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Magnetic Properties of High B_s Manganese Zinc Ferrites

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Magnetic properties of manganese zinc ferrites with high saturation magnetic flux density (B_s) were investigated. The B_s of over 520 mT at 100°C was obtained in the specimens with compositions around 65 mol%-Fe_2O_3 and they exhibited higher DC pre-magnetization characteristics. However, the specimens with Fe-rich composition showed the increase of the number of cation vacancy and the deterioration of power losses and initial magnetic permeabilities. Moreover a constricted B-H hysterisis loop, known as a "perminvar-loop", was typical at the composition. Sintering under low oxygen partial pressure was efficient to the decrease of the number of cation vacancy, but the Zn-evaporation was critical at the condition. The inhibition of the Zn-evaporation from the surface area changed the shapes of hysterisis loop and improved the magnetic properties. Not only the value of B_s, but the morphology of hysterisis loop was important factor for getting good DC pre-magnetization characteristics.
Key words: MnZn-ferrite, high saturation magnetic flux density, Zn-evaporation, B-H hysterisis loop

1. INTRODUCTION

Manganese zinc ferrites are widely used for various applications. Focusing on the choke-coils, higher DC pre-magnetization characteristics are required as regards the achievement of higher current for better efficiency and miniaturization of electric devices. Hence, the maximum magnetic field per unit volume applied to the ferrite core is expected to be increased at a practical use temperature.

An useful and well known concept in the manufacturing of MnZn-ferrite materials with the higher saturation magnetic flux density (B_s) is the higher content of magnetite in the whole spinel phases. However there are difficulties in the practical processing of the materials with Fe_2O_3-excess composition. Due to the high instability of magnetite generation reaction under the oxidizing atmosphere, some undesirable matters, such as densification delay, increase of lattice defects (cation vacancies) or decrease in resistivities, easily occur. In fact scientific reports and patents on the high B_s materials already exist, but core losses or initial permeabilities are relatively worse in almost all the cases.

Another approach to the high B_s is Ni substitution into the spinel structure. Substituting Ni ferrite for part of Mn-ferrite raise the curie temperature of the material, leading to an increase in the net B_s value at relatively high temperature (100°C)[1].

In the present work, MnZn-ferrites with high B_s have been investigated. The effects of process factors on the magnetic properties of MnZn-ferrite with large amount of excess-Fe_2O_3 were studied. Another emphasis is placed on the DC pre-magnetization characteristics with reference to the shapes of B-H hysterisis loop.

2. EXPERIMENTAL PROCEDURE

Manganese zinc ferrites were prepared by a conventional ceramic processing method. The raw materials were mixed by a tumbling ball mill, and calcined at 850°C for 3hrs in air. Arbitrary amount of dopants such as SiO_2, $CaCO_3$ and Nb_2O_5 were added. Then they pulverized to obtain a BET specific surface area between 2.5-3.0m^2/g by using a tumbling ball mill. A granulation using an aqueous solution of polyvinyl alcohol was followed. The granules were uniaxially pressed into ring-shaped compacts (outer and inner diameter of 20mm and 10mm, respectively) for a measurement of the magnetic properties and into E-shaped compacts (length of 20mm, width of 10mm) for a measurement of the DC pre-magnetization characteristics. The density of compacts was 3.0g/cm^3. The compacts were sintered at 1350℃ peak temperature for 5hrs in a tube furnace under the oxygen partial pressure of about 1%, and followed by the gradual cooling under the equilibrium oxygen partial pressure.

