JOURNAL OF MATERIALS SCIENCE 30 (1995) 504–508

Effect of glass addition and quenching on the relation between inductance and external compressive stress in Ni–Cu–Zn ferrite–glass composites

T. YAMAGUCHI, M. SHINAGAWA
Faculty of Science and Technology, Keio University, Yokohama, Japan

The stress–inductance characteristic of ferrite–glass composites has been studied with special emphasis on the effect of heat treatment and glass chemistry. The stress-inductance relation of Ni–Cu–Zn ferrite has been greatly improved by incorporating glass and by quenching from high temperature. The effect of quenching temperature on the stress–inductance characteristic is discussed in terms of the bending strength and fracture mode of the composites, and creep and microcrack formation during quenching are proposed as responsible factors.

1. Introduction

This work was undertaken to improve the stress–inductance characteristics of ferrite cores. In practical application, ferrite cores are sometimes bonded with resin or moulded in resin. Under these conditions, external stress is applied to the ferrite cores, resulting in degradation of the core magnetic properties [1, 2]. Hence, ferrite–glass composites have been developed as stress-resistant cores [3, 4]. However, there are many problems to be solved in this area, among which is the effect of thermal residual stress on the stress–inductance relation, on which our work has been focused. Quenching multiphase materials generates residual thermal stress, the amount of which depends mainly on the differences in the properties of the constituent phases. Thus, ferrite–glass composites exhibit behaviour different from glass-free ferrite cores. In view of these considerations, we studied the stress–inductance relation as a function of material and processing parameters.

Ni–Cu–Zn ferrite cores containing 0–10 vol % PbO–SiO_2 glasses with different softening points were heat-treated and subjected to inductance measurement under a compressive stress up to 400 kgf cm^{-2}. The 3-point bending strength was measured and fracture surfaces were examined by SEM. Results indicated that glass played an important role in retaining thermal residual stress when creep was operative.

2. Materials and methods

Ferrite cores containing 0–10 vol % glass were prepared by the conventional ceramic method. Two types of cores, rod and toroid, were used depending on the purpose of the experiment. Rod cores were used for studying the effect of compressive stress on inductance, since the stress is loaded in the direction normal to the magnetic flux [5]. For inductance measurement in the absence of external compressive stress, toroids were employed because of the closed magnetic circuit leading to inductance larger than that for rod cores.

2.1. Sample preparation

A calcined Ni–Cu–Zn ferrite powder containing CuO, NiO, ZnO and Fe_2O_3 in a molar ratio of 7:19:25:49 was admixed with a PbO–SiO_2 glass powder, kneaded with 3 vol % polyvinyl-alcohol (PVA), and then granulated. The granule was pressed into rods and toroids under 1 t cm^{-2} for 3 s. The glass composition and the softening point [6] are shown in Table I. The glass frits (each less than 3 μm) were made by quenching melts in water and milling with a ball mill. Pressed specimens were fired at 1000 °C for 3 h and then slow-cooled at 300 °C h^{-1}. No crystallization of glass was observed. These specimens were subjected to heat treatment and other measurements. The slow-cooled specimens were heated between 300 and 900 °C for 12 min and quenched in air.

2.2. Measurements

Inductance was measured with an LCR meter with a drive current of 0.5 mA and 100 kHz. The drive current was in the region in which the magnetization of specimens is reversible, and where the initial permeability is almost constant regardless of the drive current [7]. The initial permeability was essentially constant up to 3 MHz. The number of windings was 15 for toroids. A rod specimen was inserted into a coil and the inductance was measured with external compressive stress from 0 to 400 kgf cm^{-2}.

The maximum load was measured at a loading rate of 20 mm min^{-1} and 3-point bending strength was calculated by

$$\sigma_{3b} = 3PL/2wt^2 \qquad (1)$$

0022-2461

TABLE I Composition and softening point of glass

	PbO (mol %)	SiO_2 (mol %)	Softening point (°C)
Glass A	60.0	40.0	417
Glass B	28.8	71.2	680

