

Red Ferrite Technology-Dream or Reality

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Abstract: Search for the answer to the question, if good initial homogenization of raw materials can substitute all classic ways of homogenization such as dry mixing, pelletizing, calcination and milling brought us to the revival of the so called 'red' ferrite technology. It has been proved that it can be successfully applied in high permeability ferrite production.

Rdeča feritna tehnologija - sanje ali resničnost

Ključne besede: feriti mehki, proizvodnja, zmanjšanje stroškov, okolje, minimizacija onesnaženja, feriti rdeči, tehnologije, feriti visoko-permeabilni, MN-ZN feriti, surovine vhodne, homogenizacija, prahovi, priprava surovin, lastnosti elektromagnetne, lastnosti fizikalne, stisljivost, skrčenje, prijave patentne

Povzetek: Iskanje odgovora na vprašanje, če dobra začetna homogenizacija vhodnih surovin lahko zamenja vse klasične načine homogenizacije, kot so suho mešanje, peletiranje, kalcinacija in mletje, je naju pripeljalo do oživitve t.i. 'rdeče' feritne tehnologije. Pokazano je, da jo je možno uspešno uporabiti v proizvodnji visoko-permeabilnih feritnih izdelkov.

Introduction

In order to be competitive on the nowadays soft ferrite market one has to fulfill certain general demands: electromagnetic properties must be in specified limits being more stringent and demanding from day to day; exactness and repeatability of core dimensions is a must; yield over all parameters must be high ensuring high quality products; products must have price as low as possible; delivery time must be exact and as short as possible. Powder preparation is a part of a ferrite core production which can crucially affect the fulfillment of most of the above mentioned demands. It has pronounced influence on all of these production process properties.

There are two main branches of soft ferrite powder preparation technologies - conventional ceramic process (1-4) and wet chemical process (5-8). In the first one, dry oxide or carbonate powders are mixed, calcined, milled and dried after appropriate binder/lubricant addition. In the second one, salts such as chlorides or nitrates are soluted, coprecipitated, usually calcined afterwards, milled and dried after appropriate binder/lubricant addition. However, in both cases the general scheme is homogenization-calcination-milling-drying.

Each of these technologies can be judged not only on the basis of above mentioned general requirements but on the basis of the requirements tied to some special aspects of powder preparation such as: process ability

to lower or eliminate the influence of raw materials; number of operations is to be minimum in order to have powerful line production control loop; ease of material rework and waste material recycling is desirable; pollution by either toxic agents or dust released in the process is to be minimum; finally in the area of granulate properties - superior physical and chemical homogeneity is a must and powder compressibility should be minimum.

New 'red' ferrite technology objectives and set up

All these demands are not easily accomplished. Compromises are usually made between high magnetic properties and quality on the one side and costs, simplicity and delivery time on the other. The question is: Is it possible to set up a ferrite powder preparation technology that produces high quality products that are cheap, produces high quality products in a short time, produces high quality products in a simple and elegant way?

There is a technology which is simple enough and cheap enough, which could be the starting point for answering that question. It is so called 'red' technology. To our knowledge almost everything about that technology was denoted as poor (2):

1. poor electromagnetic properties,
2. poor dimension exactness,
3. high shrinkage,

4. impossibility to produce complicated shapes,
5. high granulate compressibility,
6. sintering equipment corrosion.

On the basis of all these statements it would never occur to anyone to even try to use this technology in high permeability ferrite production. However, this is exactly what was done and presented in this paper. Why?

In the sixties, when conventional ceramic process was developed, based on the metal oxide and carbonate production development, the quality of the iron oxide was rather poor. The impurity content of both anion and cation impurities was rather high. Specific surface area (SSA) was not reproducible, as shown in Table 1. Organic additives were not such as to provide low granulate compressibility for the powders of the average particle size $< 0.5 \mu\text{m}$. Calcination was the the only logical answer to these problems.

