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Interfacial diffusion between Ni–Zn–Cu ferrite and Ag during sintering

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The interfacial diffusion between Ni–Zn–Cu ferrite and Ag during sintering in the temperature range of 850–950 °C was investigated utilizing the scanning electron microscopy-energy–dispersive X-ray analysis technique. It was found that diffusion increased with an increase in the sintering temperature. Furthermore, some impurities in the ferrite powders, especially SiO_2 and NH_4Cl, promoted the interfacial diffusion. The interfacial diffusion of Ag can be explained by the liquid-phase formation at the grain boundary in the sintered ferrite. © *1998 chapman & Hall*

1. Introduction

Multilayered chip inductors have recently been developed as a surface mounting device. The chip inductor is produced by coating ferrite and internal Ag electrode pastes alternately and then co-firing. The properties of the chip inductor depend on the electromagnetic properties of the sintered ferrite and on the interfacial properties between ferrite and the Ag electrode. Because the melting point of Ag is relatively low (about 960 °C), high-temperature co-firing causes an unexpected lowering of the inductance due to the interfacial diffusion between the ferrite and Ag electrode. Low-temperature co-firing is necessary for suppressing the interfacial diffusion.

We studied the relationship between microstructure and the electromagnetic properties such as complex permeability in low-temperature-sintered Ni–Zn–Cu ferrite [1, 2]. It became evident that the complex permeability was determined by the sintering density (the volume loading of the ferrite) and the ferrite grain size. Permeability in the 10 MHz region was determined by both the sintering density and the ferrite grain size, while permeability in the 100 MHz region was mainly determined by the sintering density. These variations in the permeability were attributed to two different magnetizing mechanisms: spin rotation and domain wall motion.

Regarding the microstructure problem in the grain boundary, Momoi *et al.* [3] and Nakaro *et al.* [4, 5] pointed out that the differences between the thermal expansion coefficients of ferrite and Ag produced microstrains at the boundary and that these microstrains affected the permeability of the ferrite. They also proposed that the formation of the microstrain was enhanced by the presence of an intermediate phase containing Cu and Ag at the ferrite grain boundary. However, to the best of our knowledge, there are only a limited number of experimental studies on the interfacial diffusion between ferrite and Ag.

In this study, we examined the interfacial diffusion between Ni–Zn–Cu ferrite and Ag during sintering in the temperature range of 850–950 °C utilizing the scanning electron microscopy (SEM)–energy-dispersive X-ray analysis (EDXA) technique. For simplicity, the ferrite and Ag stacking discs were considered the control compound. We investigated the influences of the sintering temperature and the impurities contained in the ferrite on the interfacial diffusion, and we shall briefly discuss the method of suppressing the interfacial diffusion and the chip inductor fabrication.

2. Experiments

Ni–Zn–Cu ferrite particles were synthesized by solid-state reaction. Raw material particles of NiO, ZnO, CuO and Fe_2O_3 were mixed together by wet attrition milling, where the composition of the mixture was adjusted to $Ni_{0.28}Zn_{0.52}Cu_{0.25}Fe_2O_4$. They were filtrated and then dried at 80 °C. The obtained mixtures were calcined in air at 800 °C for 4 h and then cooled in a furnace. The calcined particles, identified as a single phase of spinel ferrite by powder X-ray diffraction, were reground by wet attrition milling, in which NiO, ZnO, CuO, SiO_2, CaO, $(NH_4)_2SO_4$ or NH_4Cl was added to the ferrite particles as a small amount of impurity (about 1 wt%). The ferrite particles and Ag particles were individually mixed with an appropriate amount of poly (vinyl alcohol) as a binder, pressed into discs at a pressure of 500 $\mathrm{kgf\,cm^{-2}}$ and stacked to form a triple-layer structure of ferrite/Ag/ferrite (with a total thickness of 6 mm and a diameter of 30 mm). They were kept in air at 500 °C for 1 h in order to decompose and vaporize the organic components and sintered in air at temperatures ranging from 870 to 950 °C for 2 h. Finally, they were cooled slowly in a furnace.

The sintered specimens were carefully fractured at right angles to the layers. The fractured surface was

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then analysed using the SEM–EDXA technique. The microstructure of the interface between ferrite and Ag layers was examined using a Hitachi S-800 scanning electron microscope, and the intensities of the Fe Kα and Ag Kα lines in the vicinity of the interface were measured along the direction perpendicular to the layers with a Kevex 7500 energy-dispersive X-ray fluorescence microanalyser.

3. Results and discussion

The results of the EDXA for the specimen sintered at 870 °C are shown in Fig. 1. From this figure, we found the relative intensity of the Ag Kα line to be approximately 50% at the interface between ferrite and Ag, and over 90% at the point 2 μm from the interface into the Ag layer. We shall designate the broadening width, ΔW, of the gradient curve as the degree of the interfacial diffusion hereafter.

