Freeze Granulation: A novel technique for low-loss Mn-Zn ferrites

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In the present work the freeze granulation technique is applied in the manufacturing process of Mn-Zn power ferrites. The powders are prepared by the solid state reaction method and a comparison between the standard industrially used spray-drying method and the freeze granulation process with subsequent freeze drying has been carried out, in terms of granulate morphology, compaction behavior and pore size distribution, sintering behavior and magnetic performance. It apeared that the freeze granulation process enables the formation of homogeneous green compact microstructures and finally leads to sintered products of good magnetic quality. Consequently, Mn-Zn ferrites with low losses of 287 mW/cm^3 (at measuring conditions f=100 kHz, B=200 mT and T=100^{0}C) are manufactured.

Index Terms—**freeze granulation, freeze drying, ferrites, power losses**

I. INTRODUCTION

MN-ZN FERRITES CONSIST an important category of ceramic magnetic materials with a wide spectrum of technological applications, in devices that in the broadest sense can be characterized as transformers, inductors or absorbers [1]. It is widely accepted within the published or patented literature that the magnetic quality of Mn-Zn ferrites in terms of high initial permeability and low power losses lies on an optimized combination of chemical and morphological homogeneity of the sintered ferrite [2]. Adequate preparation of the powder before compaction is necessary in order to achieve a pressing performance that ensures dense compaction into a homogeneous state, as the presence of defects in the green bodies often persists during sintering and therefore affects the quality of the final product [3].

The conventional spray-drying method used in production-scale processing of Mn-Zn ferrites, which is based on the spraying of the ferrite slurry droplets into a hot air vertical evaporating tube, shows significant drawbacks, such as inflation defects visible as large voids in the interior of the granule [4]. The rapid water evaporation gives rise to the development of capillary stresses that may initiate undesirable diffusion and segregation phenomena, which reduce the compositional and morphological homogeneity of the granule. Those imperfections may resist compaction and also be present in the compacted specimens. The ideal preparation of a powder suspension by applying colloidal processing combined with sufficient mechanical treatment, which provides optimal homogeneity, can be preserved by freezing and subsequent freeze-drying. The whole process is described as “freeze granulation” [5]. The process involves freezing the material by certain freezable liquids that subsequently sublime when exposed to an environment with a very low partial pressure of water to form ice crystals. The ice leaves voids producing a rigid porous product that helps in the drying process by providing pathways through the material for vapor deposition, while enabling the product to rehydrate quickly through capillary action [6]. The advantages of this procedure, which is based on the spraying of the slurry droplets into liquid N_2 followed by subsequent drying of the frozen granulate under vacuum, as found for other ceramic powders, include high yields, good control of granule density, the absence of cavities in the granules, as well as a high degree of granule homogeneity, as there isn’t any migration of small particles or binder taking place. Additionally, the freeze granulation process doesn’t involve any capillary action and shrinkage of the droplet due to elimination of the evaporation step, so the achieved homogeneity and density of the granule are retained after sublimation [7]. Finally the lower granule density and the evenly distributed pressing aid give softer granules and ensure that all granules will be broken during compaction.

Taking into account all the above mentioned characteristics of the freeze granulation process, the present study focuses on the evaluation of this technique as applied on ferrite processing. To the authors’ knowledge, there aren’t any literature references on such an evaluation, regarding the quality of the compacted specimen and, consequently, the magnetic quality of the final sintered Mn-Zn ferrite.

II. MATERIALS AND METHODS

Polycrystalline Mn-Zn ferrites of the general formula $Mn_xZn_yFe^{2+}_ZFe^{3+}_2O_{4-\delta}$ (x+y=1) are prepared using the conventional ceramic technology of solid-state reaction, which is analytically described elsewhere [8]. High-purity raw materials are selected. After mixing, the powder is prefired at 800^{0}C for 4 hours in air and is subsequently milled for 8 hours, while the appropriate amount of dopants is added. The slurry is sufficiently mixed with the appropriate amount of PVA binder (Merck, MW 72000) and then separated into two fractions, the first of which is spray-dried in a Niro (Niro atomizer, Copenhagen-Denmark) spray-drier (inlet temperature at 260^{0}C-2 nozzles). The second fraction is freeze-granulated using an LS-2 (PowderPro AB, Swedish

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Ceramic Institute, IVF, Mölndan-Sweden) lab-scale freeze granulator and subsequently freeze-dried using a Lyovac GT-2 (SRK Systemtechnik GmbH) freeze-drier, as schematically described in Fig. 1.