Table 1. History of raw material properties - calcination conditions relation

Properties of	Time period				
Fe_2O_3	1960 - 1970	1970 - 1980	1980 - 1990	1990 -	trend
PSSAT* (m^2/g)	± 2	± 2	± 1	± 0.5	± 0.5
Purity (%)	97 - 98	99.0 - 99.5	99.1 - 99.4	99.4 - 99.7	99.96 - 99.995
Anion content (%)	1 - 2	0.1 - 0.6	0.1 - 0.6	0.10 - 0.40	0.005 - 0.09
Calcination					
Temperature ($^{\circ}\text{C}$)	900 - 1150	900 - 1150	900 - 1100	1000 - 1100	750
Duration	2 - 4 h	2 - 4 h	30 min	< 1 min	15 s
Kiln type	tunnel	tunnel	rotational	spray	spray
Milling time (h)	12 - 24	12 - 24	3 - 12	≈ 1	≈ 1

*PSSAT - particle specific surface area tolerance

What happens during calcination? Release of all volatile products of red-ox reactions such as CO_2 , Cl , SO_3 . The calcinate is free from corrosive gases and all other volatile compounds that could cause cracks during sintering. Through the reaction of sintering and the reaction of spinel crystal structure formation all physical and chemical parameters are homogenized, assuring uniform microstructure and composition during sintering. Due to higher calcinate particle dimensions, granulate compressibilities approach user-friendly values of < 200 MPa.

Is there something unfavorable about calcination? Yes, it is the fact that it must be followed by milling, in order to recover calcinate reactivity by decreasing its particle size and increasing its specific surface area. What is wrong about milling? Milling introduces composition change through the iron pick-up, due to the steel ball

abrasion. The quantity of the iron pick-up changes in time as the intensity of steel ball abrasion increases. The iron pick-up can be as high as 1.3 wt % (10). Another effect of abrasion is the change of steel ball dimensions and eventually shapes, which causes the powder physical parameters not to be repeatable in time. It is very well known how deteriorating the change of composition and powder physical properties affects ferrite electromagnetic properties. So, shortly speaking, the shortcomings of conventional ceramic ferrite powder preparation include limitations on compositional control (3,10), incomplete chemical homogenization, introduction of impurities from milling, relatively coarse particles leading to pressed bodies with large and inhomogenous porosity.

In order to surpass these problems and answer to constantly higher demands regarding electromagnetic properties of ferrite materials novel powder preparation techniques (3-8) were developed as well as clean raw materials. The tendency of lowering calcination temperatures and decreasing calcination time is evident in Table 1. The direct consequence of this are shorter milling times, partially eliminating its negative effects.

The challenge we wanted to face is to produce high permeability ferrite material with the nowadays commercial raw materials by means of the simplest, shortest and cheapest process ever known. This process avoids the problems present in all technologies which incorporate calcination and subsequent milling. The main objectives of this process are to achieve sufficient composition homogeneity during the first wet mixing step, leaving spinel crystal lattice formation, grain growth and densification to sintering step and transferring everything else to the raw material and binder system level. Flow chart of the new 'red' ferrite technology, we used to produce high permeability ferrite cores is presented in Fig. 1. As evident, it follows the old 'red' ferrite processing, with the special attention paid to wet mixing optimization and the choice choice and content of organic additions (9). Sintering is another step that should be especially adjusted, due to its additional function. In this paper sintering was not adjusted to these requirements. Standard sintering

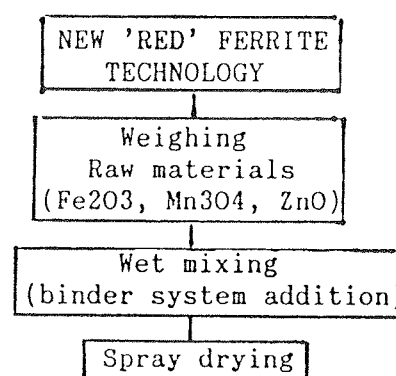


Fig. 1: Flow chart of the new 'red' ferrite process

procedure normally used in our production facilities has been used, leaving free space for future improvements.