The measurements of the magnetic properties and the other evaluations were carried out as follows. The core losses were measured at a constant frequency f=100kHz and an applied magnetic flux density of 200mT by AC B-H analyzer. The saturation magnetic flux densities and B-H hysterisis loops were measured by DC B-H tracer. The initial permeability μ_i was measured as a function of temperature with the specimens of 20 turns wound-up using an impedance analyzer. DC pre-magnetization characteristics were evaluated using an EE-cores with 50 turns wound-up. The width of an air gap provided in the magnetic circuit of the core is about 1mm. The number of cation vacancy shows one to one correspondence with the nonstoichiometric oxygen content δ, which can be written as:

$$(Zn^{2+}{}_a,Mn^{2+}{}_b,Mn^{3+}{}_c,Fe^{2+}{}_d,Fe^{3+}{}_e,Ni^{2+}{}_f)O^{2-}{}_{4+\delta}$$

$$a+b+c+d+e+f=3$$

Analyzing charges of ions (titration) and chemical compositions (XRF) gave the δ values of the specimens. Local chemical analysis on cross sections of sintered specimens was performed with EPMA.

3. RESULTS AND DISCUSSION

3.1 MnZn-ferrite materials with higher saturation magnetic flux density

To achieve the materials with higher B_s at 100°C, MnZn-ferrite including Fe_2O_3 over 60mol% were investigated. Magnetic properties mainly changed as a function of the content of Fe_2O_3 and the optimal content was around 65mol% for high B_s. Nickel substitution of about 1.5mol% at the composition resulted in the highest B_s value, B_s=525mT. The composition and magnetic properties of the high B_s material are shown in Table I and Fig. 1 shows the trilinear diagram for MnZn-ferrite materials. Compared with the major MnZn-ferrite materials for power supply use, core losses (P_{cv}) and initial permeabilities (μ_i) are lower.

Table I . Composition and magnetic properties of the high B_s material.

Composition (mol%)	Fe_2O_3	MnO	ZnO	NiO
	66	18.5	14	1.5
magnetic properties	$B_{s\ 100°C}$ (mT)	$P_{cv\ 100°C}$ (kW/m^3)		$\mu_{i\ 25°C}$
	525	1040		540

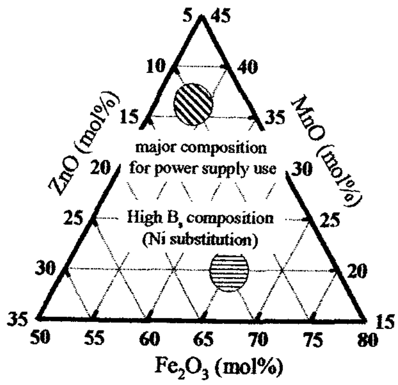

Fig. 1. Trilinear diagram of MnZn-ferrite materials.

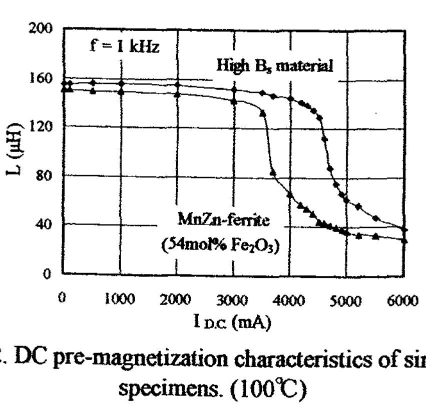

Fig. 2. DC pre-magnetization characteristics of sintered specimens. (100℃)

The DC pre-magnetization characteristics of each specimen (high B_s and Fe_2O_3:54mol%) at 100℃ are shown in Fig. 2. Their B_s values are 525 and 410mT, respectively. Showing good agreement with the development of B_s, high B_s material exhibit 27% higher DC which gives 90% inductance of initial value.

3.2 Low oxygen partial pressure sintering

In MnZn-ferrite, excessive amount of Fe_2O_3 from the stoichiometry forms maghemite or magnetite, and they exist as a solid solution in MnZn-ferrite. An existence of maghemite means a generation of lattice defect (cation vacancy) and leads to the deterioration of magnetic properties of materials. Thus, sintering MnZn-ferrite under reduced oxygen partial pressure (P_{O2}) is very efficient technique for the reduction of cation vacancies.

