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Interface reactions between SiO_2-PbO glass and Ni-Zn ferrite

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The interface reactions between SiO_2-PbO melt and Ni-Zn ferrite were studied using electron probe microanalysis and X-ray diffraction. The mechanisms of interface reaction were investigated in relation to the glass-forming region. No intermediate layers were produced at the interface between SiO_2-PbO glass and Ni-Zn ferrite because of the small amount of dissolution of Ni^{2+} ion from the ferrite. A model of the interface reaction mechanism between SiO_2-PbO melt and Ni-Zn ferrite is proposed.

1. Introduction

In recent years, not only oxide glasses but also non-oxide glasses, such as chalcogenide, have been extensively applied to electric devices [1]. For developing these devices, the behaviour of interfaces and surfaces have been investigated with various techniques of surface analysis, for example electron probe microanalysis (EPMA), Auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA). Until recently, little attention has been given to the reactions between magnetic materials and oxide glasses. It is important to reveal the mechanism of the interface reactions thoroughly for developing composite magnetic devices.

Pask and co-workers [2-12] studied the interface reaction between metals and glasses based on the concept of wettability.

Takasio [13-16] studied the interface reactions between metals and glasses from the viewpoint of thermodynamics. Tanigawa and co-workers [17, 18] reported the interface reactions between Mn-Zn ferrite and lead silicate glasses. They reported that $PbO \cdot 2Fe_2O_3$ is deposited in the mixture of Mn-Zn ferrite and SiO_2-PbO glass during heat-treatment in air. In addition, Mino and Watanabe [19] studied the interface reaction between Mn-Zn ferrite and lead silicate glasses and observed that intermediate layers with many pores are formed at the interface and the formation of those layers depends on the surface condition of the ferrite caused by polishing.

Recently, Nitta *et al.* [20] have studied the interface reactions between Mn-Zn ferrite and SiO_2-PbO melts. It was found that intermediate layers which consisted of $Pb_2(Mn, Fe)_2Si_2O_9$ and $Pb_8(Mn, Fe)Si_6O_{21}$ crystals are deposited at the interface between glass and ferrite. They suggested that these reaction processes are dominated by the dissolution of Zn^{2+} and Mn^{2+} ions in ferrite into the melts and by the viscosities of the melts.

The purpose of the present study is to investigate the interface reaction between Ni-Zn ferrite and SiO_2-PbO melts based on the concept of the glass-forming region [21]. Ni-Zn ferrite is also one of the more important magnetic mateirals as well as the Mn-Zn ferrite studied in the previous report [20].

2. Experimental procedure

2.1. Glass preparations

The glasses were prepared as described previously [20, 21]. The raw materials used were reagent-grade SiO_2 and Pb_3O_4. Batches for producing 300 g glass were placed in platinum crucibles and melted in an electric furnace in an open atmosphere at 1400° C for 2 h. The melts were cast on to a hot steel plate. The glass compositions used were $60SiO_2$-40PbO and $50SiO_2$-50PbO (mol %). These glasses are denoted hereafter for convenience as SP64 and SP55, respectively.

2.2. Interface reactions

The procedures for observing the interface reactions were almost the same as those reported previously [20]. The glasses were crushed, and remelted in alumina crucibles at 1000° C in an open atmosphere. After refining, the Ni-Zn ferrite was immersed in the melt and kept at a constant temperature for 15 or 60 min. The temperatures of heat treatment were 800, 900 and 1000° C. All experiments were performed under an open atmosphere. After heat treatment, the furnace was turned off and the glass-ferrite composite was allowed to cool slowly to room temperature. The cooling rate was approximately $2\,K\,min^{-1}$. Samples were cut out from the alumina crucible and polished into the desired shape for measurements.

2.3. SEM and EPMA observations

A scanning electron microscope (SEM) was used to observe the interface between Ni-Zn ferrite and glass. The chemical compositions at the interface were analysed by EPMA with a wavelength-dispersive

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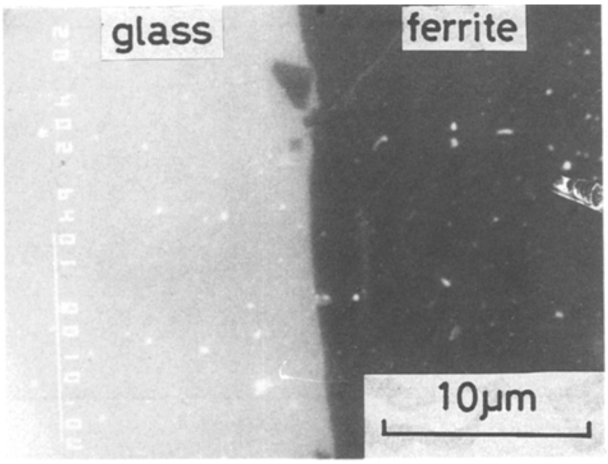

Figure 1 Scanning electron micrograph of interface between SP64 glass and Ni–Zn ferrite heat-treated at 900° C for 1 h.