Experimental procedure

The starting materials of commercial purity were spray roasted iron, manganese oxide and zinc oxide. Their properties are given in the Table 2.. Ferrite composition to be realized was $\text{MnO}_{0.49}\text{ZnO}_{0.43}\text{Fe}_{2.073}\text{O}_4$. The dry premixed starting materials are suspended in water and underwent technically superior wet-mixing step. At this stage the appropriate binder/plasticizer combination (9) was added. The slurry was then spray dried. Powder compressibility was measured as a function of a green density.

Table 2. Raw material properties

Raw material	Particle shape	Particle size (μm)	SSA (m^2/g)	Purity (%)	Anion content (%)
Fe_2O_3	spherical	0.25 ± 0.05	3.5 ± 0.5	≥ 99.4	<0.100
Mn_3O_4	spherical	0.07 ± 0.01	15 - 20	≥ 70.7	<0.027
ZnO	spherical	0.50 ± 0.10	4 - 8	≥ 99.9	<0.001

To study magnetic properties ring cores of different dimensions (FT 36/23 20, FT26/1420, FT 26/14 10, FT 22/14 07, FT 10/06 04 and test toroid FT 26/17 06) and cores RM 4 and RM 8 were dry pressed to a green density of 3.00 g/cm^3 . The samples were heated to 300°C to remove binder. Sintering was carried out in a tunnel and chamber kiln at 1350°C for about 9 h in air. In a tunnel kiln sintering was followed by cooling maintaining the stoichiometry achieved by 90 - 99 % disintegration of excess iron (11). In a chambre kiln sintering was followed by a stabilization at 1300°C for 5 h in a $0.1 \% \text{ O}_2 + \text{N}_2$ atmosphere maintaining stoichiometry achieved by 90 - 99 % disintegration of excess iron and after that by cooling. Small ring cores sintered in a chambre kiln were buried in raw ferrite powder of the same composition. After sintering, RM cores were grinded and polished to improve the quality of mating surfaces.

Ring cores were subjected to initial permeability - μ_i , loss factor value - $\text{tg}\delta/\mu$, hysteresis material constant - nB , disaccommodation factor - D_f and μ - T dependence measurements. Besides magnetic properties, dimension shrinkage dependence of ring cores on their green density was recorded as well as RM core shrinkage and warpage.

Results and discussion

Fig. 2 shows the dependence of red ferrite powder compressibility on green body density. It is evident that

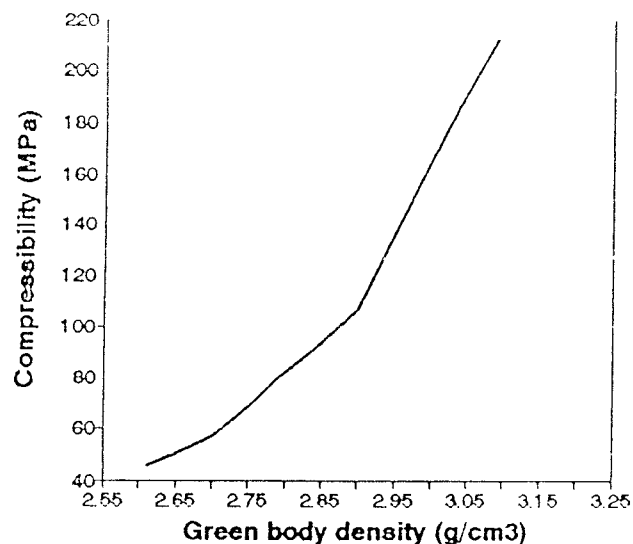


Fig. 2: Powder compressibility dependent on green body density

green densities in the range of $3.00 \pm 0.05 \text{ g/cm}^3$ can be achieved with the pressures well below 200 MPa, which is considered to be the user friendly limit for the dry pressing. Without that condition 'red' ferrite powder would not be considered usable. We suppose that one of the main reasons for such a low compressibility is spherical particle shape of the used raw materials, making the fact that their dimensions are well below $1 \mu\text{m}$ unimportant. Proper choice and content of binder/plasticizer/lubricant combination is the second one. Low 'red' powder compressibility obtained by new 'red' process discards the 5th of the 'poor' statements about red ferrite processing.