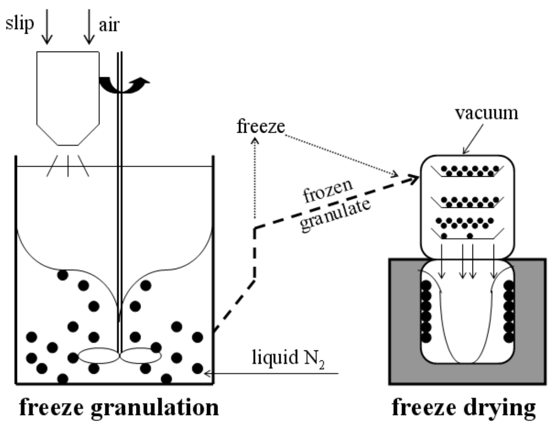

Fig. 1. Schematic description of the freeze granulation and subsequent freeze-drying technique, as applied in the case of Mn-Zn ferrite processing

The resulting dried granules are uniaxially compacted into toroids of 2.85 g/cm^3 green density and are finally sintered at 1300^{0}C for 3 hours in a specially constructed programmable kiln, under equilibrium partial pressures of oxygen [9]. The axial strength of the compacted specimens is measured using a powder testing apparatus (PTC-01, KZK Powder Technology Corp. Chantilly, VA).The densities of the sintered toroids are measured using the Archimedes' method, whereas the magnetic properties are measured using an impedance-gain analyzer (Agilent, 4284A) equipped with an oscilloscope (Tektronix, TDS 714L), a power amplifier (Crown, Microtech 600) and a frequency generator (Agilent, 33120A) on specimens wound with copper to form inductors. Additionally, cylinders of 2.85 g/cm^3 green density are prepared from each fraction and subsequently heated up to 400^{0}C and 1000^{0}C. The Pore Size Distribution of the cylinders heated at 400^{0}C is measured using an Autosorb-1(Quantachrome) BET equipment. The observation of the polycrystalline microstructure of all heated cylinders and sintered toroids is carried out using a JEOL 6300 scanning electron microscope, equipped with X-ray EDS (Oxford, ISIS 2000).

III. RESULTS AND DISCUSSION

The BET specific surface area (SSA) results, measured on the cylinders prepared from spray-dried granulate and freeze-processed granulate heated up to 400^{0}C, so that the binder was burnt out, are shown in Table I. As shown, the SSA is higher in the case of the spray-dried granulate. During the spray-drying process there is mass transfer taking place from the centre of the granule to the outer shell, when some binder and small particles migrate to the surface of the granule. Due to this procedure a density gradient is generated, leading to many small pores in the region of the outer shell (qualitatively considering as small the pores of width <100 Å). The pores become gradually larger when moving from the outer shell to the centre of the granule [10]. Taking into account that the very small pores are these mainly contributing to the SSA [11], as also indicated in Table I, it becomes predictable that the overall SSA of the spray-dried granulate in the form of compacted cylinder will be higher.

Table I. BET Specific Surface Area (m^2/g) and pore size contributions of compacted cylinders prepared from spray-dried granulate and freeze-dried granulate (small pores' width<100 Å)

	Spray-drying	Freeze-granulation
BET specific surface area (m^2/g)	3.3208	2.4108
Small pores' contribution of overall Cumulative Pore Area in sample	60.86 %	58.15 %
Small pores' contribution to BET Area (m^2/g)	**2.02**	**1.40**
Large pores' contribution to BET area (m^2/g)	1.3008	1.0108