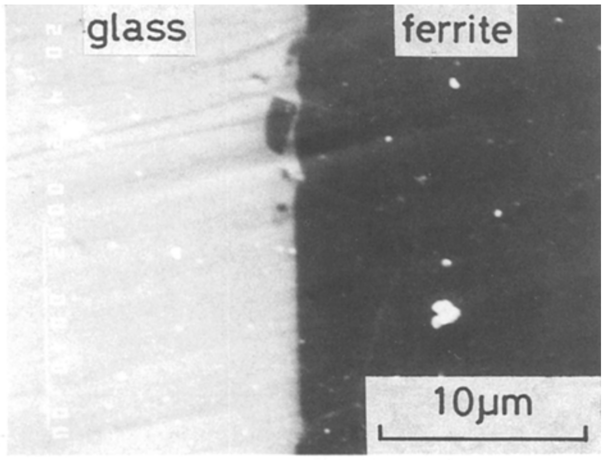

Figure 2 Scanning electron micrograph of interface between SP55 glass and Ni–Zn ferrite heat-treated at 900° C for 1 h.

X-ray spectroscopy (WDX) attachment using Fe*Kα*, Ni*Kα*, Zn*Kα*, Pb*Lα* and Si*Kα* for line traces.

3. Results

Figs 1 and 2 show scanning electron micrographs of the interface between SP64 glass and Ni–Zn ferrite and that between SP55 glass and Ni–Zn ferrite, respectively, heat-treated at 900° C for 1 h. In previous work [20] we reported that intermediate layers which consist of $Pb_2(Mn, Fe)_2Si_2O_9$ and $Pb_8(Mn, Fe)Si_6O_{21}$ crystals were precipitated at the interface between SiO_2–PbO glass and Mn–Zn ferrite. In this study, however, SEM observations show no intermediate layers at the interface between both glasses and Ni–Zn ferrite. Moreover both glasses show no signs of crystallization.

The lines traced by WDX for the interface between SP55 glass and Ni–Zn ferrite heat-treated at 900°C for 1 h are shown in Fig. 3. These results also show that there are no intermediate layers at the interface. Figs 4a and b show the images for the characteristic X-rays of Ni*Kα* and Zn*Kα*, respectively, in the same area as shown in Fig. 3. It is seen that grains separated from the bulk of the Ni–Zn ferrite contain hardly any Zn^{2+} ion although they have a strong intensity of Ni*Kα*. Figs 5a and b show a scanning electron micrograph of the interface of SP55 glass and Ni–Zn ferrite heat-treated at 1000° C for an hour and the lines traced by the characteristic X-rays of iron, nickel, zinc, lead and silicon. The white bar is the line along which the chemical composition was analysed. It is important to notice that the lines traced by Ni*Kα* and Zn*Kα* indicate a higher concentration of nickel and a lower concentration of zinc at the surface of the ferrite than those in the interior of the ferrite.

In the case of SP64 glass, EPMA shows the same result as for SP55 glass. However, the spread of the concentration gradient in ferrite is found to be narrower than in the case of SP55 glass. The concentration gradients described above were not observed at the interface heat-treated at 1000° C for 15 min.

4. Discussion

Nitta *et al.* [21] previously studied the glass-forming region of ternary SiO_2–PbO–MO (M = Fe, Mn, Ni and Zn) systems and found that the glass-forming regions of SiO_2–PbO–ZnO and SiO_2–PbO–MnO are largest and that of SiO_2–PbO–NiO is narrowest. The glass-forming region may be regarded as a measure of the solubility of a component of the ferrite in the SiO_2–PbO glass melt. Therefore, it is thought that Mn^{2+} and Zn^{2+} ions in ferrite should dissolve into the

