Preparation of Fine-grained High-μ Ferrites by Spray-roasting Nitrate Solutions

Wolfgang F. Kladnig

Maschinenfabrik Andritz-Ruthner Division, Research Center, Eibesbrunnergasse 18B, A-1120 Vienna, Austria

&

Manfred F. Zenger

Siemens Matsushita Components GmbH & Co. KG, Ceramic Components Division,
Product Developments Ferrite Materials, Balanstraße 73, D-8000 Munich, FRG

Abstract

A series of fine-grained single-phase ferrites was prepared from the system $Mn_xZn_yFe_{(2+z)}O_{(4+j)}$, where the suffixes x, y and z indicate molar contents of Mn, Zn and Fe respectively (x + y + z = 1) and j the amount of overstoichiometric oxygen in the spinel lattice. The material was formed by a thermal decomposition of aqueous nitrate solutions, in a process which is commonly called the spray-roasting process. Two compositions were selected for evaluating the soft ferrite powders made by this method in comparison to standard material. Oxide powder A is characterized by x = 0·51, y = 0·42 and z = 0·07, a range in which high permeability materials will usually be formed. Oxide powder B, on the other hand, is characterized by x = 0·68, y = 0·22 and z = 0·10. This is a composition which yields a material of high saturation magnetization in combination with low power losses and which is typically used in power devices. The characteristics of magnetic materials derived from these powders, such as initial permeability, μ_i, as well as μ' and μ'' versus frequency of material A and the power losses P_v of material B, were compared to those usually found in materials made by conventional mixing–blending technologies of single oxide powders.

Es wurde eine Reihe feinkörniger einphasiger Ferrite aus dem System $Mn_xZn_yFe_{(2+z)}O_{(4+j)}$ hergestellt, wobei die Indizes x, y und z die molaren Gehalte jeweils an Mn, Zn und Fe darstellen (x + y + z = 1) und j den

Anteil überstöchiometrischen Sauerstoffes im Spinell-gitter beschreibt. Das Material wurde durch einen thermischen Zersetzungsprozess wässriger Nitrat-lösungen gebildet, mit Hilfe eines Verfahrens, welches üblicherweise als Sprüh-Röst-Prozess bezeichnet wird. Zur Beurteilung der weichen Ferrit-Pulver, die mit Hilfe dieser Methode hergestellt wurden im Vergleich zum Standard-Werkstoff, sind zwei Zusammensetzungen ausgewählt worden: Oxid-Pulver A ist durch x = 0·51, y = 0·42 und z = 0·07 gekennzeichnet; ein Zusammensetzungsbereich also, in dem üblicherweise Werkstoffe mit hoher Perme-abilität ausgebildet werden. Oxid-Pulver B dagegen ist durch x = 0·68, y = 0·22 und z = 0·10 gekennzeichnet. Dieses ist die Zusammensetzung, die zu einem Werkstoff mit hoher Sättigungsmagnetisierung bei gleichzeitig geringen Leistungsverlusten führt und der typischerweise in power-devices Anwendung findet. Die Merkmale magnetischer Werkstoffe, die aus diesen Pulvern abgeleitet werden können, wie die Anfangspermeabilität μ_i, aber auch wie μ' und μ'' in Abhängigkeit der Frequenz für Material A und in Abhängigkeit der Leistungsverluste P_v für Material B wurden mit den Merkmalen verglichen, die bei Werkstoffen, welche mit konventionellen Misch–Blend Technologien einfacheroxidischer Pulver hergestellt werden, auftreten.

Une série de ferrites monophasées à grain fin ont été préparées à partir du système $Mn_xZn_yFe_{(2+z)}O_{(4+j)}$, où les suffixes x, y et z indiquent les teneurs molaires de Mn, Zn et Fe respectivement (x + y + z = 1) et j la

quantité d'oxygène sur-stoechiométrique dans le réseau spinel. On a formé le matériau par décomposition thermique de solutions aqueuses de nitrate, selon un procédé couramment appelé pulvérisation–calcination. On a sélectionné deux compositions pour évaluer les poudres de ferrite 'molles' produites par cette méthode, par rapport à un matériau standard. La poudre oxyde A est caractérisée par x = 0·51, y = 0·42 *et* z = 0·07, *un domaine dans lequel on forme habituellement des matériaux à haute perméabilité. La poudre d'oxyde B est caractérisée par* x = 0·68, y = 0·22 *et* z = 0·10. *Cette composition conduit à un matériau à aimantation à saturation élevée et à pertes joules faibles, qui est utilisé dans les appareils électriques. Les caractéristiques des matériaux magnétiques dérivés de ces poudres, telles que la perméabilité électrique,* μ_i, *ainsi que* μ' *et* μ'' *en fonction de la fréquence du matériau A et des pertes* P_v *du matériau B, ont été comparées à celles trouvées habituellement dans les matériaux préparés par les technologies conventielles de mélange de poudres à un seul oxyde.*

1 Introduction

Manganese–zinc ferrites, e.g. within the concentration range of 20–25 mol% MnO, 22–28 mol% ZnO and 52–53 mol% Fe_2O_3, as given in material A, are suitable for making high-permeability magnetic materials, which are used in broad-band transformer devices at low induction levels within frequency ranges of up to 100 kHz.[1] Such ceramic material is usually made by conventional mixing, milling and sintering technologies starting from oxide or carbonate material.

The Ruthner spray-roasting technology, a method of thermal decomposition of aqueous salt solutions, to make oxide powder, has found wide industrial acceptance, especially for iron oxide production. Its usual starting material is ferrous chloride in HCl solution, as provided by spent pickle liquors.[2] Its special advantage lies in the possibility of the simultaneous decomposition of mixed salt solutions, the so-called co-spray-roasting method. The special effect of a co-spray-roasted powder is offered by a very homogeneous element distribution and a fine-grained structure of the resulting oxide powder.