With different sintering procedures we achieved different high-permeability levels such as $4600 \pm 20 \%$, $6000 \pm 20 \%$ and $10000 \pm 30 \%$. Typically achieved values of $\text{tg}\delta/\mu$ @ 100 kHz are $12\text{E}-6$ for permeability levels of 4300 and 6000 and $\leq 30\text{E}-6$ for permeability level of 10000. Hysteresis losses are $\leq 1.25\text{E}-3/T$ for the permeability levels of 4300 and 6000 and $\leq 0.8\text{E}-3/T$ for the permeability level of 10000. Disaccommodation factor is $\leq 3.6\text{E}-6$ for the permeability levels of 4600 and 6000 and $\leq 0.2\text{E}-6$ for the permeability level of 10000. Fig. 3. shows respective ring core permeability - temperature dependence. Electromagnetic properties of RM cores are given in the Table 3. It is evident that all parameters both of ring and RM cores are in the world- wide accepted limits. So the 1st of the 'poor' statements is discarded. At this point we can answer the question given at the very beginning of this paper, if good initial homogenization of raw materials can substitute all classic ways of homogenization such as dry mixing, pelletizing, calcination and milling. The answer is positive. We expect even better results after adjusting the sintering to the noncalcined powder requirements.

Achieved dimension exactness and its repeatability is illustrated in Fig. 4., where the largest dimension q of RM 8 core was measured at the bottom and at the top of the

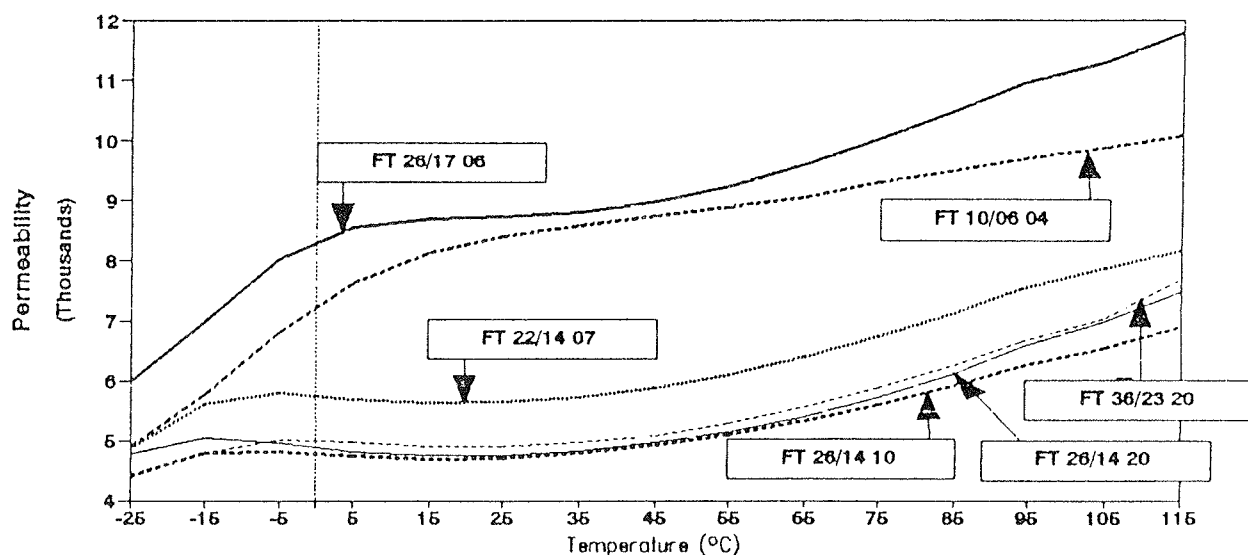


Fig. 3: Permeability dependence on temperature for different ring cores

RM core magentic properties

Core of permeability level	RM 04 4600		RM 04 10000		RM 08 4600		RM 08 10000	
	Catalogue data	New process data	Catalogue data	New process data	Catalogue data	New process data	Catalogue data	New process data
Al (nH)	+30	+20	+30	+20	+30	+20	+30	+20
	1700	1900	3690	3700	5700	6320	12500	10000
μ_{eff}	-20	-20	-20	-20	-20	-20	-30	-20
	2610	2900	5000	5030	3200	3400	5870	5500
$\mu\delta/\mu@100\text{ kHz}(E-6)$		14		14		14		30
$nB (E-3/T)$		1.16		1.19		1.12		0.96