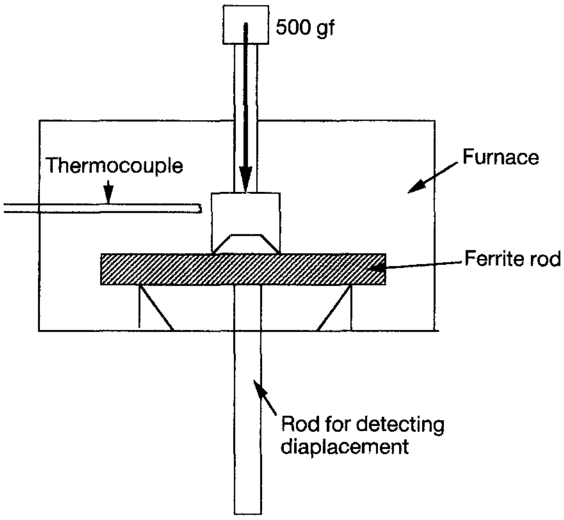

Figure 1 Apparatus for creep testing at high temperature.

where σ_{3b} is the 3-point bending strength, P is maximum load, L is the distance between lower fulcrums, and w and t are the width and thickness of the specimen, respectively. Temperature and humidity were controlled because the specimen could have been fractured by stress corrosion [8].

The fired specimen was polished to the dimensions 19.96 × 2.0 × 85.50 mm and subjected to Young's modulus measurement by the dynamic method at room temperature. A specimen polished to dimensions 10.28 × 3.00 × 47.10 mm was placed in a furnace as shown in Fig. 1, load was applied to it by the 4-point method, and then vertical displacement was detected with a rod connected to the bottom of the specimen. The specimen was heated to 900°C at 300 °C min^{-1}, and held there for 30 min.

3. Results and discussion

3.1. Stress–inductance relation

The role of glass in improving the stress-resistant properties of ferrite–glass composites was studied by analysing the effect of external stress on the magnetic permeability of slow-cooled rod specimens. The effect of residual stress was also studied using specimens quenched from different temperatures. Fig. 2 shows the effect of external compressive stress on the inductance change for slow-cooled glass-free and glass-containing specimens. These curves will be referred to as "stress–inductance relation" in this paper for the sake of convenience. In Fig. 2 the ordinate indicates the inductance change with reference to the inductance without external stress, since inductance of each specimen is different, thus making comparison difficult. The effect of glass addition on the stress-inductance relation is obvious; only 3.23 vol % of glass makes the ferrite magnetically insensitive to the external stress. The stress-insensitivity improved on further addition of glass. Another point to note is that the curves for glass-containing specimens have a maximum in the compression region. The glass-free specimen may have a maximum in the tension region, the existence of which, however, has not yet been confirmed.

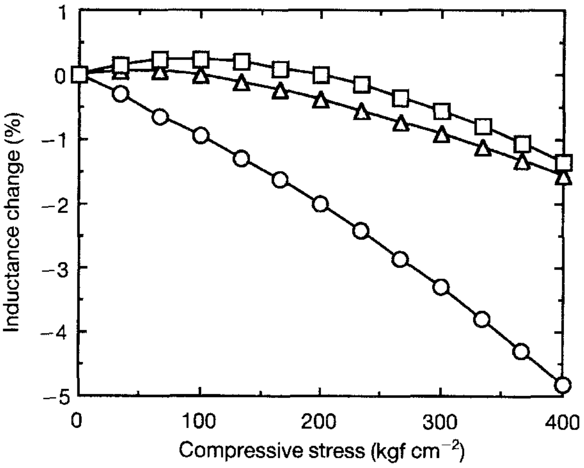

Figure 2 Effect of external compressive stress on inductance change. Glass A content: ○, 0; △, 3.23; □, 6.52 vol %.

Apparently, it was assumed that the observed effect of glass on the stress–inductance relation should be correlated with the Young's modulus of glass-containing ferrites. However, the results of Young's modulus measurement as shown in Fig. 3 did not conform to our prediction; the Young's modulus decreased with increasing glass addition, implying an increased sensitivity to the external stress. The observed decrease in Young's modulus can be attributed to the presence of pores in the specimens.

Fig. 4 illustrates the effect of quenching on the stress–inductance relation for 3.23 vol %-glass containing specimens quenched from different temperatures. Essentially quenching effect on the stress–inductance relation is not observed for the quenching temperature up to 700 °C. Quenching from 900 °C, however, resulted in an improved stress–inductance relation. Furthermore, the curve has a maximum at a higher compressive stress. Similar results were obtained for specimens containing 1.54 and 6.52 vol %-glass.

The above results imply that thermal residual stress is responsible for the stress–inductance relation. Therefore, we tried to confirm this point from fracture experiments.