The chloride system unfortunately does not allow the decomposition of certain elements, because of their high thermodynamic stability or because of their volatility even at low temperatures, which is the case with $ZnCl_2$, for example.

For this reason, today's ferrite producers who apply the co-spray-roasting method on an industrial scale[3-5] are using a mixture of $MnCl_2$ and $FeCl_2$ only to produce a very homogeneous mixture of $Mn_2O_3 . Fe_2O_3$ powder. ZnO powder, which has to be added to give the proper ferrite composition, is added afterwards by applying conventional mixing–blending techniques. Manganese–zinc ferrites which are made by this method of spray-roasting are reported to have very low power losses.[3]

A most important factor is the high grade of homogeneity achieved at least with the ferrite grain microstructure, concerning especially grain size distribution and boundary properties.[3] These special effects of a co-spray-roasted powder seem to be related to the starting condition of a very homogeneous component distribution within the molecular size range.[5] Also a high purity of the starting solution has to be provided, since a series of substances are known to affect soft ferritic properties.[1,3,4]

The present paper deals with an alternative method, investigated on a pilot-plant scale, to make in-situ ternary ferrite systems by spray-roasting aqueous nitrate solutions of the corresponding salts, such as zinc, manganese and ferrous nitrate. The spray-roasted ternary ferrite powder then received by this method was investigated in terms of its final magnetic properties and related to conventional systems.

Spray-roasting solutions to make powders have found rather limited access in the literature, but a series of methods is described such as EDS (evaporative decomposition of solution),[6] an investigation program at Pennsylvania State University, USA. Further approaches to this method has been published by Malinovsky and coworkers[7,8] and entitled 'flame-spray pyrolysis'. In some early papers the production of ferrite powders has been described, even by thermal decomposition of nitrate salts, dissolved in alcohol.[9] All these investigations, however, were on a laboratory scale and the final material was reported to yield small particle sizes of 0·02 μm and thus to have single domain structures, which led to enhanced magnetic properties, in terms of μ', μ'', B_{max}, B_{rem} and H_c.

On the other hand, methods for the thermal decomposition of nitrate salts by solid-state reaction have been published on some occasions to make rare earth oxides,[10] garnet structures,[11] ZrO_2[12] or spinels.[13] In all the cases mentioned, the temperature range of decomposition was within 300–500°C. Kinetics of nitrate salt decomposition has been reported in Ref. 10 and Arrhenius activation
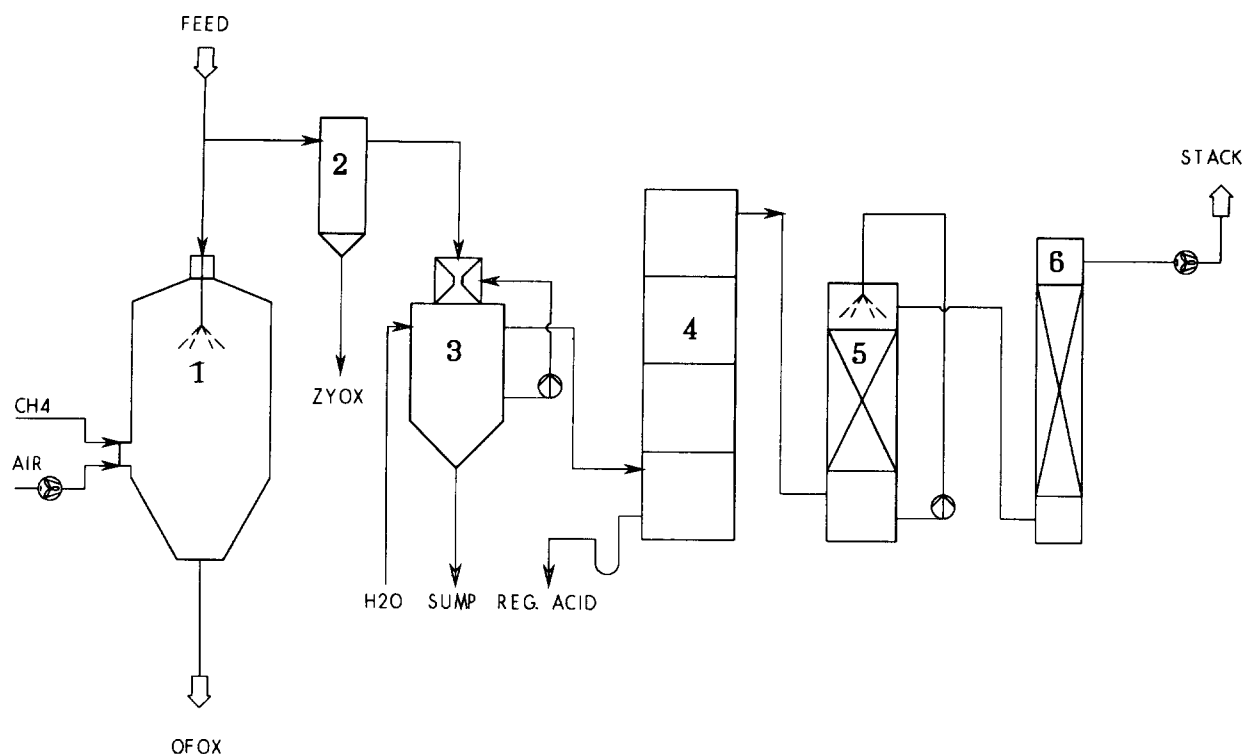
Fig. 1. Process scheme for the decomposition of nitrate salt solution in a thermal spray-roaster. 1, Reactor; 2, cyclone; 3, venturi; 4, absorber; 5, scrubber; 6, denox.