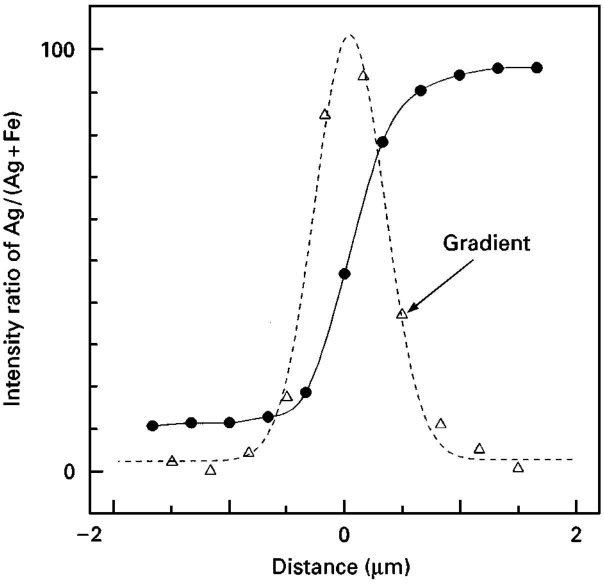

Figure 1 The spatial variation in the relative intensity ratio of Ag to (Fe + Ag) (●) and the spatial gradient (△) for the specimen sintered at 870 °C. The solid and broken curves are drawn as a guide for the eyes.

First, the temperature variation in the broadening width of the ferrite particles without additive impurity were examined. Fig. 2 shows the temperature variation in the broadening width. We found that the broadening width increases with an increase in the sintering temperature. Considering the fact that chemical reactions do not occur between ferrite and Ag, it is thought that the thermally accelerated diffusion of Ag is not due to chemical diffusion but to physical migration owing to the low melting point of Ag.

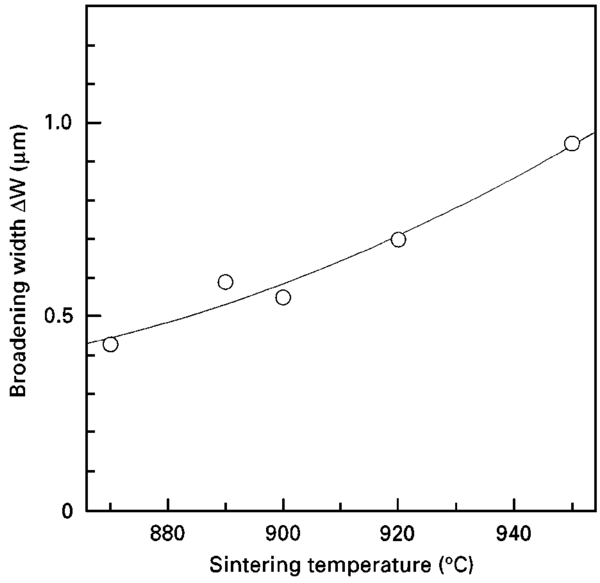

Figure 2 The temperature variation in the broadening width, ΔW. The solid curve is drawn as a guide for the eyes.

The specimen were then subjected to sintering at 900 or 920 °C, and the influence of additive impurities on the interfacial diffusion of Ag was investigated. The EDXA results are listed in Table I. In all cases where the ferrite contained an additive impurity, the broadening width is greater than that of the ferrite without the additive. This implies that the interfacial diffusion of Ag is promoted by the presence of the impurity. In particular, the presence of SiO_2 and Cl^- ions was associated with marked increases in the interfacial diffusion of Ag. It is also well known that these impurities lead to the formation of the liquid phase during the sintering, promote densifications and alter the ferrite grain growth [6, 7]. The electrode material Ag may not react directly with the ferrite particles but rather with the liquid phase. Consequently, the diffusion of Ag can be enhanced during ferrite sintering.

TABLE I The variation in the broadening width, ΔW, with the sintering temperature and the additive impurities.

Additive	Additional amount (wt %)	Sintering temperature (°C)	Broadening width, ΔW (μm)
NiO	1.0	900	0.75
NiO	1.0	920	0.85
ZnO	1.0	900	0.73
ZnO	1.0	920	0.91
CuO	1.0	900	0.60
CuO	1.0	920	0.72
CaO	1.0	920	0.97
SiO_2	1.0	920	1.33
NH_4Cl	1.0	920	1.80
$(NH_4)_2SO_4$	1.0	920	0.55

We also found that the ferrite grain growth varies with the presence of CaO and SiO_2 impurities. The SEM photographs of the fractured surface for the specimen containing CaO and SiO_2 impurities sintered at 920 °C are shown in Fig. 3. The average diameters of the ferrite grain were estimated by geometric analysis. The specimens with no additive, which were sintered at 920 °C, have an average ferrite grain size of approximately 1.0 μm. The average ferrite grain sizes of the sintered ceramics containing CaO and SiO_2 impurities are approximately 0.8 μm and 3.0 μm, respectively. It is clear that SiO_2 enhances the ferrite grain growth.

