JFE TECHNICAL REPORT
No. 27 (Mar. 2022)

MnZn Ferrite with Higher Strength

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Abstract:

For the purpose of higher strength MnZn ferrite that is strongly demanded for automotive applications in recent years, the correlation between rupture strength, precrack size and crystal structure was investigated by adopting the method of evaluating toughness of ceramics. As a result, fracture toughness value K_{Ic} was obtained as 1.3 to 1.7 $MPa \cdot m^{0.5}$. Fracture model of crack propagation through voids was estimated from the morphological observation of the fracture surfaces of sintered specimens. Furthermore, the correlation between K_{Ic} value and preexisted voids distributed inside grains was considered. On the other hand, from the investigation with actual products, crack defect behaved as the beginning point of fracture and its size was well correlated to the strength of MnZn ferrite products. Based on above knowledge, core strength was successfully increased about 30% than conventional materials by increasing toughness with controlling crystal structure and suppressing crack defect through manufacturing process.

1. Introduction

MnZn ferrite is an oxide soft magnetic material and is manufactured by a solid phase sintering reaction after mixing the main raw materials, high purity iron oxide, manganese oxide and zinc oxide[1)]. An important feature of MnZn ferrite is its resistivity, which is 10^{7-8} times higher than that of metallic soft magnetic materials. Because this makes it possible to suppress eddy current loss, MnZn ferrite is widely used in the magnetic cores of transformers, choke coils, noise filters and other components which are driven in the high frequency range of several 10 to several 100 kHz. In the past, MnZn ferrite was mainly used in the home electrical appliance field, but in recent years, with the shift to new automotive drive systems, that is, hybrid electric vehicles (HEV) and electric vehicles (EV), demand for automotive applications is also increasing.

As a soft magnetic material, MnZn ferrite cores must have high permeability or low loss. In addition to these magnetic properties, high strength is also a priority in automotive applications. Ferrite cores are usually fixed on an electrical circuit board by pressing and used under an environment subjected to constant stress. In cores for automotive power supply circuit applications, the rupture strength specification is specified so that rupture will not occur even if the core is subjected to stress several times higher than that during fixing, considering vibration while the automobile is travelling. However, since MnZn ferrite is a type ceramic, and thus is a brittle material, there is a possibility of damage due to impact not only while the core is in service, but also in the process from core manufacturing to installation in an automotive product. Therefore, MnZn ferrite with higher strength has become an important issue.

The crystal structure (spinel type) of MnZn ferrite

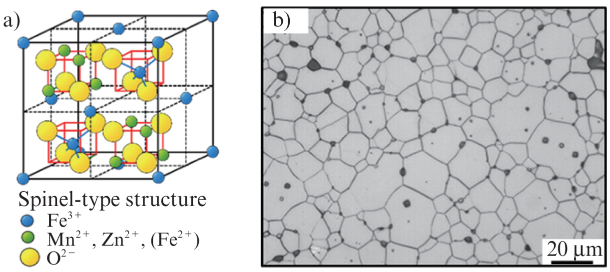

Fig. 1 Crystal structure and microstructure of MnZn ferrite

† Originally published in *JFE GIHO* No. 47 (Feb. 2021), p. 25−30

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is shown in **Fig. 1** a). The widely-used sintered cores for high frequency range are polycrystals, as shown in Fig. 1 b). This type of material has a structure in which numerous voids (pores) generated in the sintering process remain in the grains and at grain boundaries.

Many reports have examined the fracture toughness values of alumina, zirconia and other ceramics which are used in structural applications, together with techniques for their improvement[2–5]. However, knowledge of fracture toughness as a mechanical property of MnZn ferrite is limited, as the research to date has mainly consisted of a study[6] on the manufacturing conditions for suppressing pre-existing cracks in single crystal ingots, and a report[7] that the fracture toughness value, K_{Ic}, of single crystal MnZn ferrite is around 1.0 MPa-m$^{0.5}$. Voids like those shown in Fig. 1 b) are frequently seen in actual products, and it can easily be predicted that pre-existing voids will have a significant influence on the strength and toughness of MnZn ferrite polycrystals that contain such voids, but virtually no reports have examined this problem.