energies were found to be as low as 12 kcal mol^{-1}, being similar for the decomposition of nitrate salt solutions or the solid-state decomposition of crystalline nitrate salts containing physically bound water molecules. Reaction orders were found to be of the form $n = 1/2$ or $1/3$, indicating that the nitrate decomposition follows complex reaction pathways, by first evaporating water, followed by formation of

basic nitrates, which finally decompose in a first-order reaction into oxides.[10]

2 Experimental

A pilot spray-roaster apparatus of a throughput capacity of 30 litres/h was used in these experiments
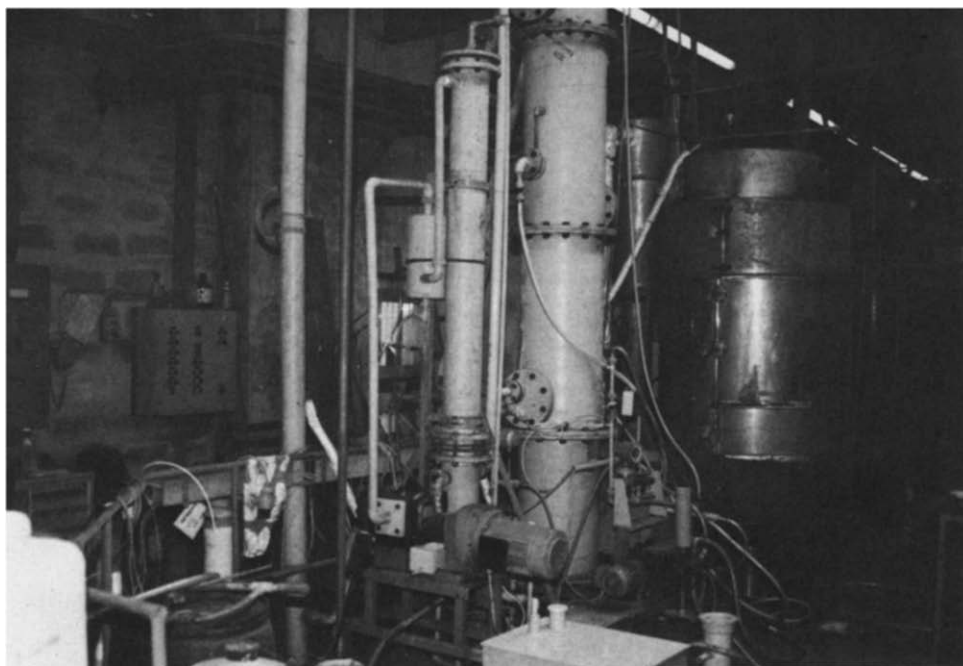

Fig. 2. Experimental process unit to produce ferritic oxide powder.

Table 1. Spray-roasting conditions for nitrate salt solutions investigated

Powder to be produced	Nitrate salt solutions (g litre^{-1})	Spray-roasting conditions	
		Pressure on spray booms (bar)	Temperature (°C)
Fe_2O_3	$Fe(NO_3)2\cdot9$ $H_2O532\cdot0$ (Fe: 86·8)	3	300–600
$(ZnO \cdot MnO \cdot Fe_2O_3)$ Sample A	Solution A		
	$Fe(NO_3)_3$ (Fe: 63·27)	3	400–500
	$Mn(NO_3)_2$ (Mn: 15·92)		
	$Zn(NO_3)_2$ (Zn: 15·34)		
$(ZnO \cdot MnO \cdot Fe_2O_3)$ Sample B	Solution B		
	$Fe(NO_3)_3$ (Fe: 49·43)	3	500–600
	$Mn(NO_3)_2$ (Mn: 15·90)		
	$Zn(NO_3)_2$ (Zn: 6·37)		

(Figs 1 and 2). Table 1 lists salt concentrations and spray-roasting conditions for these experiments.

Analysis of the oxide powders was done by inductively coupled plasma analysis (ICP) and X-ray diffraction analysis (RFA). Physical powder properties were measured including BET (single-point method, N_2/He (30%) on a Micromeritics instrument). Scanning electron microscope (SEM) analysis was performed on a Jeol JSM 6400. Particle size distribution was measured by laser granulometric statistics (CILAS method). Ceramographic analysis for grain size distribution within the ceramic material was done after proper polishing and etching procedures.

To study magnetic properties, RM6 cores (A) and ring cores (B) were made by applying conventional ceramic techniques, such as prefiring, milling, compressing the oxide powder and final sintering in appropriate N_2/O_2 atmosphere.

3 Results and Discussion

3.1 Decomposition of ferric nitrate solutions

Before starting with mixed nitrate solutions, some basic investigations were carried out to study the decomposition of Fe(III) nitrate within the spray-roaster system used, at 400°C, since the literature offers hardly anything on Fe nitrate decomposition.

Table 2 lists the physical powder parameters of the spray-roasted iron oxide powders derived from the nitrate system. The aspect of these powders was very different to those normally found by spray-roasting of the chloride system, i.e. the thermal decomposition of $FeCl_2$ solutions. The powders have a rugged surface aspect, as found in the SEM analysis, which were revealed by X-ray diffraction analysis to be composed of amorphous phases.