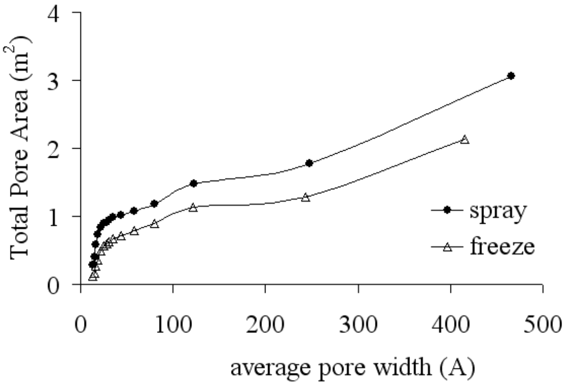

Fig. 2. Pore Size Distribution: Total Pore Area as a function of average pore width for heated cylinders prepared from freeze-granulated and spray-dried granulate

The fact that in the case of spray-drying the compacted specimen is characterized by many large pores becomes evident in Fig. 2, where the Pore Size Distribution measured on the compacted cylinders prepared from spray-dried granulate and freeze-processed granulate is given. The above results are in agreement with the SEM images presented in Fig. 3, where the morphology of the granules can be observed for each of the two granulation processes. The formation of generally large granules and the existence of inter-granular voids in the case of spray-drying, on one hand, and the formation of generally small and identically shaped granules in the case of freeze granulation, on the other hand, is evident.

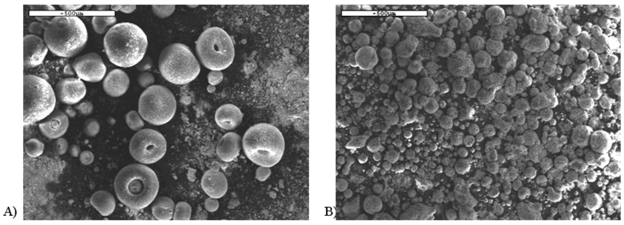

Fig. 3. SEM images of granules prepared by A) spray-drying (x70), and B) the freeze-granulation process (x70)

The results of the axial strength measurement of the green compacted cylinders are given in Table II. The much higher axial strength of the freeze-processed specimen compared to the spray-dried specimen can be attributed to the greater homogeneity of the binder and density distribution that takes place when applying the freeze granulation technique. The advantage of greater homogeneity becomes more apparent when the morphology of the compacted cylinders is observed.

Table II. Axial strength of green compacted cylinders

	Spray-drying	Freeze granulation
Axial strength (MPa)	5.3	10.4

The development of the polycrystalline microstructure, as observed on the compacted cylinders that have been heated at 400^0C and 1000^0C, is presented in Fig. 4 for both the spray-drying and the freeze granulation technique. It is shown that in the case of the spray-drying process there is a strong “memory” effect that follows the compacted specimen during the sintering process. The “shape” of the granule can be recognized in the structure of the compacted specimen. This morphological inhomogeneity is found to accompany the specimen during sintering, as the shape of the granule can be clearly identified and even the inter-granular voids can be detected. It is, therefore, most possible that the temperature increase during the sintering process until the top sintering temperature will lead to the entrapment of the voids, and, finally, to the formation of isolated intra-granular pores, which will affect the sintered density and, consequently, deteriorate the magnetic quality of the final Mn-Zn ferrite. On the contrary, the cylinder prepared from granules by freeze-granulation is characterized by a totally homogeneous polycrystalline microstructure, where any voids or cavities of potential isolated pore formation are absent. Indeed, as it is obvious in Fig. 5, where the microstructure of the sintered toroids is given, it is clear that granulate prepared by the freeze-granulation process finally leads to the development of a microstructure that is characterized by great homogeneity and high sintered density.

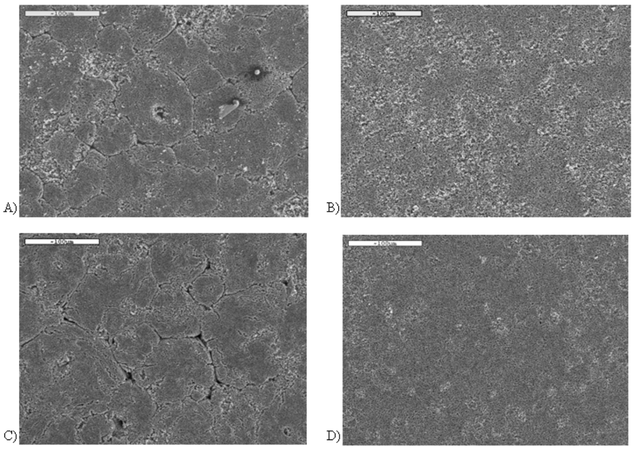

Fig. 4. SEM images of compacted cylinders, A) granulate by spray-drying heated at 400^0C (x300), B) granulate by freeze granulation heated at 400^0C (x300), C) granulate by spray-drying heated at 1000^0C (x300), and D) granulate by freeze granulation heated at 1000^0C (x300)