Therefore, in this research, we investigated the relationship among the rupture strength, precrack size and crystal structure of sintered compacts of MnZn ferrite by using a relatively simple technique called the Bridge Indentation (BI) method [8, 9] with the aim of realizing higher strength in MnZn ferrite cores used in automotive transformers, as a further expansion of demand for this product is foreseen in the future. In addition, based on the investigation results, the fracture toughness as the material for the MnZn ferrite sintered compact was evaluated, and the fracture mechanism was discussed.

Actual product cores contain locations where stress concentration occurs as a result of the product geometry, and crack-like sintering defects (hereinafter, crack defects) occur at those locations due to constriction during sintering. Since fracture originating at these crack defects occurs in fracture tests of actual products, we examined the correlation between crack defects in actual product test pieces and bending fracture strength, and implemented various measures to strengthen product cores based on a rupture model of the material. The results are reported in this paper.

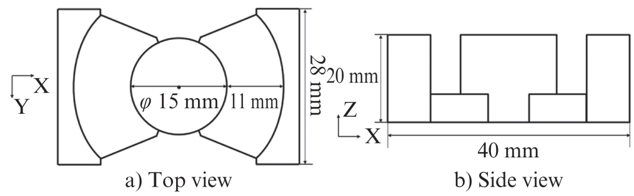

Fig. 2 Top view and side view of ERX40 shape of ferrite core

2. Experimental

2.1 Samples

The main components, Fe_2O_3, Mn_3O_4 and ZnO, were weighed, mixed and calcined. $CaCO_3$ and SiO_2 were added to the obtained calcined powder, and after pulverizing, aqueous polyvinyl alcohol (PVA) was added and the mixture was granulated. Sintered compact test pieces for toughness evaluation having a length, width and height of 35 mm×15 mm×5 mm, respectively were prepared by compacting the granulated material at a pressure of approximately 100 MPa using a press and mold, followed by sintering under atmospheric control using an electric furnace.

For measurements of the sintering defects and fracture load of the actual product cores, actual product core test pieces of the ERX40A shape[10], in