These amorphous structures which were formed especially during low-temperature (300°C) decomposition, transformed with rising temperature of spray-roasting to become more crystalline, with very small microcrystals being formed, as shown by SEM (Fig. 3(a) and (b)).
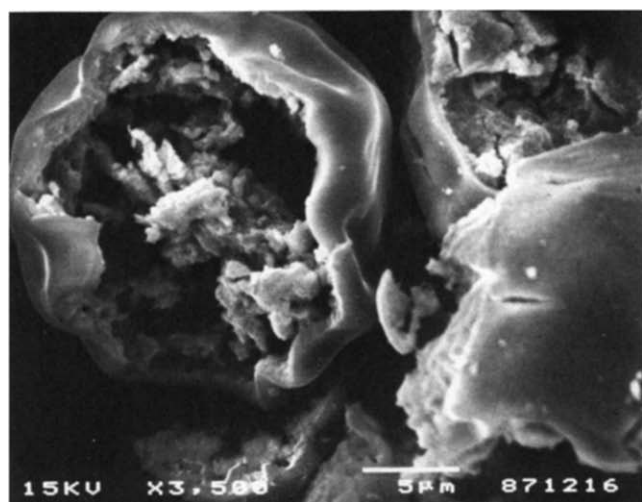
3.2 Decomposition of mixed Zn–Mn–Fe nitrate solutions

The thermal decomposition conditions for the mixed nitrate solutions in the pilot spray-roaster, as previously described, to form mixed oxide compositions of $ZnO \cdot MnO \cdot Fe_2O_3$, are given in Table 3.
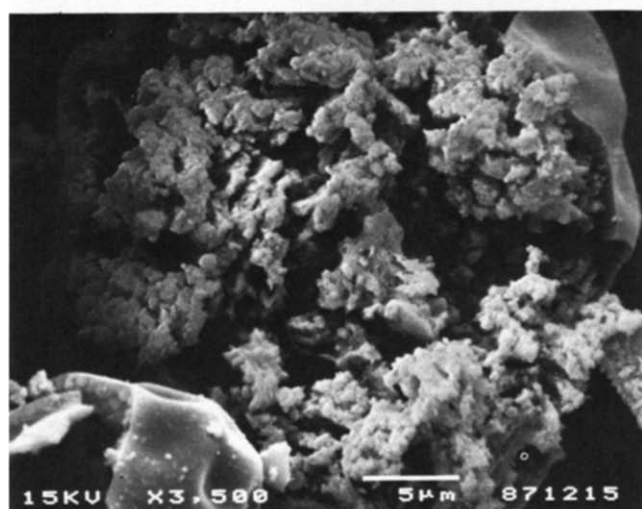
Figure 4 shows the SEM picture of some of the powders formed after milling in acetone, using steel balls as grinding media. The BET surface area of this powder was $68\, m^2\, g^{-1}$, obviously due to a high internal surface. The bulk density found was $0\cdot9\, g\, cm^{-1}$. Mean particle sizes (d_{50}) were within $10 \pm 1\, \mu m$. Before pressing into rings the material

Table 2. Physical parameters of spray-roasted Fe_2O_3 powders

Temperature of decomposition (°C)	BET ($m^2 g^{-1}$)	Bulk density ($g cm^{-3}$)	H_2O (%)	d_{50} (μm)	RDA analysis
300	55·0	0·98	3·0	25	amorphous
350	50·0	0·90	2·0	27	amorphous, crystalline α-, γ-Fe_2O_3
400	34·5	0·8	1·5	40	α-Fe_2O_3, Fe_3O_4
600	6·5	0·7	0·7	40	α-Fe_2O_3, Fe_3O_4

(a)

(b)

Fig. 3. (a) and (b) SEM pictures at $3500\times$ enlargement of Fe_2O_3 made by decomposition of $Fe(NO_3)_3$ at $T = 400°$ C.

Table 3. Zn Mn–Ferrites formed after spray-roasting of mixed nitrate solutions of two different ferrite compositions

	Composition after spray-roasting		
	Fe_2O_3 (mol%)	ZnO (mol%)	MnO (mol%)
Solution A	52·0	26·5	20·5
B	53·1	35·2	11·7

Range of impurities
(found by ICP and RFA analysis), ppm (by wt)

Al:	100–200	Cr:	100–700
Ni:	100–400	Ca:	200–300
Ti:	100–500	Na:	100–200
Mg:	200–300	SiO_2:	100–150