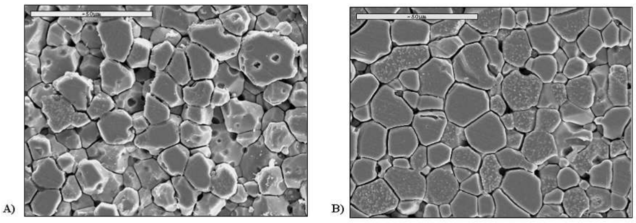

Fig. 5. SEM images of polycrystalline microstructures of sintered toroids at 1300^0C: compaction of granulate prepared by A) spray-drying, B) freeze granulation (x1000)

The magnetic performance of the toroids prepared by spray-dried and freeze-processed granulate that have been sintered at 1300^0C was evaluated. The initial permeability values at measuring conditions of 10 kHz, 0.1 mT, 25^0C as well as the power losses measured at 100 kHz, 200 mT, 100^0C are given in Table III, where the sintered density is also presented. It becomes clear that, although the press density has been the same, the sintered density of the toroid prepared from the freeze-processed granulate is higher. The difference between the two sintered densities can be attributed to the Pore size distribution that has been analytically described and explained above. Actually the remaining pores around the former granulates in the case of spray-drying, which can’t be eliminated due to the “memory effect” of the applied technique, contribute to the overall decrease of the sintered density. Consequently, the power losses of the sintered toroids prepared by the freeze granulation process are significantly lower, as indicated in Table III. The comparison between the two processes in terms of power losses at high frequencies, namely at measuring conditions of 500 kHz, 50 mT at 100^{0}C shows the significantly superior magnetic performance of the freeze-processed specimen. It is accepted that the overall power losses consist of the hysteresis losses, the eddy current losses and the residual losses. At low frequencies the major contribution to power losses comes from hysteresis, while at high frequencies the contribution of eddy current losses becomes more significant [12]. Taking into account the above facts, the evaluation of the power losses shown in Table III leads to the conclusion that the freeze-drying process gives the required morphological characteristics to the materials so that the eddy current losses are decreased, which actually reflect the condition of the grain boundaries [13]. As a result, the overall power losses at high frequencies are much more decreased in the case of freeze granulation.

Table III. Magnetic properties and densities of sintered toroids at 1300^{0}C

	Spray-drying	Freeze granulation
μ_i at 10 kHz, 0.1 mT, 25^{0}C	2020	2140
Pv at 100 kHz, 200 mT, 100^{0}C (mW/cm^3)	300	287
Pv at 500 kHz, 50 mT, 100^{0}C (mW/cm^3)	250	188
Sintered density (g/cm^3)	4.83	4.85

Based on the observation of the morphological characteristics of the samples prepared by the two granulation methods in all stages, it becomes obvious that the freeze granulation process leads to a higher quality of granulate to be compacted, in terms of great homogeneity of the binder distribution. Due to the fact that water evaporation, on which the spray-drying method is based, is substituted by sublimation in the case of freeze granulation, the migration of small particles and binder towards the outer shell of the granulate that takes place during spray-drying is now eliminated. This gain has been checked in terms of axial strength, detected by the morphological observation described above and quantitatively determined by the evaluation of the magnetic performance of the sintered toroids. The superior magnetic quality of the specimens prepared by the freeze-granulation process makes the specific method a promising technique to be applied in ferrite processing, as the gain in power losses (in low and high frequencies) in comparison to conventional spray-drying is significant. For the consideration of up-scaling of the method for industrial purposes, the issue of low bulk density must be taken into account. A possible consequence is the re-design of the pressing dies.