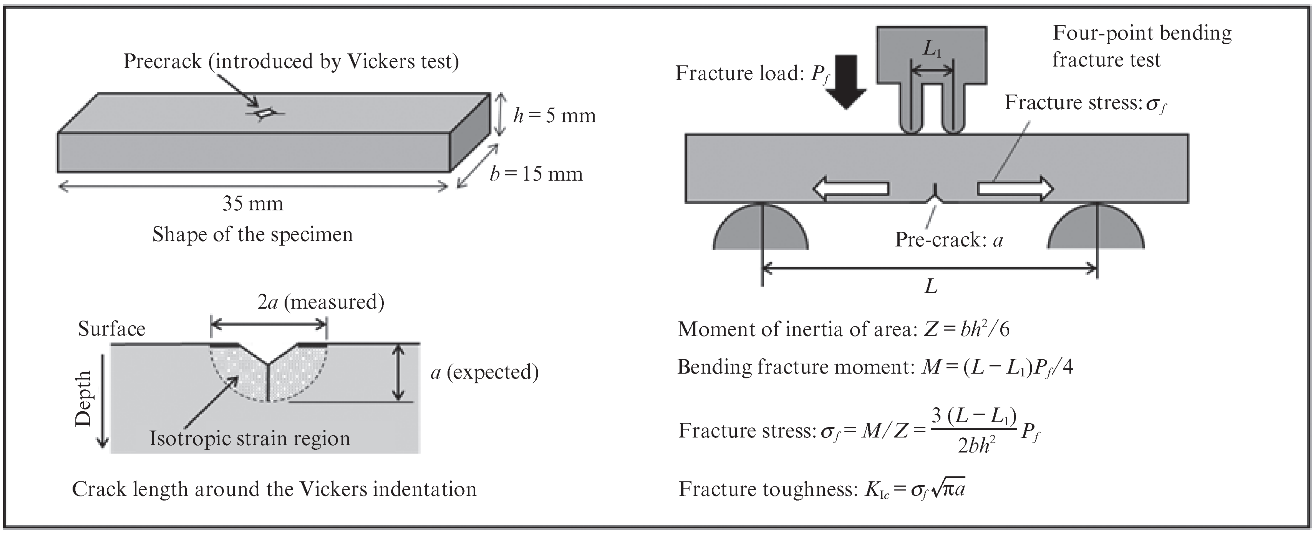

Fig. 3 Schematic diagram of evaluating toughness by Bridge Indentation (BI) method

which the length of the long side shown in **Fig. 2** is 40 mm, were compacted and sintered.

The microstructure of the prepared sintered compacts was observed and photographed with an optical microscope after cross-sectional polishing and etching, and the average grain size was calculated by image analysis. At the same time, the number of pre-existing voids remaining in grains and at grain boundaries was also counted, and the pre-existing void ratio was calculated.

2.2 Evaluation of Fracture Toughness Value: Bridge Indentation Method

Figure 3 shows the evaluation technique and principle. The center of the rectangular solid sintered test piece was indented with a Vickers hardness tester by applying different loads in the range of 500 to 5 000 gf in order to introduce precracks with different sizes. The cracks occurred similarly from each corner of the indentation. However, assuming that a semi-ellipsoid crack is formed below the indentation, the precrack depth, a, was estimated from the crack length, $2a$, measured at the surface. A 4-point bending fracture test conforming to the JIS standard[11)] was conducted with these samples, and the fracture toughness value, K_{Ic}, was calculated by the following equation from the fracture stress, σ, and the precrack depth, a.

$$K_{Ic} = \sigma_f \sqrt{\pi a} \quad \cdots\cdots (1)$$

2.3 Evaluation of Other Properties

The residual stress of the core surface, which is expected to affect fracture strength, was measured by X-ray diffraction. In this measurement, the diffraction profile of the sintered compact surface was obtained by the iso-inclination method using the Cr-Kα line with a micro-area X-ray residual stress measurement system (Rigaku; AutoMATE). Focusing on the (551) plane peak, which is assumed to appear at θ=148.40° in $MnFe_2O_4$, the residual stress was estimated from the peak shift. An elastic coefficient of 147 GPa and Poisson's ratio of 0.28 were used in the calculation of residual stress.

As the size of the sintering defects that occurred in the actual product, an actual product core with the ERX40A shape shown in Fig. 2 was cut with a micro cutter, the cylindrical midfoot root cross section was observed with an optical microscope, and the length was measured by image analysis. For the fracture load of an actual product core of the shape used in transformers, bending strength was measured by using the ERX40A shape actual core based on the method provided in the JIS standard[11)] related to ferrite. Morphological observation of the fracture surfaces of the samples was performed using a scanning electron microscope (SEM).

Table 1 List of experimental prototypese

	Average grain size (µm)	Ratio of voids inside grains※) (%)	Surface residual stress (MPa)
[A]	11.0	24.1	55.8
[B]	7.4	9.9	42.7
[C]	10.2	22.9	29.4

※(quantity of the voids inside grains)/(quantity of total voids)

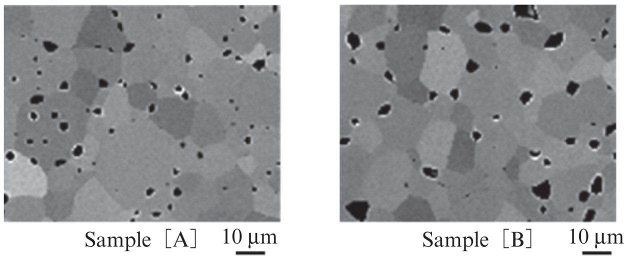

Fig. 4 Comparison of images of cross sections of samples

3. Results and Discussion

3.1 Crystal Structure of Prepared Samples

Table 1 shows the structural information for 3 types of sintered compact prototypes (hereinafter, samples [A], [B] and [C]) prepared by sintering green compacts with same composition under different sintering conditions. Samples [A] and [B] were prepared by changing the heating conditions and treatment time during sintering, and sample [C] was prepared by changing the cooling conditions during sintering used with samples [A] and [B].