In Fig. 3, the nonstoichiometric oxygen content (δ) in sintered specimens (composition is shown in Table I) are plotted as a function of P_{O2} of peak temperature during sintering. The δ value decreased with the reducing P_{O2}. Though a reduction of cation vacancies have been accomplished, an improvement of magnetic property, such as P_{cv}, has not been achieved.

The B-H hysterisis loop of two samples in Fig. 3 (P_{O2}=1%(sample A) and 0.02%(sample B)) are shown in Fig. 4. In the case of sample A, the shape of loop is constricted and curved. It is known that constricted hysterisis loop is typical in the samples with large uniaxial magnetic anisotropy, and such hysterisis is called "perminvar-loop".

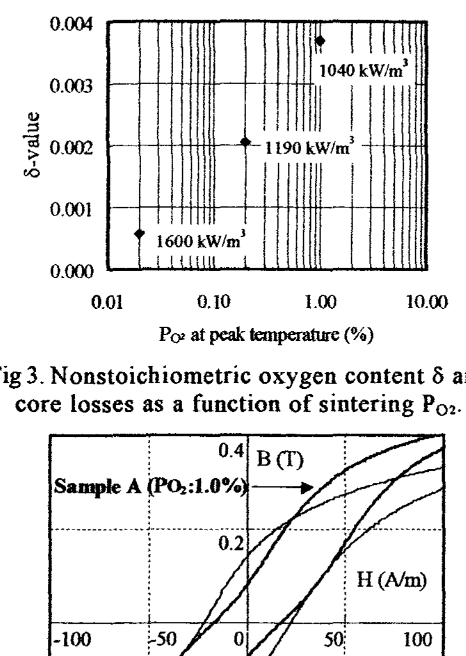

Fig 3. Nonstoichiometric oxygen content δ and core losses as a function of sintering P_{O2}.

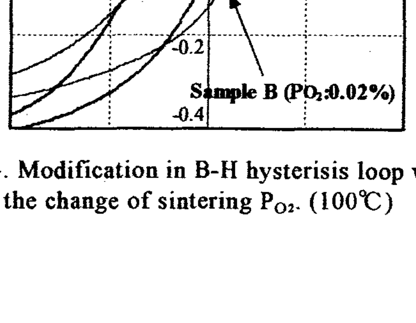

Fig. 4. Modification in B-H hysterisis loop with the change of sintering P_{O2}. (100℃)

A presence of large amount of cation vacancies or impurities in the material is one of the explanations of "perminvar-loop". On the other hand, sample B shows larger B_r and H_c value than sample A, and no constriction is observed in the loop. The difference of loop shape between "perminvar-loop" and normal loop suggests the lower induced magnetic anisotropy in sample B, and it agrees with the reduction of cation vacancies (Fig. 3). However the increase in H_c value gives us another suggestion of increasing magnetic anisotropy originated from other mechanisms, as discussed in next paragraph.

3.3 ZnO vaporization during sintering

It is known that ZnO is easily reduced and vaporizes under deoxidizing atmosphere or at high temperature. Thus, Zn vaporization has been recognized as troublesome phenomenon for processing MnZn-ferrites, especially ferrites with Fe-rich composition.

The sequential change of Zn content from the surface to the inside of sintered specimens is shown in Fig.5, measured by linear chemical analysis using EPMA.

In sample A, the intensity is stable and does not depend on the distance from the surface of specimen. It means Zn vaporization hardly occured at the sintering condition of P_{O2}=1%. In the case of sample B, Zn depletion from the surface area is obvious. Zinc content gradually approaches to the value of sample A as the distance from the surface increases. The depth of Zn vaporized layer can be evaluated as 180μm. Consequently, Zn vaporization at sample B decreased the Zn content from the original ferrite formula at the surface, resulted in deteriorative effects to the magnetic properties. One possible assumption is that the compositional slope causes the residual stress in the specimen and increases the stress-induced magnetic anisotropies. Or perhaps, the sintering P_{O2} might change the insulating grain boundary phases, average or distribution of grain size.

