JOURNAL OF MATERIALS SCIENCE 29 (1994) 2629–2632

Interface reactions between glass melts containing transition metal oxides and ferrites

A. NITTA*, T. ONO‡, T. KOMATSU, K. MATUSITA
Department of Chemistry, Nagaoka University of Technology, Kamitomiokacho, Nagaoka, Niigata-ken 940-21, Japan

The interface reactions between SiO_2–PbO–MO melts (M = Fe, Mn, Zn and Ni) and Mn–Zn and Ni–Zn ferrites were studied using electron probe microanalysis and X-ray diffraction. Ni ions in the glass melt containing NiO were localized at the interface between the glass and Mn–Zn ferrite. The Ni-rich layer was also detected at the interface between NiO containing glass melt and Ni–Zn ferrite; the composition of this layer was thought to be close to $NiFe_2O_4$. $Pb_8NiSi_6O_{21}$ crystal was deposited as the product of the reaction with the glass melt and Mn–Zn ferrite at 700 °C. As compared with Mn–Zn ferrite, no reaction products were formed in Ni–Zn ferrite at various temperatures. The dissolution length of Mn–Zn ferrite in SPN5 glass melt was found to be smaller than for other melts, and it is concluded that the NiO-rich layer at the surface of the ferrite is chemically very durable to the glass melts.

1. Introduction

It is important to investigate the interface and surface reactions between various substances for the development of many composite devices. Oxide glasses have been extensively applied for electrical industrial products, although there have been only a few investigations on the interface reactions between glasses and various materials.

Previously, Pask and co-workers [1–3] and Takashio [4–7] have studied the interface reactions between metals and oxide glasses. Concerning the reactions of magnetic materials, Tanigawa *et al.* [8, 9] and Mino & Watanabe [10] have studied the interface reactions of Mn–Zn ferrites with oxide glasses, and Matusita *et al.* [11, 12] have studied the interface reaction between Fe–Al–Si alloy (SENDUST) and various oxide glass melts, analysing the reactions based on the standard free energy diagrams of the oxidation–reduction reaction. However, more systematic studies are expected to reveal the interface reaction between oxide glasses and ferrites.

Recently, Nitta *et al.* [13–16] studied the interface reactions between some ferrites and oxide glass melts. They reported that the intermediate layers were formed at the interface between the Mn–Zn ferrite and the glass melt such as SiO_2–PbO, SiO_2–PbO–$FeO_{1.5}$, or SiO_2–PbO–MnO. However, at the interface between Mn–Zn ferrite and SiO_2–PbO–ZnO melt, no intermediate layers were observed. In this case, it was found that Zn ions in the melt diffuse from the melt into the ferrite, giving rise to the high Zn ion concentration near the interface in the ferrite.

It is necessary to reveal the effect of various components on the interface reaction mechanisms between oxide melts and ferrites for developing devices such as magnetic heads. The purpose of this report is to investigate the interface reactions between SiO_2–PbO–NiO ternary melt and Mn–Zn and Ni–Zn ferrites, and in particular, to reveal the effect of NiO on the reaction. For comparison, the effects of other components were also studied.

2. Experimental procedure

The Mn–Zn and Ni–Zn ferrites used in this study were polycrystalline, with chemical compositions of $Mn_{1.8}ZnFe_{6.2}O_{12.1}$ and $Ni_{0.7}ZnFe_4O_{7.7}$, respectively, in atomic ratio. The glass compositions used are shown in Table I and are expressed hereafter as SP64, SPM5, SPF5, SPZ5, and SPN5. The procedures for glass preparation and observation of the interface reactions were the same as reported previously [13–15]. A scanning electron microscope (SEM) and electron probe microanalysis (EPMA) with wavelength-dispersive X-ray spectroscopy (WDX) were also used to analyse the interface reactions, as reported previously [13–15].

The ferrite specimens, rectangles of 5 × 5 × 15 mm, were immersed in the glass melts in alumina crucibles and kept at 1000 °C for 15–63 min under the atmosphere. The specimens were cut out from the crucible and polished into the desired shapes for SEM and EPMA measurements. The size of the ferrite before and after the immersion in the melts was measured

Present addresses: *ALPS Electric Co. Ltd, Nagaoka Plant, 1-3-5 Higashitakami, Nagaoka, Niigata-ken 940, Japan.
‡ Corning Japan K. K., Shizuoka Operations Center, Technical Center 12117, Ohbuchi, Osuka-cho, Ogasa-gun, Shizuoka 437-13, Japan.

precisely using micrometer and photographic observation. The dissolution length was calculated from the size diminution during immersion.