Figure 4 shows the optical microscope images of the polished cross sections of samples [A] and [B]. In the microstructure of sample [A], the average grain size of the sample is large, and many small pre-existing voids remain in the grains. In sample [B], on the other hand, the average grain size is small, voids exist mainly at the grain boundary triple points, and conversely, few voids remain inside the grains.

3.2 Results of Toughness Evaluation by BI Method

Figure 5 shows the relationship between the precrack length and fracture stress obtained by the BI method on double-logarithmic (log-log) axes. The experimental results show a linear relationship analogized from Eq. (1). Although Fig. 5 shows the evaluation results of materials prepared under the three

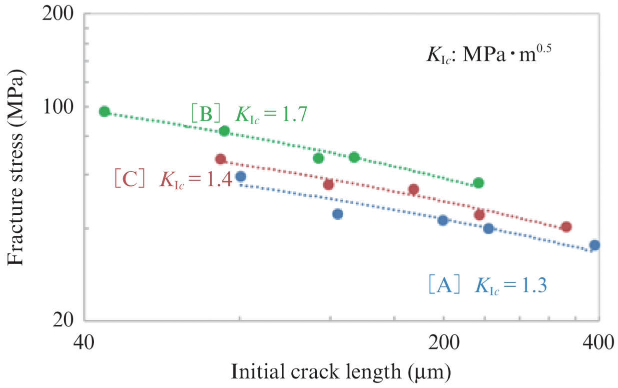

Fig. 5 Evaluation of fracture toughness by BI method

above-mentioned conditions by changing the sintering conditions, the results are stratified with almost identical slopes. The differences in the fracture toughness values among the various sintering conditions are reflected in this relationship.

The values of K_{Ic} of the MnZn ferrite polycrystal obtained by this experiment were 1.3, 1.7 and 1.4 MPa-m$^{0.5}$ in the order of sample [A], [B] and [C]. Since these values are close to the value of K_{Ic} reported for a MnZn ferrite single crystal in the past, K_{Ic}=1.0 MPa-m$^{0.5}$ [7], the fracture toughness evaluation values obtained by the BI method in this research are considered to be appropriate.

In structural ceramics such as alumina, the value of K_{Ic} is from 3 to 7 MPa-m$^{0.5}$. The value of K_{Ic} of the MnZn ferrite polycrystal is quite low in comparison with those values. Since the value for the MnZn ferrite polycrystal is on a level that slightly exceeds the 1.0 MPa-m$^{0.5}$ of glass, the MnZn ferrite polycrystal belongs to the brittle class, even among ceramics. This is thought to be because the composition and crystal structure of MnZn ferrite tend to prioritize excellent magnetic properties rather than fracture toughness because MnZn ferrite is used as a magnetic material.

3.3 Effect of Crystal Structure on Fracture Toughness Value of MnZn Ferrite Sintered Compacts

Figure 6 shows the SEM observation images of the fracture surfaces of samples [A] and [B] after evaluation by the BI method. Sample [A] fractured in a form that essentially passes through the grain, and the fracture surface was smooth. In a smooth intragranular fracture surface, a large number of pre-existing voids can be seen remaining in crystal grains, and a condition in which a linear step originating from a pre-existing void is elongated in a unform direction, is also observed. This step is estimated to be a ridge which is formed when a crack propagates by cutting across voids.

