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MODERN DEVELOPMENT TRENDS IN HIGH-PERFORMANCE SOFT FERRITES

A. Žnidaršič in M. Drofenik*

ISKRA FERITI, d.o.o., Ljubljana, Slovenia
*Fakulteta za kemijo in kemijsko tehnologijo, Univerza v Mariboru

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Abstract: This paper considers the current MnZn-ferrite development trends in high-performance soft ferrites. Today, soft MnZn ferrites play the dominant role in magnetic materials. They are produced in large quantities and are used in a wide variety of applications. As a result, research and development in both industry and research centres has made great efforts to develop new classes of soft-ferrite materials.

Novi trendi priprave visokokvalitetnih mehkih feritov

Ključne besede: elektronika, keramika magnetna, feriti mehki, trendi razvoja, zmogljivost visoka, Mn-Zn feriti, lastnosti magnetne, lastnosti električne, mikrostrukture, meje med zrni

Izvleček: V članku so podane različne razvojne smeri priprave kakovostnih MnZn-feritnih materialov. Danes predstavljajo mehki feriti pomembne magnetne materiale, ki se proizvajajo v velikih količinah in za različne uporabe. Rezultat razvojnih dejavnosti v industriji in na raziskovalnih inštitutih so nove kvalitete mehko magnetnih feritnih materialov.

1. Introduction

Ferromagnetic ceramic materials, which are mainly composed of ferric oxide, have a lower saturation magnetisation than ferromagnetic alloys, however in spite of this, ceramics have the advantage of being usable at higher frequencies because of their higher electrical resistance, higher corrosion resistance, better heat resistance and lower price.

Applications using ferrites began about 30 years after the commercialisation of the ferromagnetic soft Fe-Si alloy. The commercial ferrites did not attract much attention because their magnetic properties were considerably inferior to those of ferromagnetic alloys. However, the importance of ferrites became clear during the 1950s, as a result of new applications such as radio, television, telephones, computer and microwave devices which were rapidly expanding at that time. At the same time, physicists and electronic engineers became very interested in the magnetism and the expanded high-frequency applications of ferrites. Research scientists in chemistry, ceramics and metallurgy also started to study ferrites and become engaged in the development of new ferrites and improved ferrite-manufacturing processes. Manufacturing ferrites is a complicated process that requires more steps than the manufacturing of ferromagnetic alloys. Because ferrites are frequently used as electronics parts, there are strict requirements in terms of the accuracy of their dimensions and the uniformity of their properties. Consequently, extremely good quality control is necessary during their manufacture.

Ferrites are mistakenly believed to be fully developed in all fields of science, technology and applications. Ferrite materials are now being recognised and crucial to the further development of electronics and it is believed that the production levels of ferrites will increase year by year as their applications become more diverse. Reviewing the history of ferrites and accurately analysing their present situation will help with further development in the future.

The electromagnetic properties of ferrites depend on the method of production and the resulting micro- and nanostructures. MnZn ferrite is designed to have a high permeability and to be used in power application. A high initial permeability over 15 000 at 10 kHz was recently achieved by using pure spray-roasted iron oxide. However, hand low power losses are also of prime importance for power applications. Control of the grain-boundary chemistry and the grain size by the appropriate selection of additives and firing conditions is required to achieve low power losses at high frequencies.

The magnetic characteristics of ferrites are sensitive to chemical composition, impurities, firing conditions, and so on. Much effort has been devoted to investigating these parameters in order to achieve the best properties in the limit of a conventional process. In order to go beyond these limits, attempts involving new processes for ferrite powders have recently been made. Hydrothermal synthesis, which is one of these new processes, is a process under consideration. This process may be particularly useful to producing low-cost high-performance power ferrites for high-frequency switching power supplies.

Finally, the parameters that determine the magnetic losses in MnZn ferrites, such as the purity of the raw materials, the influence of the dopant and the sintering process are considered in terms of their effect on the final magnetic properties.

2. MnZn FERRITES

MnZn ferrites are generally classified into three groups: i) high-permeability materials for wide-band and pulse transformers, ii) low-loss materials for inductors and telecommunications uses and iii) high-saturation-flux-density materials for power applications.

The performance of ferrites is not determined only by the high value of the initial permeability. The other characteristics such as a low loss value, a high saturation flux density, a high sintered density and frequency characteristics are also important. In many cases, these requirements are not satisfied at the same time, so a compromise material has to be selected in such cases.