IV. CONCLUSIONS

The freeze granulation technique has been applied in Mn-Zn ferrite processing and has been evaluated in terms of morphological homogeneity of the resulting granulate, and magnetic quality of the final sintered material, in comparison to the conventional spray-drying method. It is shown that freeze granulation leads to the formation of granules of better morphological homogeneity and superior sintering performance. This is attributed to the higher quality of the compacted specimen.

REFERENCES

[1] V.T. Zaspalis, V. Tsakaloudi and M. Kolenbrander, "The effect of dopants on the incremental permeability of MnZn-ferrites", *Journal of Magnetism and Magnetic Materials,* vol. 313, pp. 29-36, 2007.

[2] A. Goldman, *Handbook of Ferromagnetic Materials*, Kluwer Publ., London, 1999, pp. 59-70.

[3] M. Uppalapati and D.J. Green, "Effect of External Lubricant on Mechanical Properties of Dry-Pressed Green Bodies", *Journal of the American Ceramic Society,* vol. 88, issue 6, pp. 1397-1402, 2005.

[4] K. Rundgren, O. Lyckfeldt and M. Sjöstedt, "Freeze granulation for the processing of silicon nitride ceramics", *Key Engineering Materials,* vol. 264-268, issue I, pp. 281-284, 2004.

[5] K. Rundgren, O. Lyckfeldt and M. Sjöstedt, "Improving Powders with Freeze Granulation", *Ceramic Industry*, pp 40-44, Apr. 2003.

[6] A. Stapley and C. Rielly, "Advances in unconventional freeze drying technology", *Chemical Engineer,* vol. 790, pp. 33-35, Apr. 2007.

[7] B. Nyberg, E. Carlström and R. Carlsson, "Granulation of Ceramic Powders for Pressing by Spray-Freezing and Freeze-Drying", *EuroCeramics II*, vol. 1, Deutsche Keramische Gesellschaft, pp. 447-451, 1993.

[8] V. Tsakaloudi and V.T. Zaspalis, "A New Mn-Zn ferrite for High-Speed Data Transmission Applications in Telecommunication Networks", *Journal of Magnetism and Magnetic Materials,* vol. 310, pp. 2540-2542, 2007.

[9] R. Morineau and M. Paulus, "Chart of PO_2 versus Temperature and Oxidation Degree for Mn-Zn Ferrites", *IEEE Ttransactions on Magnetism,* vol. 5, pp.1312-1316, 1975.

[10] Y. Iwamoto, H. Nomura, I. Sugiura, J. Tsubaki *et al.,* "Microstructure Evolution and Mechanical Strength of Silicon Nitride Ceramics", *Journal of Materials Research*, vol. 9, issue 5, pp. 1208-1213, 1994.

[11] Y. Liu and L.X. Meng, "The Mathematical Description and Analysis on the Characteristics of Pore Structure of Porous Calcium Oxide", *Proceedings of the Chinese Society of Electrical Engineering,* vol. 22, issue 7, pp. 145-149, July 2002.

[12] D. Stoppels, "Developments in soft magnetic power ferrites", *Journal of Magnetism and MagneticMaterials,* vol. 160, pp. 323-328, 1996.

[13] V.T.Zaspalis, E. Antoniadis, E. PApazoglou, V. Tsakaloudi *et al.,* "The effect of Nb_2O_5 dopant on the structural and magnetic properties of MnZn ferrites", *Journal of Magnetism and Magnetic Materials,* vol. 250, pp. 98-109, 2002.

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FREEZE Granulation:A novel technique for low-loss MnZn ferrites.

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It is widely accepted that the magnetic quality of MnZn ferrites in terms of high initial permeability and low power losses lies on an optimized combination of chemical and morphological homogeneity of the sintered ferrite[1]. This study focuses on the evaluation of freeze granulation and subsequent freeze-drying,a novel technique applied on ferrite processing, on the quality of the compacted specimen and, consequently,on the magnetic quality of the final sintered MnZn ferrite.