On the other hand, in sample [B], the fracture surface is polygonal, and extremely uneven. In this case, it is estimated that the fracture followed the grain boundaries. This is a remarkable difference from sample [A], which displayed a smooth fracture surface. As shown in Table 1 and Fig. 4, in sample [B], the number of pre-existing voids remaining in crystal grains is small and the number of voids on the grain boundaries is large. The difference in the condition of the fracture surfaces in Fig. 6 shows a good correspondence with the differences in the existing position and amount of pre-existing voids. Moreover, as mentioned in section 3.2, the fracture toughness value of sample [B] is high in comparison with that of sample [A]. This result is thought to be related to the difference in the fracture surface condition shown in Fig. 6.

Figure 7 shows a schematic diagram of the fracture model of the MnZn ferrite polycrystal estimated on the basis of these results. Because remaining pre-existing voids are strongly related to fracture of the MnZn ferrite polycrystal, it is thought that a crack is induced

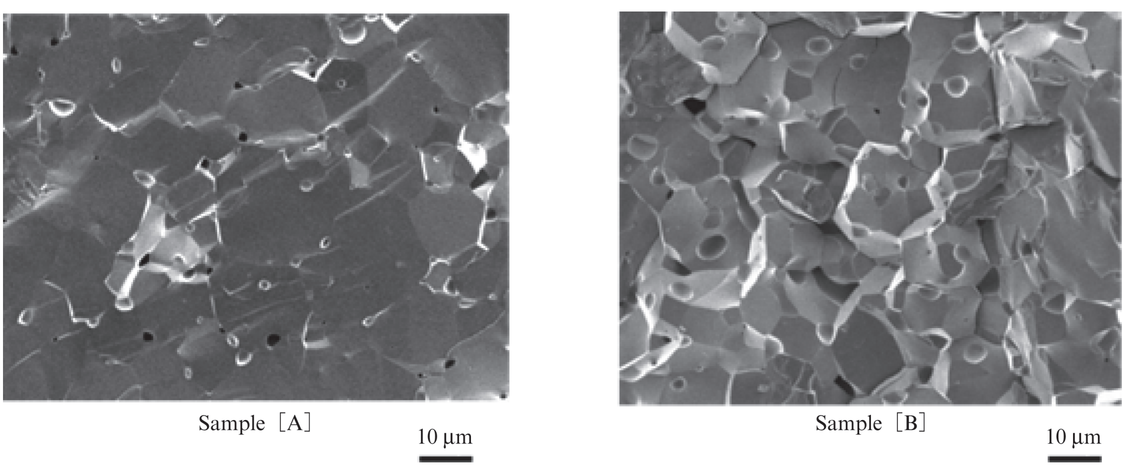

Fig. 6 Comparison of SEM images of fracture surfaces

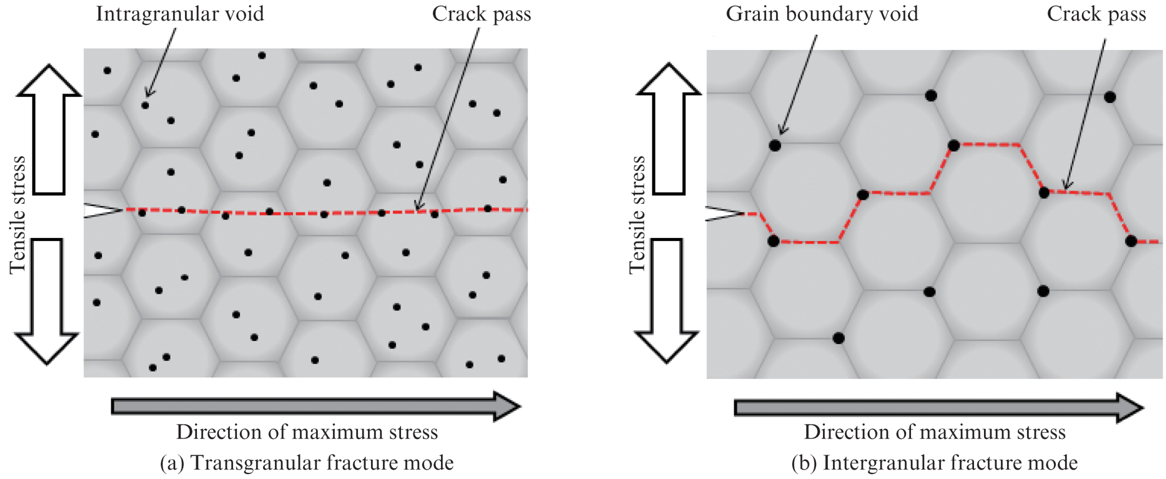

Fig. 7 Schematic diagram of fracture model of polycrystal MnZn ferrite

by a void and fracture expands by the growth of that crack. Even when a material is subjected to the same tensile stress, differences can occur in the microscopic crack propagation path, corresponding to the position where pre-existing voids exist. In sample [A], which contains many pre-existing voids inside grains, the crack propagates linearly in the direction of the maximum principal stress, but in sample [B], which contains few pre-existing voids inside grains, the pre-existing voids on the grain boundaries are controlling, and the crack propagates while circumventing the direction of maximum principal stress.

The energy required for fracture of a material is considered to be equal to the energy necessary to form the fracture surface[12], and can be regarded as the product of the area of the newly-formed surface caused by the fracture and the surface energy per unit of surface area.