3. Results and discussion

Fig. 1 shows SEM photographs and the lines traced by WDX of the interface between SPN5 glass and Mn–Zn ferrite, heat-treated at 1000 °C for 1 h. As seen in Fig. 1, the lines traced by characteristic X-rays of Fe and Zn monotonically change in close vicinity to the interface, while the concentration of Mn is high in this interface region. In contrast, the concentration of Ni shows a maximum at the interface between glass and ferrite, indicating that Ni ions in the melt localize at the interface. It is obvious that Ni ions in the melt diffuse into the ferrite, suggesting that the Ni ions in the melt have high chemical potential. This coincides with the narrow glass-forming regions of the SiO_2–PbO–NiO ternary system compared with the wide glass-forming regions of SiO_2–PbO–MO (M = Mn, Fe, and Zn) systems [17].

According to X-ray diffraction (XRD) analysis of powder mixtures of SPN5 glass and Mn–Zn ferrite heat-treated at 700 °C for 1 h, $Pb_8NiSi_6O_{21}$ crystal was found as the reaction product, but no reaction

TABLE I Glass Composition (in mol %)

Glass	SiO_2	PbO	MnO	$FeO_{1.5}$	ZnO	NiO
SP64	60	40	–	–	–	–
SPM5	55	40	5	–	–	–
SPF5	55	40	–	5	–	–
SPZ5	55	40	–	–	5	–
SPN5	55	40	–	–	–	5

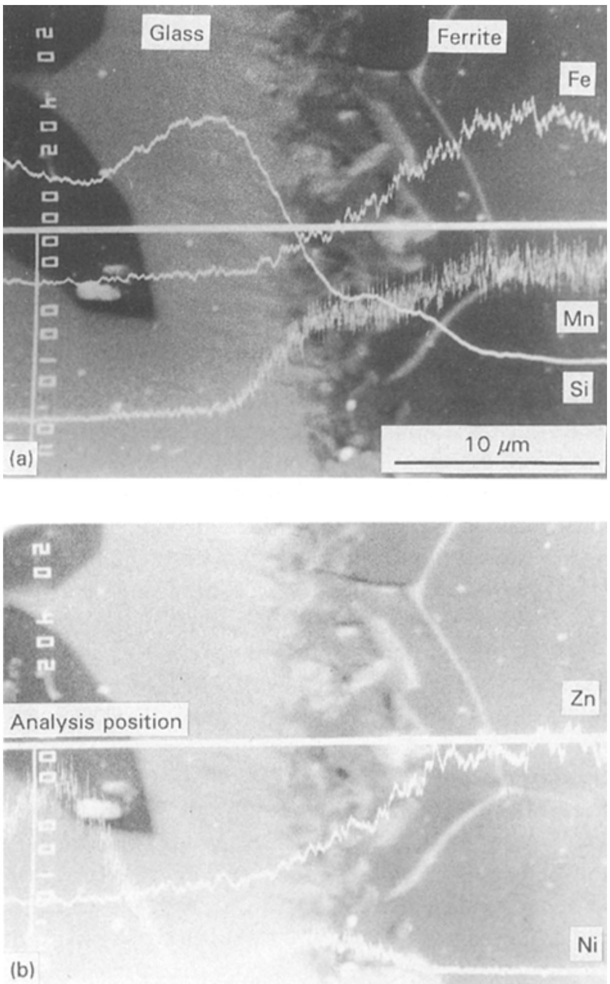

Figure 1 Line traced by characteristic X-rays of Fe, Mn, Si, Zn, and Ni across the interface between SPN5 glass and Mn–Zn ferrite heat-treated at 1000 °C for 60 min.