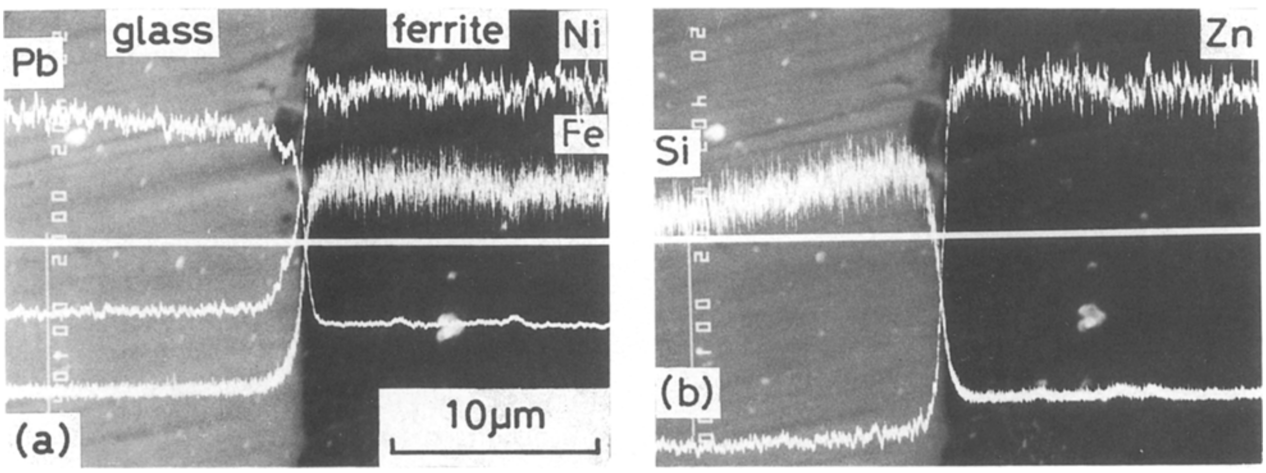

Figure 3 Lines traced by characteristic X-rays across the interface between SP55 glass and Ni–Zn ferrite heat-treated at 900° C for 1 h: (a) iron, nickel and lead; (b) zinc and silicon.

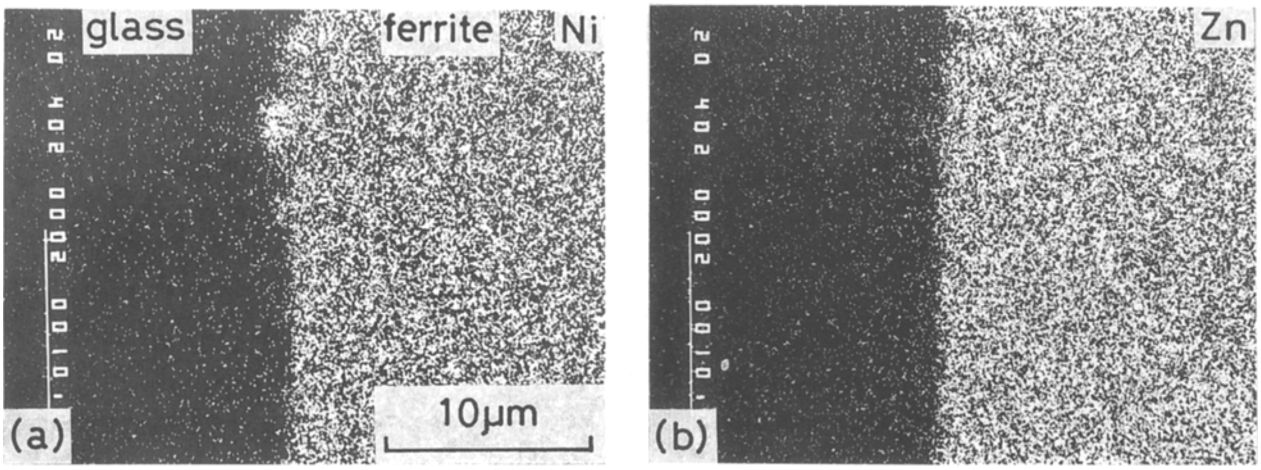

Figure 4 Images of same area as Fig. 3 using X-rays: (a) nickel, (b) zinc.

SiO_2–PbO melt very easily and Ni^{2+} ions should remain in the ferrite. Based on these concepts, Nitta *et al.* [20] analysed the interface reactions between SiO_2–PbO melt and Mn–Zn ferrite at high temperatures at which intermediate layers were found.

In the present study, we may discuss the interface reaction between SiO_2–PbO melt and Ni–Zn ferrite on the basis of the same concept. As shown in Fig. 5, the intensity of the characteristic X-rays for nickel in the ferrite increases near the interface, while that of zinc decreases. Figs 4a and b also show the same behaviour relating to the concentrations of nickel and zinc in crystal grains separated from the ferrite body. As remarked above, Zn^{2+} ions in Ni–Zn ferrite easily dissolve into the melt and diffuse fast, giving rise to a uniform concentration in the melt. Ni^{2+} ions tend to remain in the ferrite, and accordingly Fe^{3+} ion would not dissolve into the melt as easily as in Mn–Zn ferrite. Therefore, intermediate layers are not formed at the interface between Ni–Zn ferrite and SiO_2–PbO melt as they are in the case of Mn–Zn ferrite.

