Interface reactions between manganese zinc ferrite single crystals and SiO2PbOZnO ternary systems

Hae June Je, Do Kyung Kim, Chong Hee Kim, Kug Sun Hong, Byeong Won Park et al.

Related Articles

Enhancement of perpendicular magnetic anisotropy through reduction of Co-Pt interdiffusion in (Co/Pt) multilayers
Appl. Phys. Lett. 100, 142410 (2012)

Organic salts as super-high rate capability materials for lithium-ion batteries
Appl. Phys. Lett. 100, 091905 (2012)

A unified interdiffusivity model and model verification for tensile and relaxed SiGe interdiffusion over the full germanium content range
J. Appl. Phys. 111, 044909 (2012)

Insulation and diffusion barrier characteristics of spin-on-glass layer on a stainless steel substrate
J. Renewable Sustainable Energy 4, 011603 (2012)

How do InAs quantum dots relax when the InAs growth thickness exceeds the dislocation-induced critical thickness?
J. Appl. Phys. 111, 013709 (2012)

Additional information on J. Appl. Phys.

Journal Homepage: http://jap.aip.org/

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: http://jap.aip.org/authors

Interface reactions between manganese zinc ferrite single crystals and SiO_2-PbO-ZnO ternary systems

Hae June Je,[a] Do Kyung Kim, and Chong Hee Kim
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

Kug Sun Hong
Department of Inorganic Materials Engineering, Seoul National University, Seoul 151-742, Korea

Byeong Won Park and Sung Do Jang
Division of Ceramics, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

Interface reactions between Mn-Zn ferrite single crystals and SiO_2-PbO-ZnO ternary systems were investigated using scanning electron microscope, electron probe microanalyzer, and x-ray diffractometer. The addition of ZnO in a SiO_2-PbO glass resulted in inhibition of formation of the intermediate phase and suppression of dissolution of the ferrite. The interface morphology became a dendrite structure with increase of ZnO concentration in the glass. Appearance of the anomalous concentration profile of Zn and Mn at the ferrite adjacent to the interface was investigated in terms of the dissolved quantity of Mn and Zn ion. It was found that Zn ion has dissolved from the ferrite into the glass melt during the reaction and Mn ion in the ferrite dissolved into the glass melt more than Zn ion, resulting in changing the undissolved ferrite adjacent to the interface into a Zn-rich Mn-Zn ferrite, $Mn_{0.16}Zn_{0.85}Fe_2O_4$, after reaction with $57SiO_2$-$38PbO$-$5ZnO$ (in mol %) glass. It was considered that the source of the hump of Zn concentration at the ferrite adjacent to the interface would be the undissolved, remaining Zn ions. A microscopic model was suggested. © *1995 American Institute of Physics.*

I. INTRODUCTION

The unique magnetic properties and the outstanding wear resistance of manganese zinc ferrite (Mn-Zn ferrite) single crystals have promoted their use as a material for VCR heads.[1,2] The track part of the magnetic heads for VCR interchanging magnetic signals with magnetic tapes is composed of the very thin (~30 μm) ferrite single crystal surrounded by a bonding glass. The magnetic properties of the ferrites surrounded by the glass are degraded by the residual stress due to thermal expansion mismatch[3] and by the chemical reaction between them.[4] Therefore, it is important to reveal interface reactions between ferrites and glasses thoroughly. Only a few studies on interface reactions between polycrystalline ferrites and glasses have been reported.[5-13]

Previously, Tanigawa *et al.*[5,6] found that $PbO \cdot 2Fe_2O_3$ crystal was formed in mixtures of Mn-Zn ferrite and lead silicate glasses heat treated in air. It was reported that the grain boundary diffusion of the glass elements was dominant at the ferrite adjacent to the interface during the reaction and the magnetic properties of the diffusion layer were abruptly degraded.[7,8]