In sample [A], in which intragranular fracture occurred, both the area of the newly-formed surface required for propagation of a unit length of a macroscopic crack and the energy dissipation for enlargement of the fracture surface are small, and as a result, it is thought that the toughness values is low. As the reason why intragranular fracture is the main fracture mode, because the grain size is large and the intragranular pre-existing void ratio is high, as shown in Table 1, it is considered that the crack propagates as though "short-circuiting" through voids, which have a high probability of existence in the high stress region ahead of the crack.

On the other hand, in sample [B], which had an extremely rough fracture surface, the newly-formed surface area required for propagation per unit of length is large and larger energy dissipation is required for fracture surface enlargement. In this case, the difference in the microscopic crack propagation path is thought to be reflected in the difference in the fracture toughness value. From this, it can be inferred that a crystal structure in which the pre-existing voids remaining in grains are reduced and voids are controlled to the grain boundary triple point, like that in sample [B], is effective for improving the fracture toughness value. However, the magnetic properties of MnZn ferrite are greatly affected not only by the main composition, but also by the crystal structure[1]. Therefore, care is necessary, as excessive change in the crystal structure to improve the fatigue toughness value may simultaneously cause a loss of the key feature of MnZn ferrite, that is, its excellent magnetic properties.

3.4 Effect of Residual Stress on Fracture Toughness Value of MnZn Ferrite Sintered Compacts

In comparison with sample [A] and sample [C], which have almost identical grain sizes and intragranular pre-existing void ratios, the residual tensile stress of the surface has been relaxed in sample [C] by partially changing the cooling conditions during sintering. On the other hand, the fracture toughness value of sample [C] is higher than that of sample [A]. Considering the fact that samples [A] and [C] have almost the same grain sizes and intragranular pre-existing void ratios, it can be thought that the difference in the fracture toughness values of samples [A] and [C] is the result of the difference in the residual stress due to sintering.

Because MnZn ferrite sintered compacts do not undergo plastic deformation like general metallic materials, residual stress is not released until fracture occurs. Moreover, as MnZn ferrite is a typical brittle material, tensile stress controlled-type fracture occurs, mainly with a pre-existing microscopic crack defect on the surface as the point of origin. In this case, the