2.1. High initial permeability materials

The initial permeability of high-permeability materials depends to a large extent on the mobility of the Bloch' s domain walls. To obtain high permeability it is important to lower the anisotropy and the magnetostriction. During the development of high-permeability MnZn ferrites in the past, much effort was devoted to the parameters which govern the bulk properties such as composition, microstructure and porosity /1/. To achieve a high permeability the composition of MnZn ferrite must be selected from a relatively narrow composition range where a zero crystalline anisotropy and a zero average magnetostriction can be expected. Studies of the grain-boundary chemistry in combination with grain-boundary structural analyses revealed that the grain boundaries are usually a source originating from ZnO evaporation and the presence of a glassy phase at the grain boundary and the segregation of aliovalent ions /2/. Firing conditions and additives are also important for achieving good properties, Fig.2. However, the most important microstructural parameter when it comes to achieving a high magnetic permeability is large and inclusion-free ferrite grains.

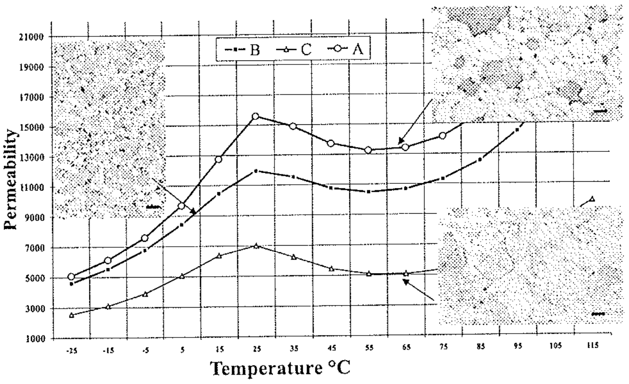

Fig. 1: Effect of liquid-phase-forming additives on the μ - T characteristics of sintered MnZn ferrites; A - doped with Bi_2O_3, SiO_2 > 200 ppm; B- doped with Bi_2O_3, SiO_2 < 200 ppm and C - doped with Bi_2O_3, SiO_2 < 500 ppm . The micron marker is 30 μ m.

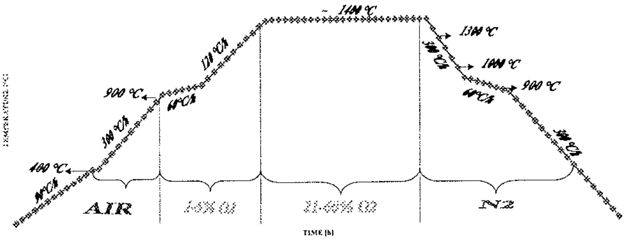

Fig.2: Typical firing program used for sintering of high performance high permeability ferrites

In order to increase the average grain size in MnZn ferrites the mobility of the grain boundaries must be promoted by using a proper additions that form a liquid phase during sintering such as Bi_2O_3 or SiO_2. In order to take the advantage of the presence of the liquid phase in ferrites during sintering, solid-state diffusion must be the prime mechanism at a constant amount of liquid phases until the total grain-boundary surface area decreases to such an extent that a liquid-phase film of a critical thickness d_0 is formed and solution-reprecipitation starts /3/.

The coarse grains in samples C, with intragranular porosity can be easily attained by discontinuous grain growth when the critical liquid-phase film is achieved at an early state of sintering when the average grain size is relatively small. Pores in large grains make no contribution to the magnetisation and decrease the free path length of domain walls during magnetic polarisation thus decreasing the magnetic pemeability.

Continous grain growth in the samples B is a key to achieving a relatively high permeability due to the intergranular porosity and the formation of grains free of non-magnetic inclusions. However, the average grain size obtained after just the solid-state sintering is usually about 30 μ m unless long sintering times are used. Long sintering times increases the average grain size but are detrimental to the permeability due to the evaporation of ZnO (4). Here, sample B contains an insufficient amount of liquid-phase-forming impurities or additions that would otherwise induce a liquid-phase film to provoke the anomalous grain growth.

In sample A the formation of a critical liquid-phase film was delayed as long as possible and the solution-reprecipitation processes started at a time when the total surface grain-boundary area decreases during solid-state sintering, accompanied by a grain size increase to about 30 μm. Here, during this sintering step the driving force is already "exhausted" and the pore size has increased and he pores were more resistant to being entrapped during the exaggerated grain growth. This all leads to a microstructure with larger average grain size and pore-to-pore distance and consequently to a higher magnetic permeability.

2.2. Low-loss Power Ferrites

Power ferrites should have low-power- loss characteristics under driving conditions. Low-power- loss MnZn ferrites should have uniformly sized fine grains and a high fired density. Thus far, the power-loss characteristics of ferrites were improved mainly by additives and a suitable sintering profile. Additives and impurities responsible for the grain-boundary chemistry have a remarkable effect on the grain boundaries properties, particularly on the grain-boundary resistance /5/. In order to obtain a sintered body with uniformly sized fine grains, which would be suitable for achieving low power losses, grain growth should be suppressed especially in the initial stage of sintering.