3.2. Effect of quenching on bending strength

Fig. 5 shows the bending strength of glass-free and 3.23 vol % glass-containing specimens as a function of quenching temperature. The effect of glass addition is remarkable for quenching temperatures higher than 600 °C. For glass-free specimens the bending strength decreases with decreasing quenching temperature to 800 °C and then increases at 1000 °C. For

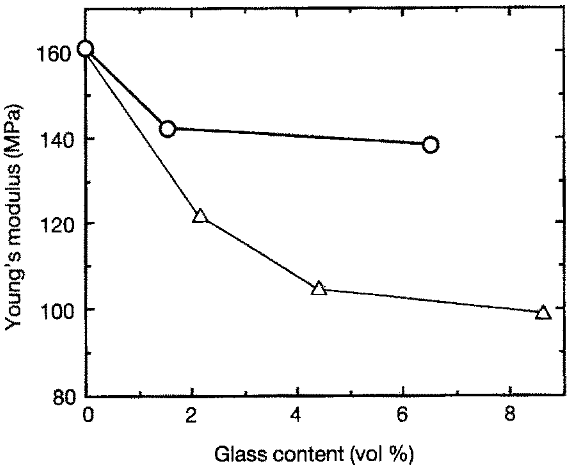

Figure 3 Effect of glass addition on Young's modulus of ferrite. Glass A, ○; glass B, △.

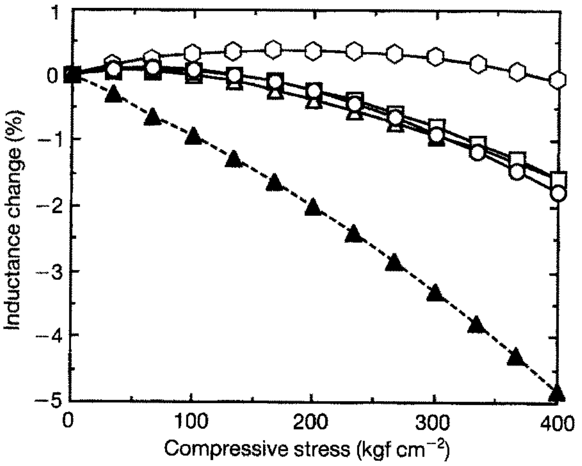

Figure 4 Effect of quenching temperature on the stress–inductance relation. ○: slow cool, quenched from △, 500 °C; □, 700 °C; ⬡, 900 °C. Dashed line: glass-free ferrite; solid line: 3.23 vol % glass A-containing ferrite.

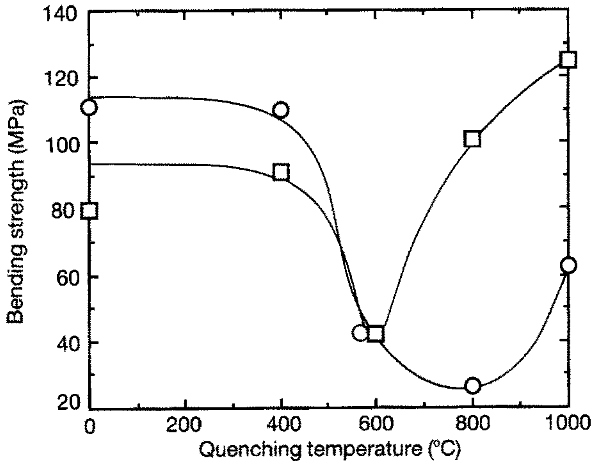

Figure 5 Effect of quenching temperature on the 3-point bending strength. Glass content: ○, 0; □, 3.23 vol %.

glass-containing specimens, on the other hand, the minimum bending strength was observed at a quenching temperature of 600 °C, and further increase in quenching temperature resulted in increased strengths. It is to be noted that the 1000 °C-quenched specimen has a bending strength higher than that of the slow-cooled specimen.

In order to analyse the behaviour observed with glass-containing specimens, fracture mode was observed by SEM. Examination of fracture surfaces revealed that slow-cooled specimens were characterized by intragranular fracture, but that quenched specimens were characterized by mixed-mode fracture (Fig. 6); the fractional area of intergranular fracture increased with increasing quenching temperature. Moreover, the central area of the specimens was characterized by intragranular mode regardless of the quenching temperature. These findings suggested that the observed decrease in bending strength is closely associated with the microcrack formation in grain boundary areas during quenching, and that the extent of the microcrack increases with a rise in quenching temperature.

For glass-containing specimens, the sharp increase in bending strength at quenching temperatures above 600 °C is probably due to the behaviour of glass, because the fracture mode was intergranular regardless of the quenching temperature. Therefore, we studied the creep behaviour.