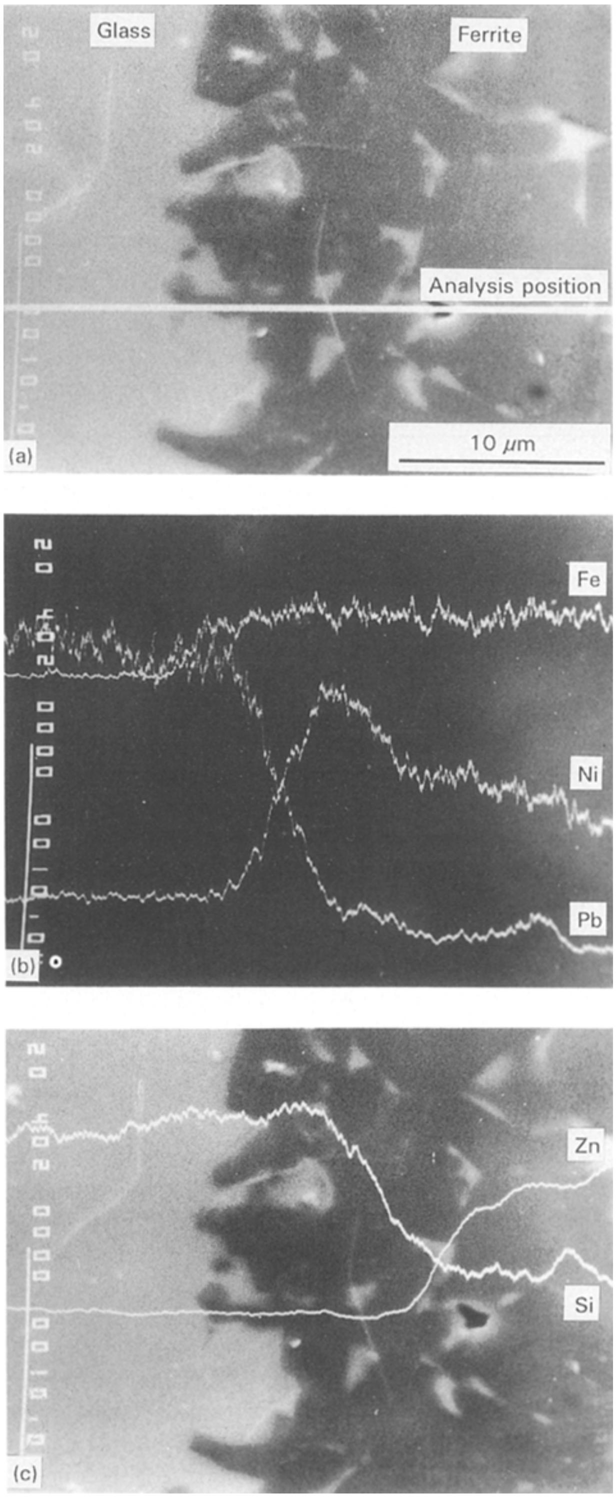

Figure 2 Line traced by characteristic X-rays of Fe, Ni, Si, and Pb across the interface between SPN5 glass and Ni–Zn ferrite heat-treated at 1000 °C for 60 min.

products were detected in the specimens heat-treated at above 800 °C.

Fig. 2 shows SEM photographs and the lines traced by WDX of the interface between SPN5 glass and Ni–Zn ferrite, heat-treated at 1000 °C for 1 h. As seen in Fig. 2, Ni ions also localized at the interface between glass and ferrite, although Fe and Zn ions change almost monotonically in close vicinity of the interface. It is thought that Ni ions diffuse into Ni–Zn ferrite from the glass melt because of the high chemical potential of Ni ions in the melt [17]. As a result, the composition of the ferrite should be close to $NiFe_2O_4$ at the interface.

Figs 3 and 4 show the relationship between reaction time and dissolution length of Mn–Zn and Ni–Zn ferrites, respectively, immersed in various glass melts at 1000 °C. It is seen that the slope of the dissolution length of Mn–Zn ferrite in Fig. 3 is steeper than that of Ni–Zn ferrite in Fig. 4, indicating that Ni–Zn ferrite is more durable to the glass melt. It is noticeable, however, that the dissolution rate of Mn–Zn ferrite is remarkably low in the melt containing NiO, compared with those in NiO-free melts, as seen in Fig. 3. This indicates that the Ni-rich layer formed at the interface between SPN5 melt and Mn–Zn ferrite is chemically durable to the melt.

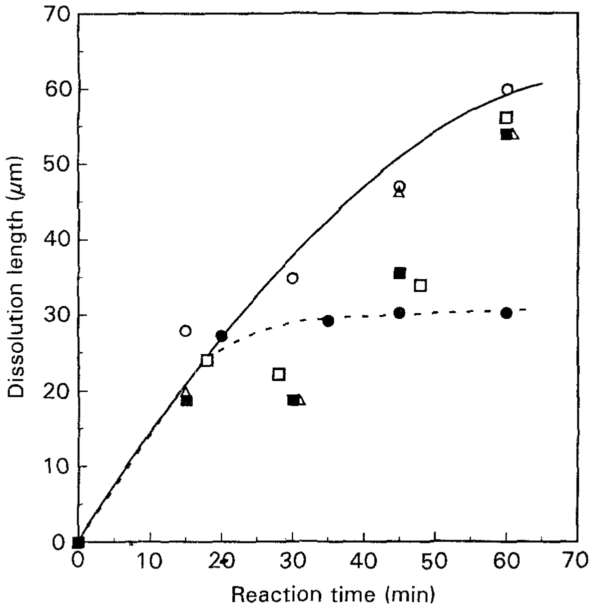

Figure 3 Relationship between reaction times and dissolution lengths of Mn–Zn ferrite immersed in various glasses at 1000 °C. ■, SP64; ○, SPF5; △, SPM5; ●, SPN5; □, SPZ5.