The conventional spray-drying method, used in production-scale processing of MnZn ferrites,shows significant drawbacks,such as inflation defects visible as large voids in the interior of the granule.Moreover,the rapid water evaporation gives rise to the development of capillary stresses that may iniate undesirable diffusion phenomena that reduce the compositional and morphological homogeneity of the granule. Those imperfections may resist compaction and also be present in the compacted specimens[2].Freeze granulation on the other hand,is based on the spraying of the slurry droplets into liquid N_2 followed by subsequent freeze-drying.It is advantageous in terms of homogeneous granule density,absence of cavities in the granules,since due to elimination of the evaporation step it doesn't involve any capillary action and shrinkage of the droplet.The achieved homogeneity and density of the granule are retained after sublimation[3].

In this study, MnZn ferrite powders have been prepared by the conventional ceramic route as reported elsewhere[4].After mixing,prefiring and milling,binder is added to the slurry of the milled powder that is separated in two fractions.The first fraction is spray-dried,while the other is freeze-granulated and subsequently freeze-dried.The quality of granulates is compared through compaction testing,electron microscopy observation of granulates and compacted cylinders after BBO,pore surface area determination and power loss measurement of sintered toroids under equilibrium partial pressures of oxygen[5].

The observation of the microstructure of pre-sintered pressed cylinders so that the binder is burnt out,has shown that in the case of spray drying there is a strong "memory effect" that follows the compacted specimen during the sintering process.The granule structure can be recognized in the structure of the compacted specimen.This morphological inhomogeneity is now found to accompany the specimen during the sintering process,as the granule area can be clearly seen and even the intragranular void can be detected.It is,therefore,most possible that the temperature increase during sintering will lead to the entrapment of the voids and,finally,to the formation of isolated intragranular pores which will affect the sintered density and,consequently deteriorate the magnetic quality of the final MnZn ferrite.On the contrary,the cylinder prepared form granules after freeze-granulation is characterized by a totally homogeneous microstructure,where any voids or cavities of potential isolated pore formation are absent.

The Pore Size Distribution presented in Figure 1 of pre-sintereds pecimens compacted from the spray-dried and freeze-granulation processes confirms the above characteristics.In the case of the spray-drying process the total pore surface area remaining is much larger than in the case of freeze-granulation.The increased pore surface area will most probably lead to a decreased sintered density and lower magnetic quality of the final MnZn ferrite.The magnetic characterization of the sintered toroids at 100 kHz-200 mT indicated that freeze granulation leads to sintered toroids with lower power losses at lower densities,in comparison to the spray-dried granules,as presented in Figure 2.

The above results indicate that the novel technique of freeze granulation offers advantages in the MnZn ferrite manufacturing since it leads to better green compact microstructures and finally to better magnetic quality products.A draw-back of the process is the low bulk density of the granulated matter.This will have as unavoidable consequence a re-design of the pressing tools.

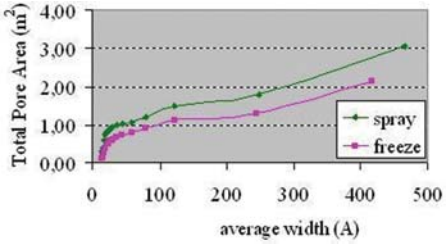
[1] A.Goldman, Handbook of Ferromagnetic Materials, Kluwer Publ., London 1999

[2] V.Zaspalis, V.Tsakaloudi, J. Am. Ceram.Soc. 87, 5 (2004) 824-829

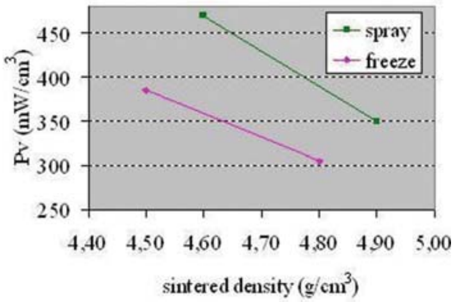
[3]. B.Nyberg et al, Euro-Ceramics II, Vol.1, Deutsche Keramische Gesellschaft, 1993

[4]. V.Tsakaloudi, V.Zaspalis, J. Magn .Magn. Mater. 2, 3 (2007) 2540-2542

[5]. R.Morineau, M.Paulus, IEEE Trans. Magn. 5 (1975) 1312-1316



Pore size distribution in pre-sintered cylinders prepared from spray-dried and freeze-processed powders.



Power loss comparison at 100 kHz-200 mT-100<0>C between spray-dried and freeze-processed sintered toroids.

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