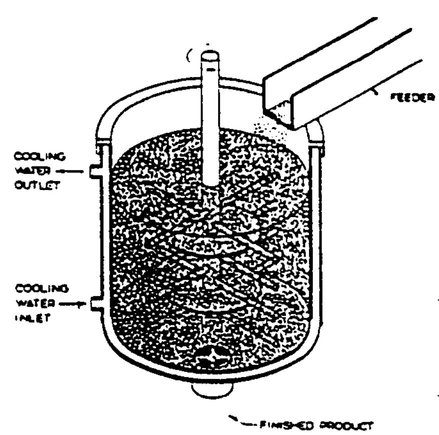

Figure 2 Continuous Attritor

reduction results when the material to media ratio is optimized. The objective is to control the retention time in the mill just long enough to reduce the particles to the desired size. Variables affecting the achievement and control of this condition include:

Feed rate - An accurate feeding system must be used to dispense material into the top of the mill.

Discharge rate - A specially designed metering valve is located at the base of the mill and can be adjusted to discharge the same amount of material as is being added to the top.

Torque - A sensor is fixed to the rotating shaft with a display indicating applied torque. By operating within a narrow range of torque variation, one can be assured that process conditions are stable. An ammeter displaying motor current can be used in a similar fashion.

Media Charge - Regular maintenance of media size and charge level must be performed to assure a process with tightly controlled conditions.

In addition to monitoring and recording these 4 variables regularly, control charts can be generated for average particle size of in-feed versus product materials.

Figure 3 illustrates the particle size distribution which is typical of in-feed material versus product from a continuous dry attrittor and a continuous ball mill for iron oxide application.

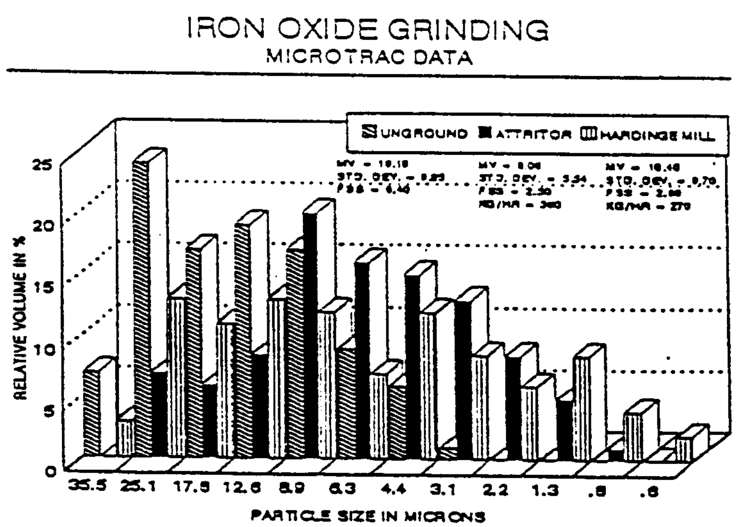

Figure 3 Particle Size Distribution for Iron Oxide Grinding

MIX/CALCINE

The finely ground iron oxide is now mixed with selected metal oxides or carbonates to formulate the desired ferrite. High intensity dry mixing is commonly followed by a moisture addition to aid the formation of pellets. Pelletization of the raw mix is desirable to aid material transfer to the calcine operation. Pellets can be formed by compaction, extrusion, or high speed rotation in the mixer pan. Each of these pelletizing methods will yield a different average pellet size. Pellet size variation will affect the uniformity of the structure and friability of the calcined pellets. The desirable pelletizing process yields small, uniform pellets with minimal dust content.

Calcining typically is conducted in ambient air at temperatures around 1,000° C. During calcination carbonate raw materials decompose and oxides react to form the desired spinel structure. Calcination provides a dense, low surface area material which can subsequently be milled to a small average particle size with a narrow distribution. Process variables must be controlled during calcination to render a consistent density and proper oxidation state both of which effect calcine friability.

CALCINE MILLING

Several objectives are addressed during calcine milling. The first objective is the controlled improvement of reactivity through reduction of calcined pellets to small uniformly sized particles. The exact particle size target will vary depending on the application of the final product. It is always best to mill to a particle size target rather than for a fixed time because the extent of milling depends on milling efficiency as well as milling time. A second objective is to produce a manageable slurry that is well suited for spray drying. This will involve introducing organic additives including dispersents, defoamers, binders and plasticizers which aide slurry rheology and improve pressing characteristics. The last objective is to measure and adjust, if necessary, the final chemical formulation. Major components are typically held to ± .1% on a molar basis of a nominal target value. Additives used as modifiers for electrical properties are sometimes introduced and dispersed during the milling process.

The same options of milling methods and equipment types presented for iron grinding exist for calcine grinding. A wet, batch-type milling process must be used to produce a slurry for spray drying and to allow composition adjustment. Ball mills and attrittors are both capable of meeting the process objectives for calcine milling, but the attrittor offers several advantages. The attrittor creates both impact and shearing forces, consumes less power, requires less floor space, and is capable of finer grinds in shorter grind times; typically ten times faster than conventional ball mills. The attritor also allows more reproducible results, and yields a narrower particle size distribution. Attritors allow inspection of the material during the grinding cycle and material additions without stopping the machine. (See Figure 4).