Green densities (100 MPa compression),
  $g cm^{-3}$ 3·05 (A)
             2·90 (B)
Sintered densities (1 350 C firing),
  $g cm^{-3}$ 4·88 (A)
             4·70 (B)
Core form RM6 cores (A) ring cores (B)
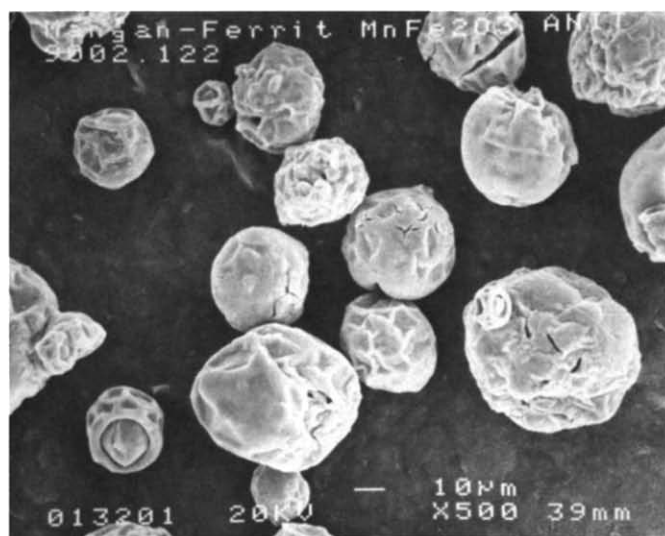
(a)
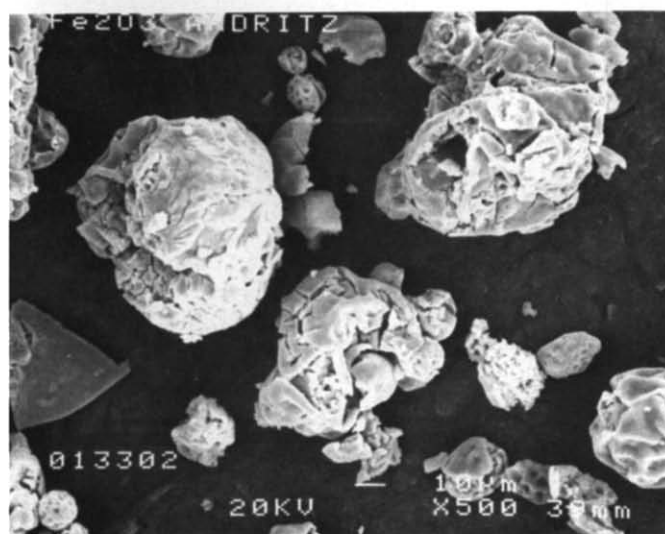
(b)
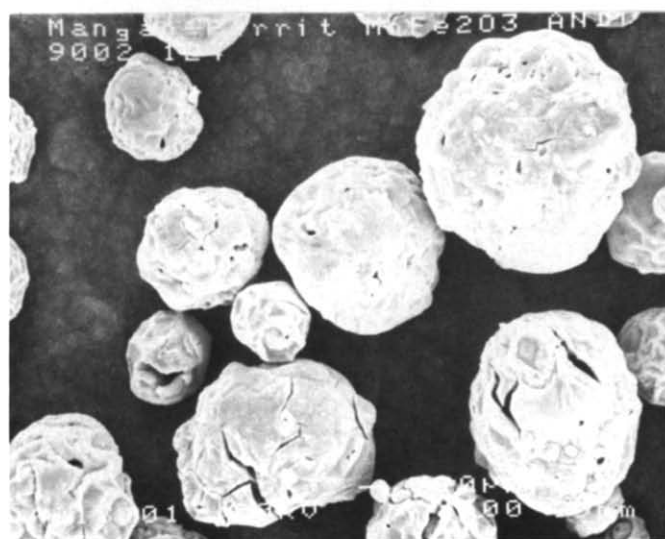
(c)

Fig. 4. (a), (b) and (c) Fe_2O_3 powder particles made by thermal decomposition of nitrate solution, after proper milling in acetone.
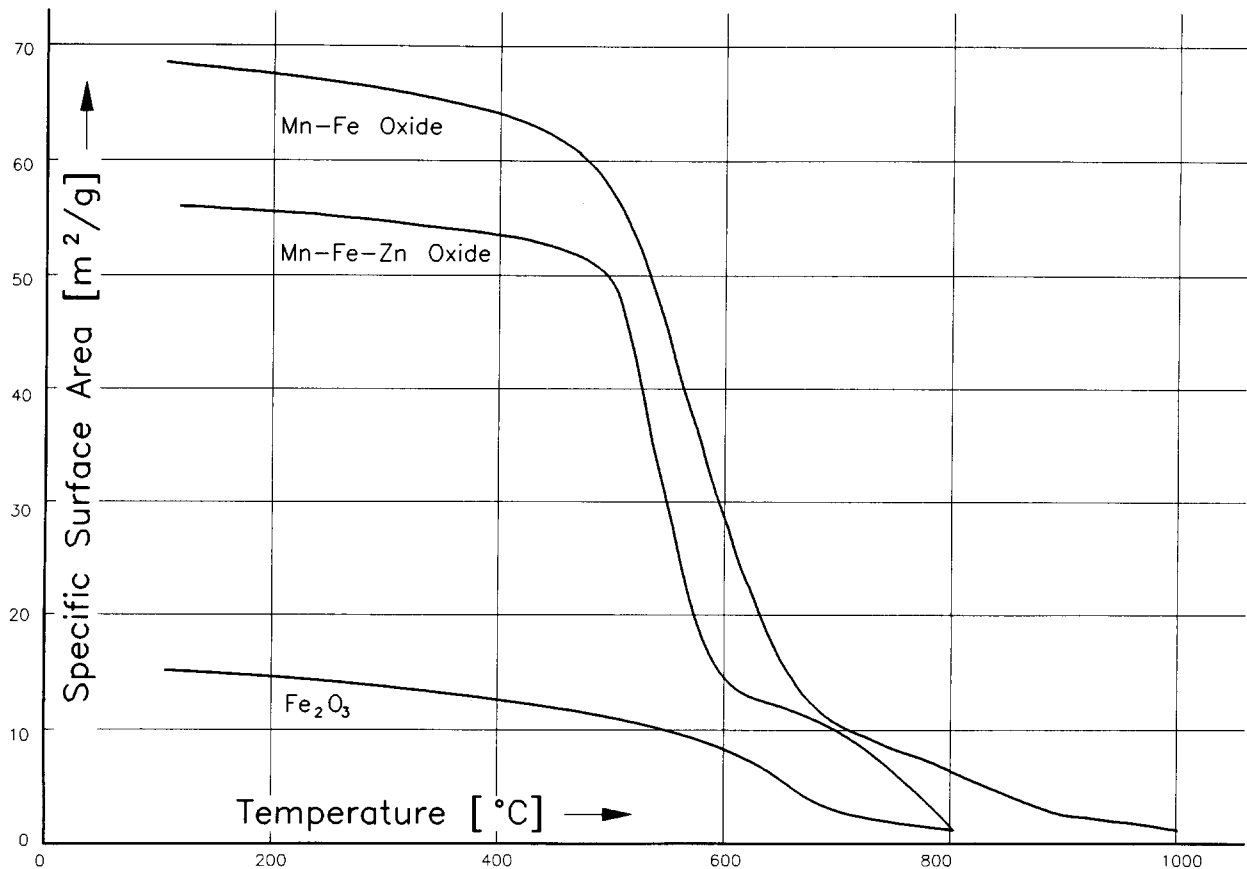
Fig. 5. Correlation of specific surface area (BET) of spray roasted Fe_2O_3, $MnO \cdot Fe_2O_3$ and $ZnO \cdot MnO \cdot Fe_2O_3$ powders, derived from spray-roasting nitrate solutions, with the temperature of post-treatment.
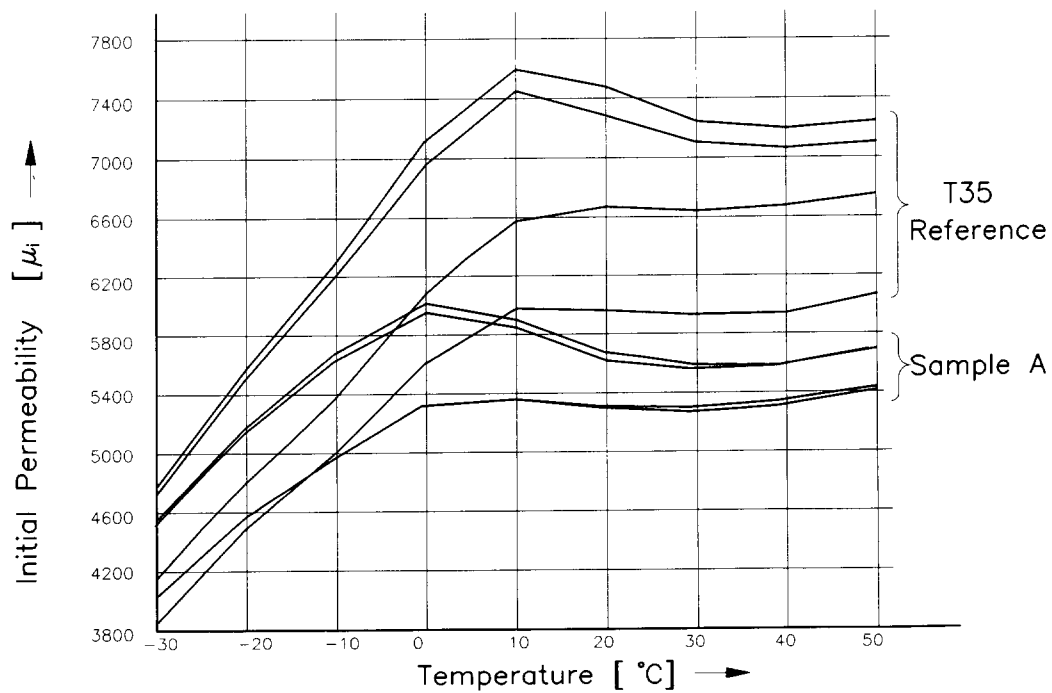