A development of the magnetic properties in MnZn-ferrite could be obtained if an inhibition of Zn vaporization and a decrease of cation vacancies achieve simultaneously. To inhibit the Zn vaporization from the surface of the specimens during sintering, it is necessary that surrounding gas phase on the solid surface is strictly controlled. A schematic model of the stacking condition of ferrite cores for sintering are shown in Fig.6, and inhibition of the Zn vaporization was achieved in sample C.

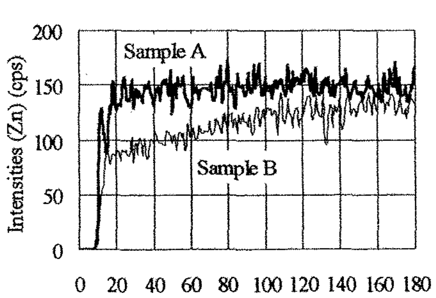

Fig. 5. Sequential change in Zn content at the surface area of sintered specimens. (EPMA)

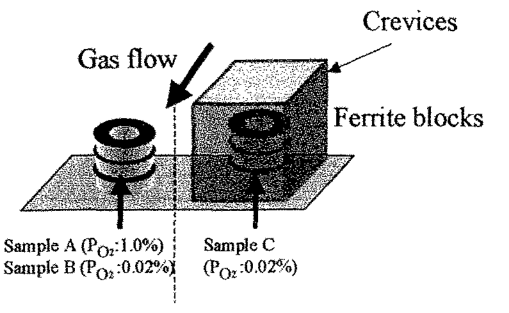

Fig. 6. Schematic model of stacking conditions of cores.

By surrounding ferrite cores with sintered ferrite blocks, Zn vapor pressure around cores increased temporarily during sintering and suppressed the decomposition reaction of Zinc oxide.

The result of EPMA linear chemical analysis at the surface area of specimens is shown in Fig. 7 and B-H hysterisis loops are shown in Fig. 8. In Fig. 7, the curves for sample A and C have overlapped, and it can be confirmed that Zn has not vaporized in sample C as in sample A. As mentioned before, Zn vaporization influences the shapes of B-H hysterisis loop (Fig. 8). Inhibition of Zn vaporization resulted in the decrease of Hc value and the steep inclination of the loop. The δ value of sample C was 0.009, similar to δ value of sample B (0.006). This result shows that surrounding ferrite blocks did not interrupt the reduction of cation vacancies of the specimen, and agree with the non-constricted loop-shape of sample C. In addition, inhibition of Zn vaporization also resulted in the improvement of magnetic properties. P_{cv} was lower (860kW/m^3 at 100℃) and μ_i was higher (shown in Fig. 9) in sample C than in sample B. The temperature dependence of initial permeabilities for each sample is shown in Fig. 9. Sample C presented the highest maximum value and the lowest temperature of secondary permeability. It is well known that the temperature of the maximum secondary permeability decreases with increasing Fe^{2+} content. There is a qualitative agreement between the result of permeability and δ value. Moreover secondary permeability peak shift to higher temperature in sample B suggests that Zn vaporization enhanced a negative anisotropy to the material.

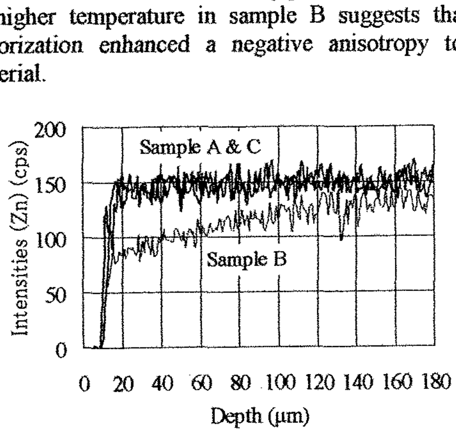

Fig. 7. Sequential change in Zn content at the surface area of sintered specimens. (EPMA)