Fig. 7 illustrates the deformation of rod specimens as a function of temperature as they were heated at

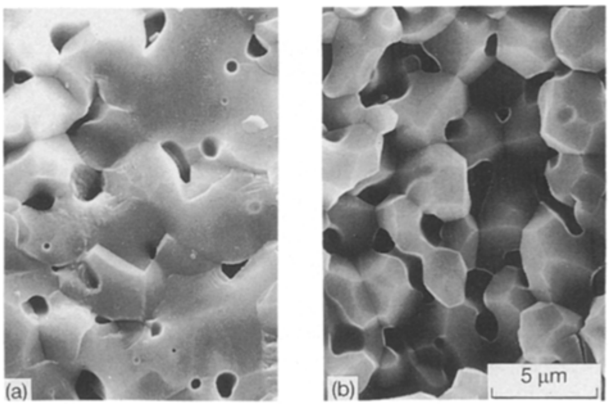

Figure 6 SEMs of fracture surfaces of glass-free specimens quenched from 900 °C, illustrating (a) intragranular fracture and (b) intergranular fracture.

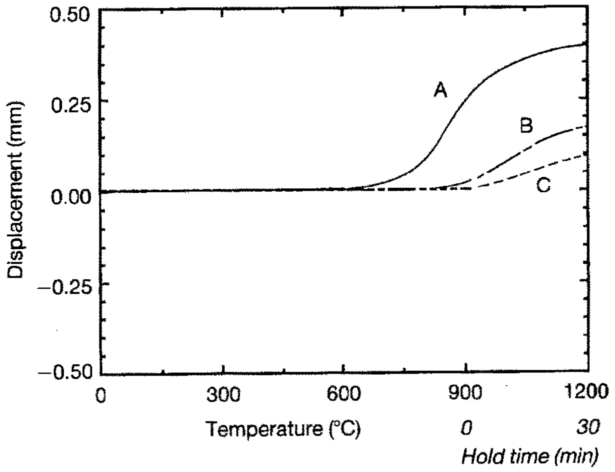

Figure 7 Effect of glass addition on the displacement as a function of temperature. A, glass A-containing ferrite; B, glass B-containing ferrite; C, glass-free ferrite.

a rate of 300 °C h^{-1} while being loaded. The glass-free specimen did not creep until a temperature of 900 °C was reached. Addition of glass decreased the temperature of creep onset; creep started for the glass A-containing specimen at a temperature lower than that for the glass B-containing specimen. This is explained by the difference in the softening points (see Table I).

Summarizing the above findings it can be concluded that quenching from the temperature region in which microcrack formation is suppressed results in retention of thermal residual stress. The increased bending strength for the glass-containing specimen quenched from 900 °C supports this view. When quenched from below 700 °C, however, the thermal stress is dissipated in forming microcracks. The improved stress–inductance relation for the 900 °C-quenched specimen is probably explained by these factors. The progressive decrease in bending strength observed for glass-free specimens with increasing quenching temperature can be interpreted in terms of increased microcrack formation. A slight increase in bending strength for the 1000 °C-quenched specimen (Fig. 5) is possibly explained by densification during the heat treatment.

3.3. Effect of glass composition

Exactly the same experiments as above were conducted using glass B. The effect of glass composition will be discussed with emphasis on the difference arising from the chemistry of glass. Fig. 8 shows the effect of glass content on the stress–inductance relation for glass B-containing specimens. In comparison with the results for glass A in Fig. 2 the inductance changes at high compressive stresses shifted upward progressively with increasing glass content. On the other hand, a small amount of glass A is sufficient to make the specimen stress-insensitive. This behaviour is probably due to the difference in chemistry, as will be discussed later.

Fig. 9 illustrates the effect of quenching temperature on the stress–inductance relation. Quenching from 900 °C did not modify the relation significantly in comparison with the case for glass A (Fig. 4). Similar results were obtained for 4.34 and 8.68 vol % glass additions. As a matter of fact, the specimen containing 8.68% glass gave essentially a flat stress–inductance curve.