Fig. 6. Initial permeabilities of RM6 rings made from the ferrite powder A, in comparison to the T35 reference material.
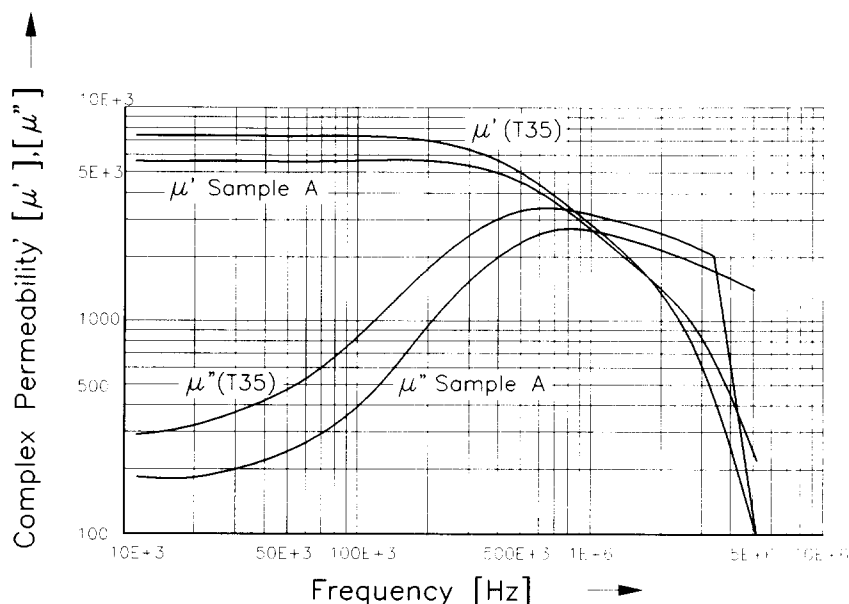
Fig. 7. Complex, relative permeabilities μ' and μ'' derived from RM6 rings of powder A and compared with reference material T35.

was presintered for 1 h at 800°C and milled again for 2 h in acetone with steel balls to obtain a proper surface area of finally $2-3 \, m^2 \, g^{-1}$.

Figure 5 shows the surface area degradation of Fe_2O_3 and $Zn \cdot Mn \cdot Fe_2O_4$ with rising calcination temperature up to 800°C starting with around $60 \, m^2 \, g^{-1}$, which is reduced to some $1-2 \, m^2 \, g^{-1}$. As pressing aid 2% PVA solution was used. The pressing strength applied was 100 MPa.