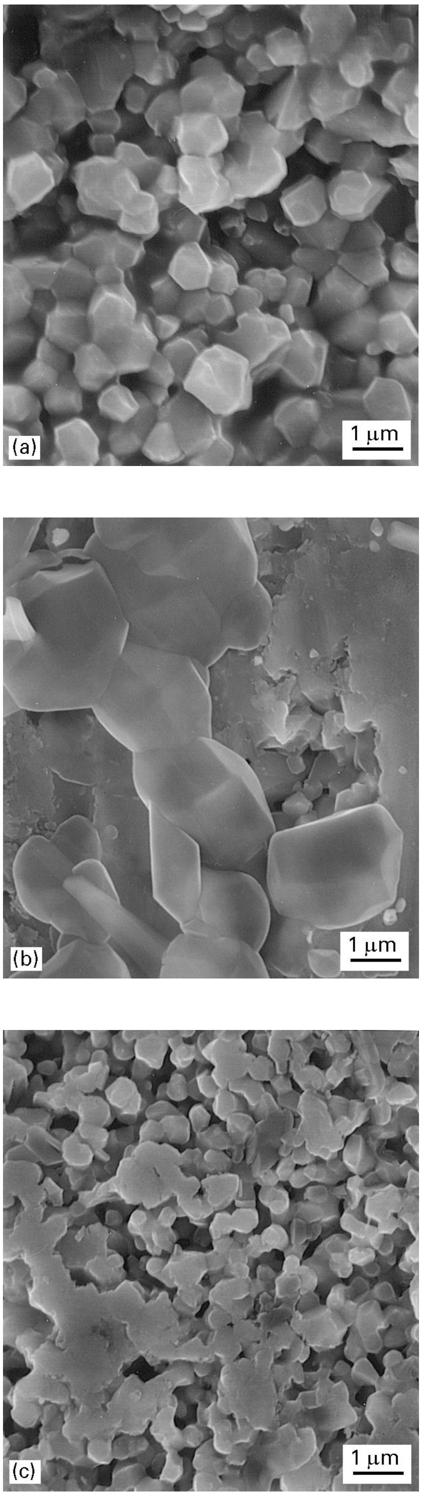

Figure 3 Scanning electron microphotographs of the fracture surface of the sintered ferrite: (a) sintered at 920 °C without the additive; (b) sintered at 920 °C with SiO_2 addition of 1 wt%; (c) sintered at 920 °C with CaO addition of 1 wt%.

Conversely, the presence of CaO slightly suppresses the ferrite grain growth.

As the Ag electrode material diffuses into the polycrystalline ferrite, the interface between ferrite and Ag increases and provides increases in the residual stress. This stress is produced during the cooling process and is due to the difference between the thermal expansion coefficients of ferrite and Ag [3–5]. In general, the residual stress is sensitive to the cooling rate, and its presence affects the permeability. Therefore, the interfacial diffusion causes poor reproducibility in the character of the chip inductor devices.

From these experimental results, we have made the following observations. Even though NiO, ZnO and CuO are constituting elements of the ferrite, an excess amount of these elements promotes diffusion. This implies that, in order to suppress the interfacial diffusion of Ag, complete ferrite formation is required before the co-firing process. As the concentrations of CaO and SiO_2 (typical impurities in the ferrite) increase, the Ag diffusion also greatly increases. This shows that attention must be paid to the purity of the starting materials. We also found that, of the impurity anions originating from the Fe source material (ferrous sulphate or ferric chloride), Cl^- is more likely to enhance the interfacial diffusion of Ag than SO_4^{2-} Fe_2O_3 particles synthesized from ferrous sulphate can be utilized for this.

Since chip inductor devices are becoming more and more compact, it has become necessary to obtain high-permeability ferrite sintered ceramics. From the results of our previous studies on the permeability spectra of polycrystalline ferrite [1, 2], it became evident that both a high sintering density and large ferrite grains are necessary for the synthesis of high-permeability ferrite. It is thought that both these can be obtained through the liquid-phase formation during the sintering process. Therefore, the liquid-phase formation is considered necessary for the synthesis of the high-permeability ferrite. However, the liquid phase formation causes diffusion of the Ag electrode material during the sintering and, consequently, leads to residual stress during the cooling process, which in turn results in a decrease in the permeability. Accordingly, it is necessary to select carefully the kind and the quantity of the liquid phase, and the sintering temperature, and to take into account both the microstructure of the sintered ferrite and the Ag–ferrite interfacial properties in order to fabricate ferrite chips practically.

4. Conclusion

We used the SEM–EDXA technique to study the interfacial diffusion between Ni–Zn–Cu ferrite and Ag electrode material during the co-firing process at temperatures ranging from 850 to 950 °C. We found that the interfacial diffusion of Ag electrode material, which was not chemical diffusion but physical migration, was enhanced with an increase in the sintering temperature. We also found that the interfacial diffusion was promoted by the presence of some impurities, especially SiO_2 and Cl^- ions. These ions were closely associated with the liquid-phase formation during the sintering process. This liquid-phase formation was suitable for the synthesis of high-permeability ferrite ceramics but unfavourable for the suppression of the interfacial diffusion of the Ag electrode material. Accordingly, it was necessary to select carefully appropriate preparation conditions, such as the chemical impurities of the ferrite powders and the sintering temperature.

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