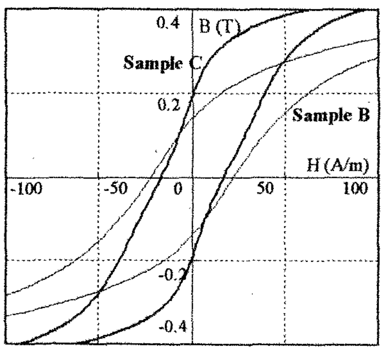

Fig. 8. Modification in B-H hysteresis loop with inhibited Zn vaporization. (100℃)

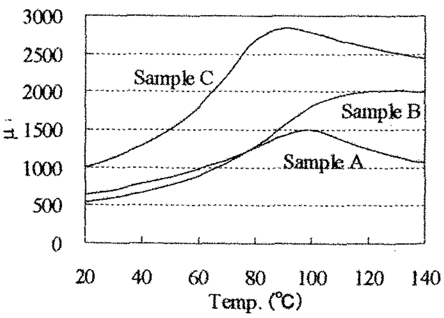

Fig. 9. Initial permeabilities as a function of temperature.

3.4 Relationship between the morphology of hysteresis loop and the DC pre-magnetization characteristics

Fig. 10 and 11 shows the B-H hysteresis (full-loop) and the DC pre-magnetization characteristics, respectively, of sample A and B. Though sample A and B show a similar B_s value, their magnetization behavior and the corresponding DC pre-magnetization characteristics differ remarkably. In Fig.11, the inductance of sample B gradually decreases as the applied DC increase. On the other hand, inductance of sample A remains stable till the DC exceeds 3000mA. Direct current that gives 90% inductance of initial value is 4300mA and 3550mA in sample A and B, respectively. Probably this results reflected the different curvature of B-H hysteresis, especially at the shoulder, B range of 0.3 to 0.5T.

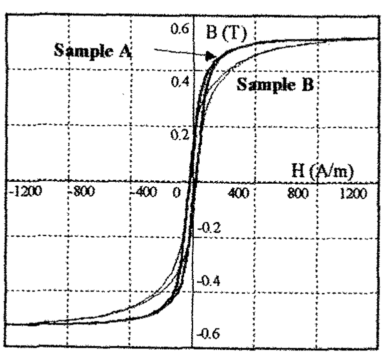

Fig. 10. B-H hysteresis loop of specimens. (100℃)

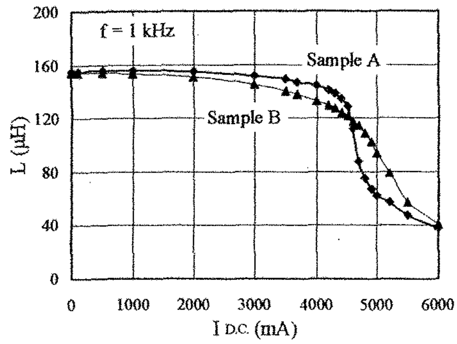

Fig. 11. DC pre-magnetization characteristics of sintered specimens, showing a gradual decrease of inductance in sample B. (100℃)

Usually the DC pre-magnetization characteristics are explained from B_s value of the material. But there are some cases that the magnetization behavior, which appears in the shape of hysterisis loop, play an important role in the DC pre-magnetization characteristics. Further research is required to provide a satisfactory explanation about the relationship between the magnetization behavior and the DC pre-magnetization characteristics.

4. CONCLUSIONS

Manganese zinc ferrites with high saturation magnetic flux density have been investigated. The optimal amount of Fe_2O_3 was 66mol%, and B_s of 525 mT at 100°C was obtained at the composition. As the sintering oxygen partial pressure reduced, cation vacancies in the specimens decreased. However Zn evaporated from the surface of the cores during sintering and magnetic properties of MnZn-ferrite degraded.

By surrounding specimens with MnZn-ferrite blocks during low P_{O_2} sintering, amount of Zn vaporization was remarkably decreased and magnetic properties improved.

Amount of cation vacancies or Zn vaporization changes the magnetic anisotropy and affect to the magnetization behavior. As a result, the DC pre-magnetization characteristics were also influenced by them.

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