The average grain size during sintering can be decreased when a suitable sintering profile is applied, Fig. 3. This program is a combination of an initially high oxygen concentration and then, above 900°C, a low oxygen concentration /6/. At an oxygen concentration of above 20 vol % the microstructural development in MnZn ferrites is dominated by exaggerated pore growth /7/, while at a lower oxygen concentrations, below about 20 vol % the grain-boundary mobility in MnZn ferrites during sintering is promoted because of the increase in the concentration of oxygen vacancies which are the slowest moving species and hence promote volume diffusion. On the other hand, grain growth in ceramics is largely determined by the attachment or separation of pores from grain boundaries, which depends on the ratio of pore size to grain /7/. Thus, a combination of an intial high oxygen partial pressure, which promotes exaggerated pore growth, and a subsequent low oxygen partial pressure, which enhances volume diffusion, can inhibit grain growth and consequently decrease the average grain size in MnZn ferrites and increase the final sintered density.

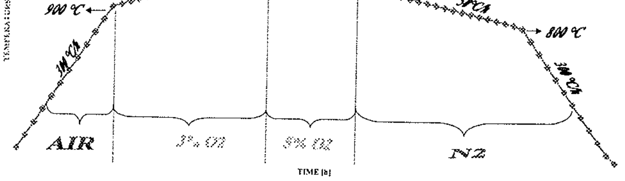

Fig. 3: *Typical firing scheme for of high-performance power ferrite*

The selection of high-grade raw materials with low level of impurities is of special importance in the production of MnZn ferrites with optimised microstructural properties. Ca and Si are well known to control the microstructural properties. This means that the raw materials have to be checked for existing levels of Ca and Si impurities. Both ions strongly influence the microstructure of MnZn ferrites. Furthermore, the total resistance of MnZn ferrites increases due to the precipitation of silicate phases at the grain boundaries. This has the advantage that CaO and SiO_2 are doped in a defined amount in the ferrite mixture and their effect can be optimised without being influenced by further impurities. In addition to the concentration of impurities, the reactivity of raw materials is a fundamental parameter when optimising the production process /9/.

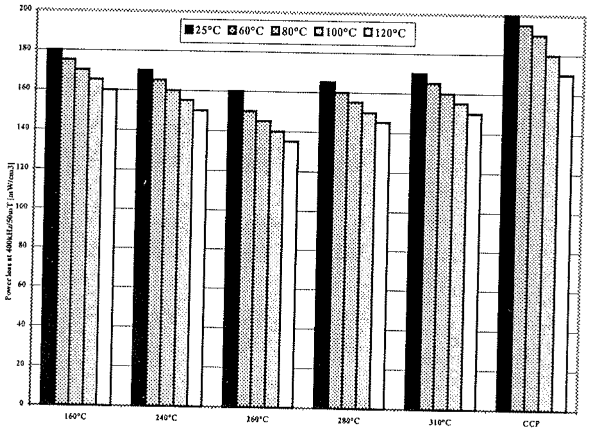

Fig. 4: *Temperature dependence of the power loss of samples prepared by hydrothermal synthesis at various temperatures and a time of 10h versus a conventional ceramic processing; labeled as CPP.*

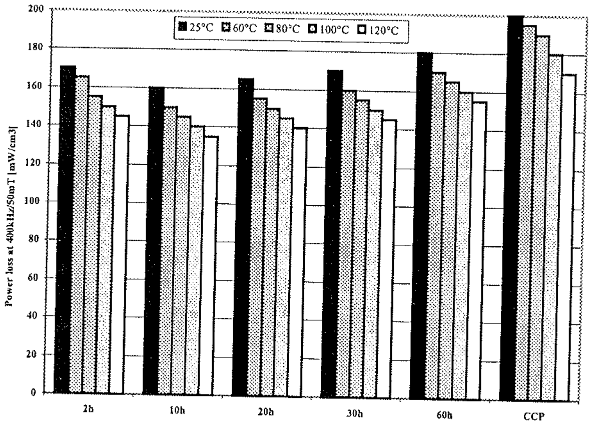

Fig. 5: *Temperature dependence of the power loss of samples prepared by a hydrothermal synthesis under the same temperature conditions 260°C and different times versus a conventional ceramic processing, labeled as CPP.*

The power loss of samples prepared by the hydrothermal processing method is shown in Fig.4 and Fig.5. Samples synthesised at 260°C and 10 ^{h} exhibit the lowest power losses.

The large-scale production of MnZn-ferrite ceramic materials is based on ceramic technology involving pre-sintering of a homogenized mixture of appropriate starting oxides at temperatures around 900 - 1000 °C in air. The pre-sintered material is subsequently milled to produce the ferrite powder. The pre-sintering step has the following effects on the ferrite powder (i) oxides are partially transformed into various spinel phases, (ii) the variations in reactivity of the individual starting oxides are reduced and (iii) the starting mixture is homogenized.