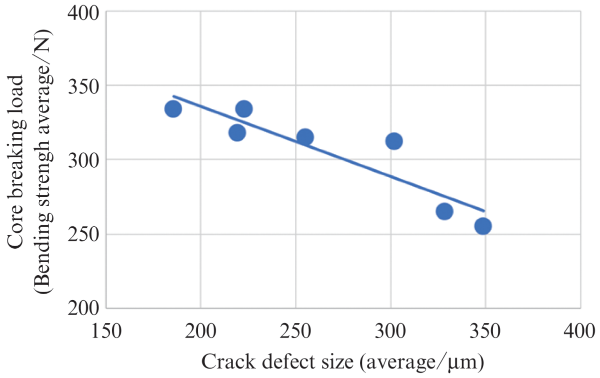

Fig. 8 Effect of crack defect size on core breaking load

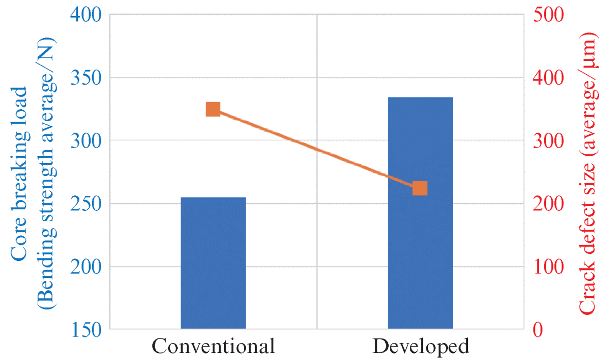

Fig. 9 Effect of higher strength by increasing toughness and suppressing crack defect size

driving force of fracture is stress, in which an external force is superimposed on the residual stress. This means that crack propagation originating from a surface defect can be suppressed by relaxing the tensile residual stress at the surface, and as a result, the fracture toughness value will increase.

It is possible to relax surface residual tensile stress not only by changing the sintering conditions, as in the case of sample [C], but also by dip treatment of the sintered compact in an oxidizing liquid such as nitric acid. However, treatment that achieves an equilibrium of magnetic properties and fatigue toughness is necessary because excessive treatment will change the surface properties of the MnZn ferrite, and as a result, its magnetic properties will also deteriorate significantly[1].

3.5 Effect of Pre-existing Crack Size on Core Breaking Load of MnZn Ferrite Product

Microscopic crack defects occur on the surface of actual product cores, and in bending tests of products, fracture occurs with these surface defects as the point of origin. Therefore, as analogized from Eq. (1), in addition to increasing the fracture toughness value, K_{Ic}, of sintered compacts, reducing the size, a, of the crack defects that occur on the surface of actual product cores is also effective for increasing the core breaking load of products.

Multiple actual product cores, in which the sintering defect size was intentionally changed, were prepared by changing the sintering contraction behavior of the compacts by making various changes in the sintering conditions. **Figure 8** shows the relationship between the size of those sintering defects and the breaking load. There is a clear correlation between the two, and the core breaking load of the actual product cores is increased remarkably by reducing the size of the sintering defects.

In addition to changing the sintering conditions, other techniques for suppressing the size of crack defects are also available. One such technique is control of the surface state in the powder compacting process. The surface properties of the green compact have a large influence on the initiation and growth of crack defects in the sintering process. The surface roughness of the green compact can be reduced and the crack defects of product cores after sintering can be suppressed by smoothing the surface of the mold used in powder compaction or using a proper amount of an appropriate lubricant.

3.6 Confirmation of Strengthening Effect

Figure 9 shows the core breaking load of a prototype MnZn ferrite actual product (i.e., the developed product) prepared by improving the fracture toughness of the sintered compact as material and suppressing the crack defects that occur during sintering due to the product shape compared with the breaking load of the conventional material. In comparison with the conventional material, the average breaking load of the developed product was successfully improved by approximately 30 % while maintaining the feature of excellent magnetic properties. Comparing the size of the crack defects in the two samples, it can be understood that the crack defects in the developed product are approximately 35 % shorter than those in the conventional product. It should be noted that the conventional product was sintered under the conditions of sample [A], while the developed product was sintered under the conditions of sample [C]. Thus, the improvement of the breaking load shown in Fig. 9 is the result of superimposing the effects of precrack size reduction in the sintering process and improvement of the fracture toughness of the original material.

4. Conclusion

With the aim of achieving higher strength in MnZn ferrite cores, the relationship among the fracture stress, precrack size and crystal structure of sintered compacts was investigated using the Bridge Indentation (BI) method, which is one method for evaluating the toughness of ceramics. As a result, the following knowledge was obtained.