The final ferrites had, after proper corrections, the formulas:

$$Mn_{0.51}Zn_{0.42}Fe_{2.07}O_{4-j}$$

and

$$Mn_{0.68}Zn_{0.22}Fe_{2.10}O_{4+j}$$
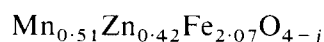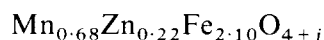
With these materials initial permeability values were found to be 6000 (sample A) and up to 3000 (sample B) respectively.

4 Discussion

4.1 Powder A

The magnetic properties measured on RM6 cores as previously described, indicate that the method of co-roasting of ternary ferrite systems, starting from their respective nitrate salts in aqueous solutions, can be well applied to the production of ferrite materials of high initial permeability (μ_i of about 5000, as a minimum). Figures 6 and 7 describe the initial permeability found versus temperature and μ', μ'' versus frequency of the RM6 cores, respectively both compared with the standard material T35 (Siemens-Matsushita, Munich, W. Germany).

Investigations of the grain structure both of the skin and of the ground and etched internal surface show good homogeneity without pores being present inside or outside the grains, which have a disastrous effect on achieving high permeability values (see Figs 8 and 9).

The values of initial permeabilities (Fig. 6) should be higher if purer nitrate solutions than those investigated here (Table 3) were used. Special
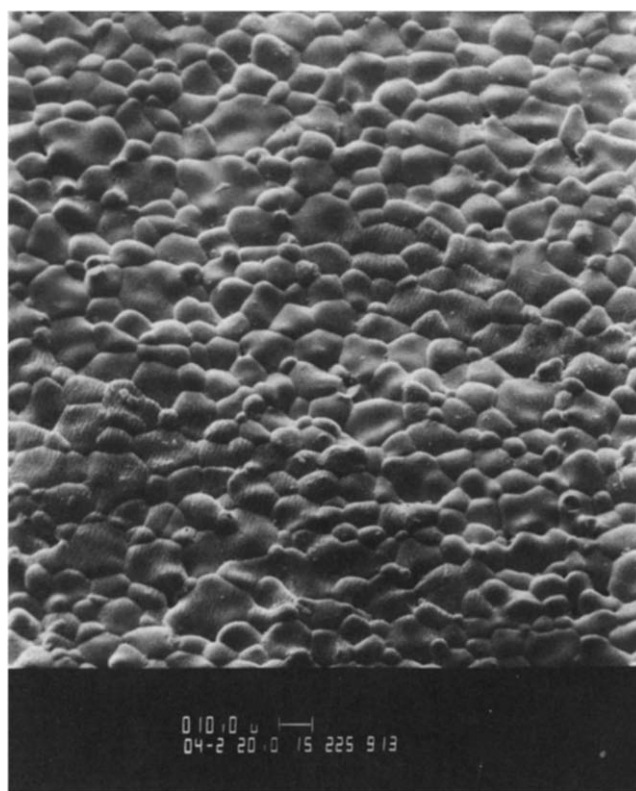

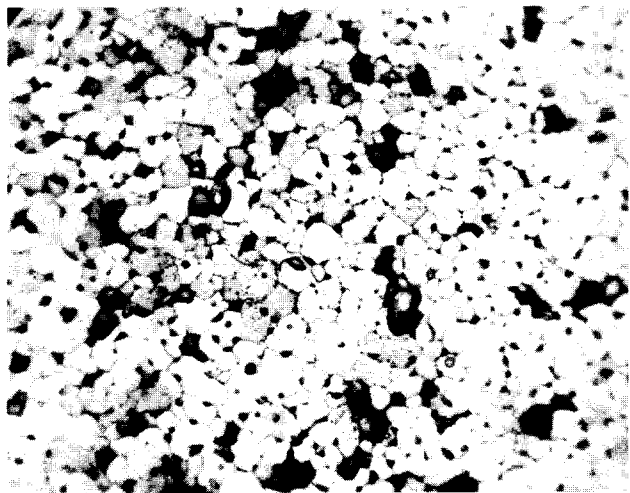**Fig. 8.** SEM picture of the ferrite surface made from powder A.

Fig. 9. Ceramographic picture of ground and etched surface of a ferrite made from material A.

Fig. 10. Powder losses of ring cores made from material B, at 25 and 100 kHz, compared to those of reference material N41.

negative effect makes the influence of Ca impurities which unfortunately are usually found to some extent in commercial nitrate salts and could only be avoided by dissolving the pure metals or pure oxides in nitric acid. Thus the maximum permeability values of such spray-roasted powders, provided less than 100 ppm impurities like Ca, Mg, Cr, Ni, could be expected to range around 10·000.

4.2 Powder B

The physical parameters of the power losses of material B do not need further discussion because of their similarity to those of the high-permeability material A.

Prefiring the spray-roasted powder up to 700°C was again necessary in order to get the very high surface area of the powders first down to approximately $1\,m^2\,g^{-1}$ and then by milling again up to $2\text{–}3\,m^2\,g^{-1}$, using steel balls as grinding media, in order to enable the desired level of green density and avoiding too high rates of shrinkage. The rather smooth surfaces of the powder spheres (Fig. 4) did obviously not result in higher green densities, because of their rather hard surfaces.