Table 3: Electromagnetic properties of RM cores for 19G, 22G and 12G quality

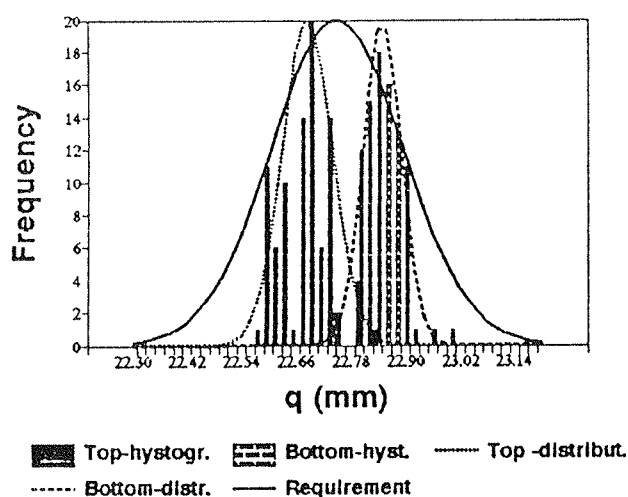


Fig. 4: Dimension exactness and repeatability RM 8 length - q

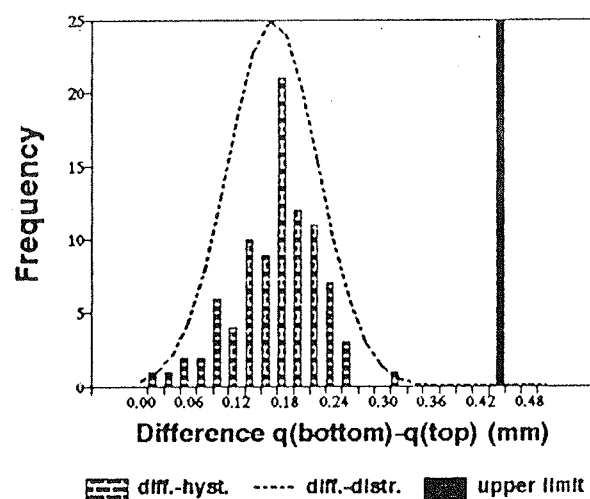


Fig. 5: Warpage of RM 8 outer walls; measurement of RM 8 length - q

CRITERIA	TECHNOLOGY					
	New 'red' (9)	Conventional dry mixing(1)	Conventional wet mixing(2)	Spray firing (3,4)	Co-spray roasting (5,6)	Coprecipitation (7,8)
RAW MATERIAL INFLUENCE						
Particle physical properties	■	■	■	■	■	■
Cations	■	■	■	■	■	■
Anions	■	■	■	■	■	■
PROCESSING						
Number of processing steps	3	6	6	5	5-6	6-7
Line production control loop	○	○	○	○	○	○
Yield of toxic agents	■	■	■	■	■	■
Recycling of waste materials	○	○	○	○	○	○
Rework possibility	○	○	○	○	○	○
Reduction of dust	○	○	○	○	○	○
Adaptation with conv. ferrite prod.	○	○	○	○	○	○
POWDER						
Homogeneity physical	■	■	■	■	■	■
chemical	■	■	■	■	■	■
Workability	○	○	○	○	○	○
CORE PROPERTIES	■	■	■	■	■	■
COST	○	○	○	○	○	○


 more, better


 favorable


 less, worse


 unfavorable

Table 4: Comparison of new 'red' ferrite processing with the other ones

RM outer walls on arbitrarily chosen 80 out of the series of 3000 pieces. It is obvious that dimension exactness is satisfactory, process capability measure C_p being >1.33 for both of the measuring points. This proof discards the 2nd of the 'poor' statements.