(1) The toughness values of the MnZn ferrite polycrystal evaluated by the BI method were in the range of $K_{Ic} \fallingdotseq 1.3$ to 1.7 MPa-m$^{0.5}$. Although this belongs to the brittle class, even among ceramics, it was possible to stratify the fracture toughness values based on the sintering conditions.

(2) Intragranular fracture occurred in samples with low fracture toughness values, and intergranular fracture was observed in samples with high values. The fracture surface in intragranular fracture was smooth, while the fracture surface in intergranular fracture was polygonal and extremely uneven, suggesting a difference in the crack propagation resistance of the two types of samples.

(3) Although pre-existing voids inevitably occurred in these sample materials during sintering, it was found that the difference in crack propagation resistance noted in (2) above was the result of the position of the pre-existing voids, i.e., whether the voids existed predominantly inside the grains or at the grain boundaries.

(4) The results of a bending fracture test of actual products revealed that the origin of fracture is crack-like sintering defects, which occur depending on the product shape.

(5) Based on the knowledge outlined above, the fracture toughness of MnZn ferrite sintered compacts was improved by controlling the crystal structure, and the manufacturing process was optimized with the aim of suppressing the crack defects that occur during sintering of product cores. As a result, prototype product cores with an approximately 30 % higher average breaking load than those manufactured by the conventional process were produced successfully, while maintaining the excellent magnetic properties of MnZn ferrite.

The authors hope to realize higher strength in actual product cores by developing this technology to the actual production process.

References

1) Hiraga, T.; Okutani, K.; Ojima, T. Ferrite. Maruzen Publishing Co., Ltd, 1986, 246p.
2) Suzuki, T.; Uchikoshi, T.; Sakka, Y. Anisotropic Science and Technology for Bulk Ceramics. Ceramics Jpn. 2012, vol. 47, no. 4, p. 243–248.
3) Lange, F. F. Transformation toughening. J. Mater. Sci. 1982, vol. 17, issue1, p. 225–254.
4) Kitazumi, J.; Taniguchi, Y.; Hoshide, T.; Yamada, T. Characteristics of Strength and Their Relations to Flaw Size Distribution in Several Ceramic Materials (Part1: Static Strength). J. Soc. Mater. Sci., Jpn. 1989, vol. 38, no. 434, p. 1254–1260.
5) Hayashi, K.; Gotoh, K.; Nishikawa, T. Grain Size Dependence of Fracture Toughness in Polycrystalline Alumina. J. Ceram. Soc. of Japan. 1991, vol. 99, no. 1151, p. 620–624.
6) Nishikawa, T.; Okamoto, Y.; Inagaki, S. Fracture Toughness of Mn-Zn Ferrite Single Crystal. J. Ceram. Soc. Jpn. 1983, vol. 91, no. 1052, p. 149–156.
7) Nagata, S.; Matsuzaki, S.; Echizenya, K. Large Sized MnZn Ferrite Single crystals for Magnetic Heads of VTR. Kawasaki Steel Giho. 2002, vol. 34, no. 3, p. 32–36.
8) Sadahiro, T.; Sobata, K. Fracture Toughness Determination of Hard Materials by Bridge Indentation Method. J. Jpn. Soc. Powder Powder Metall. 1986, vol. 33, no. 8, p. 422–425.
9) Awaji, H.; Yamada, T.; Okuda, H. Results of the Fracture Toughness Test Round Robin on Ceramics. J. Ceram. Soc. of Japan. 1991, vol. 99, no. 1149, p. 417–422.
10) JFE Ferrite Co. Website. http://www.jfe-frt.com/products/
11) JIS C 2560–2. Cores made of ferrite -- Measuring methods
12) Nishida, T.; Yasuda, E. Evaluation of Mechanical Characteristics of Ceramics. The Nikkan Kogyo Shimbun, Ltd.,1986, 240p.

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