4.3 Magnetic properties

Due to the relatively high iron content the minimum of the total power losses is located at a temperature of approximately 50°C. The high initial permeability of 2500 is also a consequence of the high iron content. Thus material B is comparable to the well-known Siferrit material N 41 (Siemens-Matsushita). In Fig. 10 the power losses versus temperature are given for two different frequencies of 25 kHz and 100 kHz of material B, both measured at an induction level of 200 mT (200 gauss).
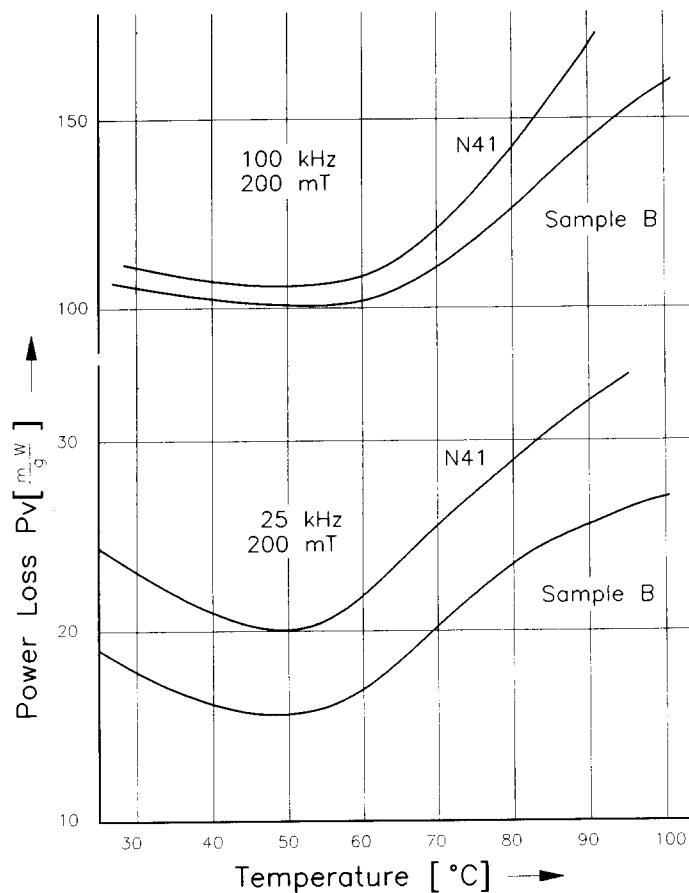
5 Conclusions

This research work was aimed at investigating the possibility to make ternary ferrite systems by a in-situ co-spray-roasting process. The present paper proved that the co-roasting method can be applied to make ferrites of the type $Zn\text{–}Mn\text{–}Fe_2O_4$, by starting from nitrate solutions of homogeneously mixed salts. The materials having formulations corresponding to a high-permeability material (sample A) and to a low-loss one (sample B) had magnetic properties similar to those of materials prepared by conventional techniques. With material B of a formulation of a typical power loss material even improved values of losses, compared to the standard N41 material (Siemens-Matsushita) were obtained.

The method thus applies for industrial production of ferrite material, provided that there is proper absorption of the NO_x gases, which are formed from the nitrate salts being decomposed and which happen to escape from the absorption and scrubbing procedures, by proper selective catalytic reduction (SCR). Further work will be necessary to investigate in detail the magnetic parameters of starting

materials of higher purities than those applied in the present investigation.

References

1. Roess, E., Soft magnetic ferrites and application in telecommunication and power conversion. *IEEE Trans. Magnetics*, **MAG 18**(6) (1982) 1529–34.
2. Kladnig, W. & Karner, W., Pyrohydrolysis for the production of ceramic raw materials. *Ceram. Bull.*, **69**(5) (1990) 814–17.
3. Ochiai, T. & Okutani, K., Ferrites for high-frequency power supplies. In *Proc. IVth Int. Conference on Ferrites*, San Francisco, California, 1984, *Advances in Ceramics*, Vol. 16/II, ed. W. P. Holbrook. American Ceramic Society, Westerville, Ohio.
4. Okutani, K. & Mori, T., Recent topics in soft ferrites. Tutorial Session I. Ferrite processing and manufacturing. In *Vth. Int. Conference Ferrites*, Bombay, 1989. Elsevier Science Publishers, Amsterdam.
5. Ruthner, M. J., Richter, H. G. & Steiner, I. L., Spray-roasted iron oxide for the production of ferrites. In *Proceedings of the 1st International Conference on Ferrites (ICFI)*, Kyoto, Japan, 1970, pp. 75–8.
6. O'Holleran, T. P., Evaporative decomposition process for the production of reactive fine ceramic powders. PhD Thesis, Penn State University, University Park, PA, 1980.
7. Malinovsky, W. W. & Babbitt, R. W., Fine-grained ferrites. I. Nickel ferrite. *J. Appl. Phys., Suppl. Vol.*, **32**(3) (1961) 273 S–238 S.
8. Malinovsky, W. W., Babbitt, R. W. & Sands, G. C., Fine-grained ferrites. II. $NiZnFe_2O_4$. *J. Appl. Phys., Suppl. Vol.*, **33**(3) (1962) 1206–7.
9. Wenckus, J. F. & Leavitt, W. Z., Preparation of ferrites by the atomizing burner technique. In *Proc. AIEE Conf. on Magnetism and Magnetic Materials*, 1952, Special Publ. T 91 526 ff, 1957.
10. Wendlandt, W. W., The thermolysis of the rare earth and other metal nitrates. *Analytica Chimica Acta*, **15** (1956) 435–9.
11. Messier, D. E. & Gazza, G. E., Synthesis of $MgAl_2O_4$ and $Y_3Al_5O_{12}$ by thermal decomposition of hydrated nitrate mixtures. *Am. Ceram. Soc. Bull.*, **51**(9) (1972) 692–7.
12. Arean, C. O., Fernandez Colinas, J. M., Arjona, A. M. & Villa Garcia, M. A., Effect of high temperature treatment in air on the surface area and porous texture of zirconium dioxide prepared by thermal decomposition of the nitrate. *J. Chem. Tech. Biotech.*, **32** (1982) 882–7.
13. Markov, L. & Petrov, K., Nickel–cobalt spinels prepared by thermal decomposition of Ni(II)–Co(II) hydroxide nitrates. *Reactivity of Solids*, **1** (1986) 319–27.