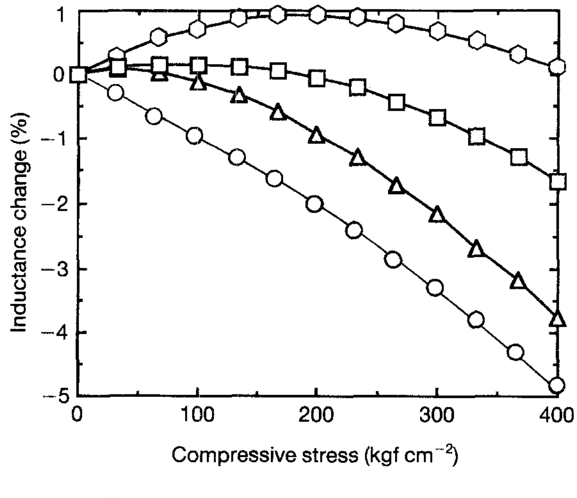

Figure 8 Effect of external compressive stress on inductance change. Glass B content: ○, 0; △, 2.17; □, 4.34; ⬡, 8.68 vol %.

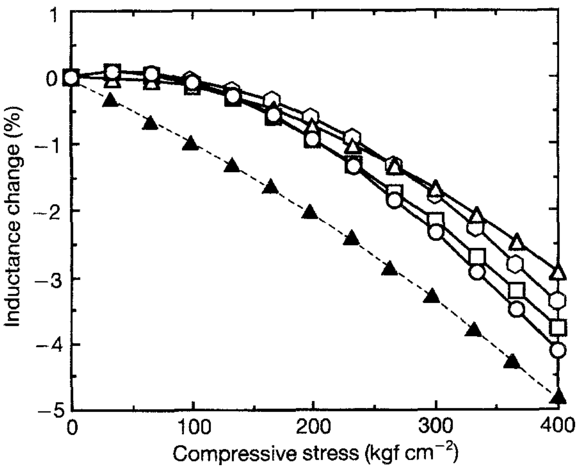

Figure 9 Effect of quenching temperature on the stress–inductance relation ○; slow cool, quenched from △; 500 °C, □; 700 °C, ⬡; 900 °C. Dashed line: glass-free ferrite; solid line: 2.17 vol % glass B-containing ferrite.

The results of bending strength measurements yielded curves similar to those for glass A in Fig. 5. Here, it must be noted that minimum bending strength was observed at 800 °C, approximately 200 °C higher than that for glass A. Such a difference can be explained by the difference in the softening point between glasses A and B. Indeed, this point of view was supported by the creep behaviour shown in Fig. 7. Also, the results in Fig. 8 can be explained along these lines: a relatively small amount of glass is sufficient for covering ferrite grains for a glass having a low softening point, whereas a larger amount of glass is required for extensive coverage with a glass having a higher softening point. We assumed that the behaviour of glass is governed by the viscosity rather than by the interaction between glass and ferrite. Another point to note with regard to the effect of quenching is that the bending strength of the specimen quenched from 900 °C was lower than that of the slow-cooled specimen, implying that a larger part of the thermal residual stress was dissipated in microcrack formation. Thus, in glass B-containing specimens, creep plays a minor role relative to glass A-containing specimens.

4. Conclusions

1. The stress–inductance characteristic is improved by incorporating glass and by quenching from high temperature.
2. The improvement in the stress–inductance characteristic is explained by thermal residual stress. Results of bending strength measurements support this view.
3. Glass chemistry, especially the softening point, determines the magnetic behaviour of ferrite–glass composites under the influence of compressive stress.

Acknowledgement

This work was supported by the TDK company, Japan. The authors are grateful to Y. Ikeda, K. Kinoshina, M. Kumagai and S. Murayama of TDK Corp. for their assistance in experimental work and valuable discussions.

References

1. G. MIAN and T. YAMAGUCHI, *J. Magn. Magn. Mater.* **68** (1987) 351.
2. *Idem., J. Mater. Sci.* **26** (1991) 1775.
3. M. KUMAGAI and Y. IKEDA, in "Advances in Ferrites", Proceedings of the 5th International Conference on Ferrites, Bombay, January 1989, edited by C. M. Srivastava and M. J. Patni, p. 625.
4. S. MURAYAMA, M. KUMAGAI and Y. IKEDA, in Proceedings of the 6th International Conference on Ferrites, Tokyo, September 1992 (Japan Soc. Powder and Powder Metallurgy) in press.
5. N. P. BANSAL and R. H. PORENUS, in "Handbook of Glass Properties" (Academic Press, Orlando, FL, USA 1986).
6. J. SMIT, and H. P. J. WIJN, in "Ferrites" (Philips' Technical Library, Eindhoven, 1965) p. 262.
7. D. J. CRAIK, in "Magnetic Oxides Part 2" (Wiley, London, 1975) p. 633.
8. B. F. BROWN, *Metallurgical Reviews*, Review 129 (The Institute of Metals, London, 1968) 171.

Received 30 March
and accepted 9 June 1994