Warpage of complicated ferrite cores might be the reason why complicated cores can not be successfully produced as stated in the 4th of the 'poor' statements. One of the ways to estimate the warpage is to measure the difference of the largest RM dimension q at the bottom and at the top of the RM outer wall. The frequency distribution of this difference is shown in Fig. 5. The average difference is 0.18 mm being sufficiently below the tolerance of 0.45 mm. Such an extent of warpage is

usual with standard calcined ferrite RM cores. The 4th of the 'poor' statements is discarded as well.

Finally, Fig. 6 presents the dependence of ring core dimension shrinkage on its green density. Shrinkage of the ring core height is $15.0 \pm 0.5 \%$, while shrinkage of its outer and inner diameter is $16 \pm 0.5 \%$ for the green density in the interval $3.00 \pm 0.05 \text{ g/cm}^3$. This shrinkage is exactly the same as the one corresponding to the calcined ferrite powders with approximately equal binder content, being sintered under approximately the same conditions. The 3rd of the 'poor' statements is discarded.

The 6th of the 'poor' statements concerns sintering equipment corrosion. This one holds, but let us see to

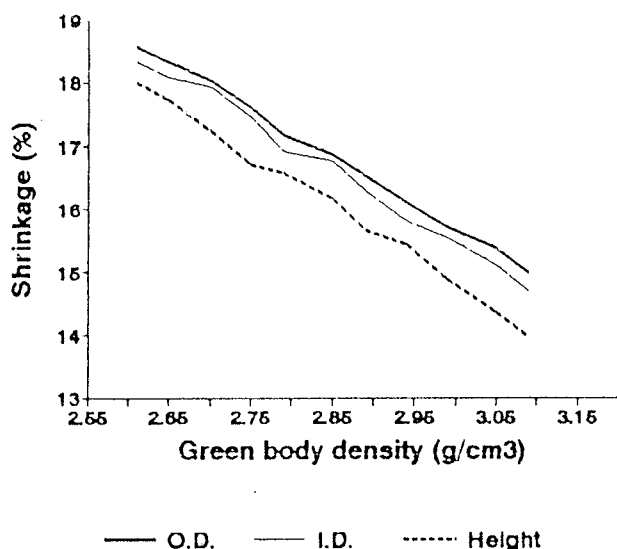


Fig. 6: Shrinkage as a function of a toroidal green body density

what extent and if that problem can be solved. Iron oxide we use incorporates Cl. According to U. Wagner (12) chlorides completely evaporate in the temperature range from 400 - 1000°C. This means that probable corrosion problem can be solved on the furnace hardware level in that range of temperatures, using corrosion resistant and gas tight ceramic insulation, stainless steel exhaust piping and finally corrosion resistant heating elements, all available in the market. Using higher purity materials for reliable production of ferrite materials of permeabilities ≥ 10000 the 6th of the 'poor' statements practically disappears.

Let us consider other aspects of the new 'red' technology - the economy and pollution related aspects. Even a glance thrown on the new 'red' process flow chart reveals the following. It is the shortest, the simplest, the cheapest and the best controllable ferrite core processing ever used. Dust pollution is minimal. Comparison of the new 'red' ferrite powder preparation technology with the other ones taking into consideration all of the criteria given in the Introduction is given in Table 4. Judgement of other technologies has already been given by U. Wagner (3).

Conclusion

With the example of high permeability ferrite ring and RM core production by new 'red' technology, all of the 'poor' features of old 'red' ferrite technology are shown

to be nonexistent, such as poor electromagnetic properties, high shrinkage, high powder compressibility etc, or easily solvable such as corrosion. New 'red' ferrite processing is the simplest, the shortest and the cheapest ferrite production technology ever known. Moreover, this technology overcomes classical shortcomings of the conventional ceramic ferrite technologies. Are we entering the new era of 'red' ferrite processing? The time will show whether this orientation is the right one !

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