An alternative method involves the preparation of ferrite powders by the hydrothermal treatment of starting oxides /10,11/. During the hydrothermal treatment, chemical reactions between oxides occur in an autoclave at elevated temperatures around 260 °C under a high pressure, normally at an equilibrium water pressure. As a result of the hydrothermal treatment, a homogeneous mixture of some residual reactants (Fe_2O_3, Mn_3O_4) and ferrite spinel products $Zn(Mn)Fe_2O_4$ is obtained. Hydrothermally derived powders are much finer and more homogenous than conventionally prepared powders using pre-sintering.

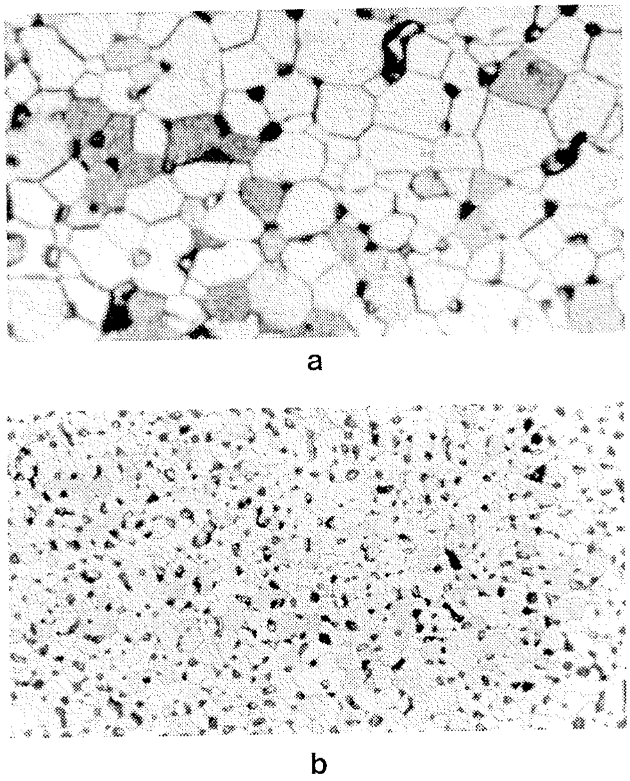

Fig. 5: Typical microstructures of samples; a) prepared by a conventional ceramic process, and b) by a hydrothermal process.

Raw-material quality is a very critical factor in ferrite processing. Other factors to be taken into account are reactivity, particle size distribution, chemical homogeneity, impurity content, impurity distribution and consistency between lots. In conventional processing the raw materials are mixed, pelletized, calcined and then milled to break up agglomerates. The disadvantages of this form of processing are poor homogeneity, a wide particle size distribution and the introduction of impurities during milling. The hydrothermal process eliminates the pelletizing, calcining and milling steps of the conventional process and leads to the formation of a fine, homogeneous powder with good reactivity.

3. Future Prospects for Ferrites

As described at the beginning, no-one doubts that the amount of ferrite produced will continue to increase each year. If researchers and engineers who work on MnZn ferrites take a closer look at the future prospects for MnZn ferrites and focus on important areas, of great value, the future for ferrites will be bright.

Most researchers who have studied the basic science of ferrites are now woking in other areas. The reason for this is that when we want to prepare ferrites with better properties or to find a new application, we may find that there is insufficient knowledge available from basic research. For example, when we want to achieve a value as close as possible the theoretical value for the magnetic or poweloss characteristics of MnZn ferrites by changing the heatreatment conditions, we would need a more precise understanding of the equilibrium between the phase and oxygen partial pressure, as well as the oxidation and the reduction kinetics of the ferrites.

It is not easy to develop novel, exiting new ferrite materials. At present, however, some promising materials are under investigation and their future development is anticipated.

The demand for soft ferrites has been growing and ferrites will expand considerably in both quantity and extent of application as the need for ferrites of higher quality increases. Raw materials and the improvement of technology, of which iron oxide is a major constituent, plays a decisive role in improving the quality as well as lowering the costs of ferrites. With a combination of improved raw materials, compositional and processing improvements, a new class of soft ferrite will be developed.

Furthermore, new applications of ferrites such as toners for photocopier application, new microwave ferrite material at a frequency of several tens of GHz and biomedical applications will be developed as a new research category.

Research on the application of ferrites for protecting the natural environment is being actively investigated. Applications include a washer disposal method for factory drains and the transformation of solar energy into hydrogen energy using ferrites as catalysts. We hope that some of these studies will become practical application in the near future /12/.

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Andrej Žnidaršič
Iskra Feriti, d.o.o.
Stegne 29, 1000 Ljubljana

Prof. dr. Miha Drofenik
Fakulteta za kemijo in kemijsko tehnologijo
Univerza v Mariboru
Smetanova 17, 2000 Maribor

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