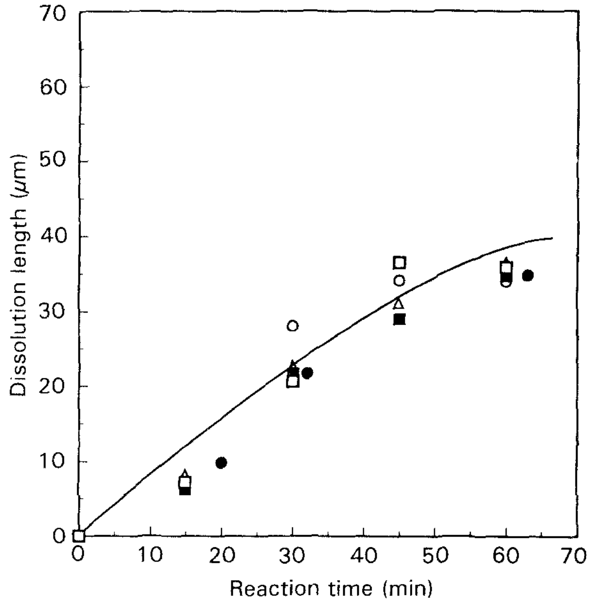

Figure 4 Relationship between reaction times and dissolution lengths of Ni–Zn ferrite immersed in various glasses at 1000 °C. ■, SP64; ○, SPF5; △, SPM5; ●, SPN5; □, SPZ5.

Nitta *et al.* [15] previously studied the interface reaction between Ni–Zn ferrite and SiO_2–PbO melt. They reported that the Zn ions dissolve from the ferrite into the melts and the Ni ions remain in the ferrite, giving rise to the formation of a durable layer of NiO high concentration at the interface.

4. Conclusion

The interface reactions between SiO_2–PbO–MO melt (M = Fe, Mn, Zn and Ni) and Mn–Zn and Ni–Zn ferrites have been investigated. It was found that in the reaction of SPN5 melt and Mn–Zn ferrite, Ni ions in the melt localized at the interface, indicating that the Ni^{2+} ions in the melt diffuse into the ferrite. Moreover, even in the reaction in SPN5 melt and Ni–Zn ferrite, the Ni^{2+} ions in the melt were found to diffuse into the ferrite.

It was also found that the dissolution length of Mn–Zn ferrite in SPN5 melt is smaller than that in any other melts, indicating that the Ni-rich layer is chemically durable to the glass melt.

Acknowledgements

The present work was supported by the Japanese Ministry of Education, Science and Culture with a Grant-in-Aid for Science Research of fiscal years 1991/1992. The authors wish to express their sincere thanks to ALPS Electrical Company for financial support and encouragement.

References

1. M. P. BOROM and J. A. PASK, *J. Amer. Ceram. Soc.* **49** (1966) 1.
2. C. E. HOGE, J. J. BRENNAN and J. A. PASK, *ibid.* **56** (1973) 1.
3. J. J. BRENNAN and J. A. PASK, *ibid.* **56** (1973) 58.
4. H. TAKASHIO, *Yogyo Kyokaishi* **82** (1974) 248.
5. *Idem, ibid.* **84** (1976) 383.
6. *Idem, ibid.* **84** (1976) 548.
7. *Idem, Bull. Ceram. Soc. Jpn* **15** (1980) 427.
8. H. TANIGAWA, T. UENO and K. FUKUSHIMA, *Bull. Gov. Ind. Res. Inst., Osaka* **25** (1974) 142.
9. H. TANIGAWA, T. UENO and Y. NISHIDA, *ibid.* **27** (1976) 68.
10. M. MINO and H. WATANABE, *J. Jpn. Soc. Precis. Engng* **44** (1978) 685.
11. K. MATUSITA, M. SATOU, T. KOMATSU and A. NITTA, in Proceedings of the International Conference on Science and Technology for New Glasses, Tokyo, October 16–17 1991, Tokyo, edited by S. Sakka and N. Soga (Ceramic Society of Japan) p. 163.
12. K. MATUSITA, M. SATOU, T. KOMATSU and A. NITTA, *J. Mater. Sci.* **28** (1993) 6333.

13. A. NITTA, H. NAKAMURA, T. KOMATSU and K. MATUSITA, *J. Amer. Ceram. Soc.* **72** (1989) 1351.
14. A. NITTA, T. KOMATSU, K. MATUSITA and A. INADA, in Proceedings of XV International Congress on Glass in Leningrad, July 3–7, 1989 **Vol. 3b** edited by O. V. Mazurin (Nauka, Leningrad, 1989) p. 326.
15. A. NITTA, H. NAKAMURA, T. KOMATSU and K. MATUSITA, *J. Mater. Sci.* **25** (1990) 2857.
16. *Idem, J. Appl. Phys.* **71** (1992) 1992.
17. A. NITTA, T. MIURA, T. KOMATSU and K. MATUSITA, *J. Amer. Ceram. Soc.* **72** (1989) 163.

Received 2 April
and accepted 1 November 1993