According to these results, we suggest a mechanism of reactions between SiO_2–PbO melt and Ni–Zn ferrite as shown in Fig 6. First, Zn^{2+} ions in Ni–Zn ferrite dissolve fast into the SiO_2–PbO melt while few Ni^{2+} ions dissolve, so the melt contains few Fe^{3+} ions. After dissolving in the melt, Zn^{2+} ions diffuse away from the interface and the concentration becomes uniform in the melt. As a result, Ni^{2+} ions are accumulated near the interface region in the ferrite.

5. Conclusion

The interface reactions between SiO_2–PbO melt and Ni–Zn ferrite have been investigated. No intermediate layers were produced at the interface between SiO_2–PbO glass and Ni–Zn ferrite because there was little dissolution of Ni^{2+} ions. Among the components of ferrite, Zn^{2+} ions dissolve into the melt easily and Ni^{2+} ions remain in the ferrite, giving rise to surface layers of ferrite in which the nickel concentration is high and the zinc concentration is low. In addition, grains separated from the Ni–Zn ferrite body have a low concentration of zinc at below 1000° C.

The diffusion of Zn^{2+} ions in the melt dominates the reaction between SiO_2–PbO melt and Ni–Zn ferrite as well as Mn–Zn ferrite. We suggest a model mechanism of reaction between SiO_2–PbO melt and Ni–Zn ferrite.

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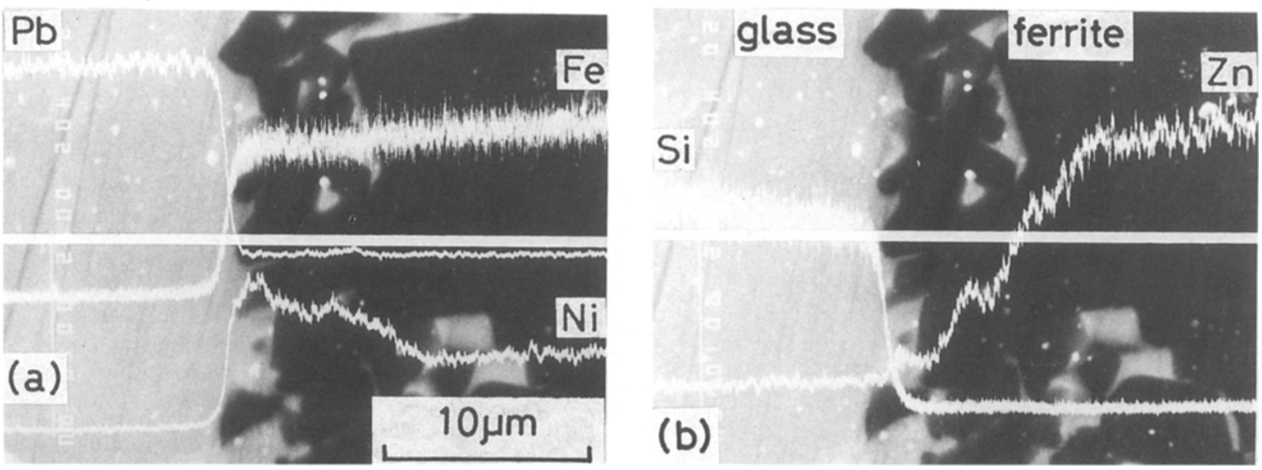

Figure 5 EPMA for interface between SP55 glass and Ni–Zn ferrite heat-treated at 1000° C for 1 h: (a) traces for iron, nickel and lead; (b) traces for zinc and silicon.

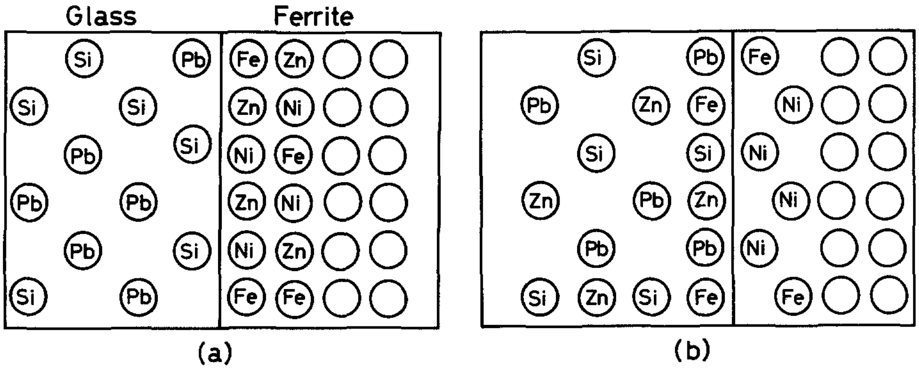

Figure 6 Model mechanism of reaction between SiO_2–PbO melt and Ni–Zn ferrite: (a) before interface reaction. (b) after interface reaction.

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