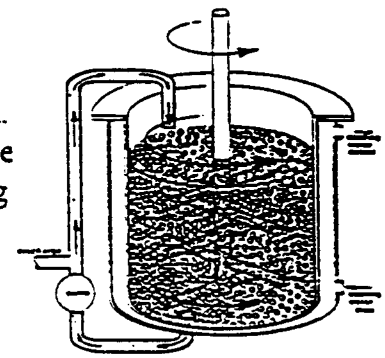

Figure 4 Batch Attritor

A circulation attritor provides an even narrower particle size distribution and allows processing of larger batch sizes with lower capital investment. A circulation system combines the attritor with a large holding tank which is generally about ten times the size of the attritor (see Figure 5). The circulation attritor rapidly pumps the slurry through a confined bed of grinding media so that the entire contents of the holding tank passes through the attritor about eight times per hour. The fast pumping stream makes the agitated media act as a dynamic sieve, allowing the fine particles to pass quickly through while the coarser particles follow a slower path and are subjected to additional milling forces resulting in a narrower particle size distribution.

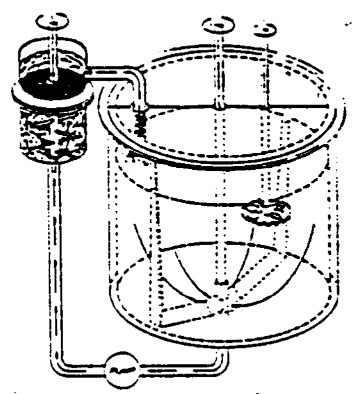

Figure 5 Circulation Attritor

Low carbon or chrome steel is again the obvious media choice. The circulation attritor typically uses media from 2 to 6 mm in diameter. Since a dry feed material can not be charged directly into the circulation attritor and since the size of the calcined pellet may not be adequately broken down by 6 mm media, a two stage milling operation is required.

If attritors are being purchased to upgrade conventional ball milling, a ball mill can be used in a coarse milling step to produce a pumpable slurry ready to transfer to the circulation attritor holding tank. Multiple coarse mills can be transferred to the holding tank as needed to satisfy the requirements of the fine grind tank capacity.

Following is an example of this type of approach. Initially, four 3,630 kg ball mill charges were processed to create a 14,520 kg tank. Milling time to reach target particle size averaged 20 hours/mill or 80 hours mill time for 1 tank. Currently, two 3,630 kg ball mill charges are pre-milled for three hours and then transferred to a circulation attritor for seven hours additional mill time. This two stage milling process is repeated to generate the same 14,520 kg tank in 26 hours total mill time. Ignoring transfer times, the initial method processes 181 kg/hour and the current method processes 558 kg/hour. Remember also that with 7 hours processing time in a circulation attritor the total residence time in the grinding chamber is only 35-40 minutes. Comparing 40 minutes residence time for 7,260 kg of slurry to 34 hours in the ball mill provides a 50 to 1 improvement in milling efficiency. Figure 6 represents particle size distributions of a) a pre-milled slurry; b) a ball milled slurry with 25 mm media; and c) an attritor milled slurry with 6 mm media. As a further comparison of the two distributions, a quality factor can be calculated which takes into account particle sphericity and tightness of distribution. Using the mean value (MV) from Microtrak data and theroetical density and assuming monosize spherical particles, a calculated surface area (CSA) can be derived.

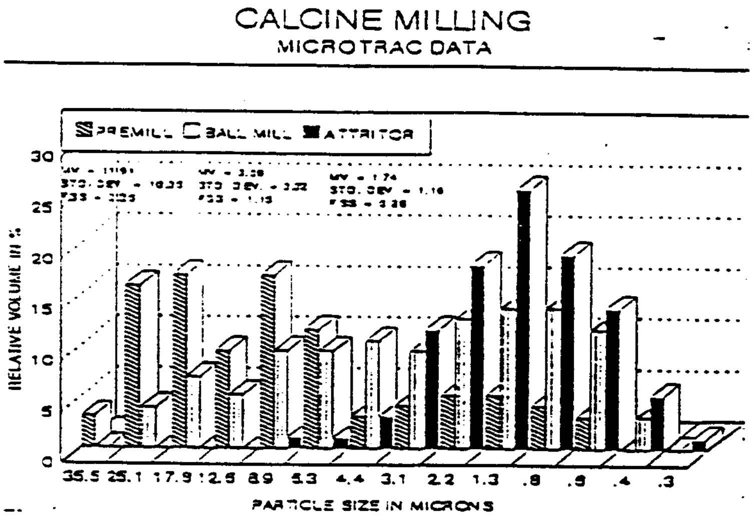

Figure 6 Particle Size Distribution for Calcine Milling

$$CSA = \frac{\text{Surface Area / part.}}{(\text{Density})\ (\text{Volume / part.})} \quad m^2/g$$

The Quality Factor (Q.F.) then becomes the ratio of actual surface area (BET) to calculated surface area (CSA). Table II illustrates the difference in the two samples from figure 6.

PROCESS COMPARISON
Quality Factor

BALL MILL	ATTRITOR
MV - 3.6 μ	MV - 1.7 μ
CSA - .32 m^2/g	CSA - .69 m^2/g
BET - 4.60 m^2/g	BET - 5.36 m^2/g
Q.F. = $\frac{BET}{CSA}$ - 14.4	Q.F. = $\frac{BET}{CSA}$ - 7.8

Table II Process Comparison - Quality Factor

To completely eliminate the conventional ball mills from the process, another method must be used to produce a slurry transferable to the circulation attrittor. A batch-type attrittor can be charged with dry material if in-feed pellets can be broken down by 10mm. media. A dry pre-milling step can be used successfully if a rapid, high shear agitator is used to produce a slurry. In this method, water is added to a holding tank first and then rapidly stirred as pre-milled particles are gradually metered in from the top.

SUMMARY

Any ferrite manufacturing process in today's market must strive for consistent, reproducible processing. Parameters must be identified at every process step and controlled within the narrowest tolerances in order to minimize process variability. Grinding of iron oxide and milling of calcine can be performed with adequate process controls such that up-stream variation is reduced and spray dried powder can be sintered into a product with uniform ceramic phases.

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Attrittor Figures courtesy of
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