Recently, more systematic studies to reveal interface reactions have been performed by Nitta *et al.*[9-13] They reported that the intermediate layers, mixtures of $Pb_2(Mn, Fe)_2Si_2O_9$ and $Pb_8(Mn,Fe)Si_6O_{21}$ crystals, were formed at the interface between the Mn-Zn ferrite and the glass such as SiO_2-PbO binary system,[10] and SiO_2-PbO-MnO or SiO_2-PbO-$FeO_{1.5}$ ternary system.[12] However, no intermediate lay-

ers were observed at the interface between the Mn-Zn ferrite and the SiO_2-PbO-ZnO ternary system[12] and between the Ni-Zn ferrite and the SiO_2-PbO-NiO ternary system.[13] In these cases, they found an anomalous concentration profile that the concentrations of the transition elements (Zn, Ni ion) contained in the glass increased sharply at the ferrite adjacent to the interface. The reason of the hump of Zn or Ni concentration was thought that Zn or Ni ion in the glass has diffused into the ferrite even though Zn or Ni ion concentration in the glass was lower than that in the ferrite. They considered that the diffusion was caused not by the difference in concentration but by the difference in chemical potential. There was, however, no evidence that the chemical potential of Zn or Ni ion in the glass is higher than that in the ferrite.

The purpose of this article is to investigate thoroughly the interface reactions between the Mn-Zn ferrite and the SiO_2-PbO-ZnO ternary systems and the mechanism of the chemical reaction. The effect of the interface reactions on the morphology of the ferrite at the interface can also be investigated using the Mn-Zn ferrite single crystal instead of the polycrystalline ferrite.

II. EXPERIMENTAL PROCEDURE

A Mn-Zn ferrite single crystal used in this study was grown by composition-controlled Bridgman technique[14] to obtain crystal with a uniform composition. The chemical composition of the Mn-Zn ferrite was $Mn_{0.55}Zn_{0.37}Fe_{2.08}O_{4.04}$. The (100) plane of the Mn-Zn ferrite single crystal was reacted with glasses as the case of the practical magnetic head for VCR.[2] The glass compositions used in this study were shown in Table I. The amount of ZnO

---

[a]Present address: Division of Ceramics, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea.

TABLE I. Glass composition of SiO_2-PbO-ZnO ternary system.

z	SiO_2 (mol %)	PbO (mol %)	ZnO (mol %)
0	60.0	40.0	...
05	59.7	39.8	0.5
5	57.0	38.0	5.0
12	52.8	35.2	12.0

in glasses was varied from 0 to 12 mol % and those glasses were expressed hereafter as 0, 05, 5, and 12Z. The molar ratio of SiO_2 to PbO was fixed as 60:40 in all glass compositions. The concentration of ZnO was controlled within 12 mol % because the glass containing more than 12 mol % ZnO was devitrified after heat treatment. The raw materials of glass were reagent-grade SiO_2, PbO, and ZnO. After dry mixing the powders for 12 h, batches of glass were placed in platinum crucibles and melted at 1350 °C for 4 h in air. The melts were cast onto a steel mold.

A mirror-polished ferrite crystal with dimension of $6\times4\times1$ mm was sandwiched by glass specimens with dimension of $8\times6\times3$ mm. They were heat treated at 700, 800, 900, and 1000 °C in a platinum crucible. After heat treatment, ferrite crystals were surrounded by the glass. The heating and cooling rate was 5 °C/min. All specimens were heat treated under nitrogen atmosphere using a high-purity N_2 gas (>99.999%) in order to prevent the oxidation of ferrite crystals. Heat treatment implies the same meaning as the chemical reaction in this study.

Morphology of the interface between the ferrite crystal and glass was observed by scanning electron microscope (SEM). The chemical composition at the interface was analyzed by electron probe microanalyzer (EPMA) with a wavelength dispersive x-ray spectroscopy (WDX). The intermediate phases formed at the interface between the ferrite crystal and the glass were analyzed by x-ray powder diffractometer (XRD). In order to analyze the intermediate phases more clearly, the crushed powders of the ferrite crystal and the glasses were mixed at the same weight ratio. The mixtures were heat treated under the same conditions.

The sizes of the ferrite crystal before and after heat treatment were measured precisely using micrometer and SEM. The dissolution length was calculated from the size diminution during the reaction. When the ferrite crystal was locally corroded the base line of the dissolution length was the tip of convex, undissolved ferrite.

III. RESULTS

A. Effect of ZnO concentration

Figure 1 shows SEM micrographs and the lines traced by a WDX of the interface between the Mn-Zn ferrite single crystals and 0, 05, 5, and 12Z glasses heat treated at 900 °C for 1 h. The intermediate layer is observed at the interface between the ferrite and 0Z glass but not observed in the case of the glasses containing ZnO. With the increase of ZnO concentration in the glass, the interface morphology becomes a dendrite structure due to the local corrosion of the ferrite.
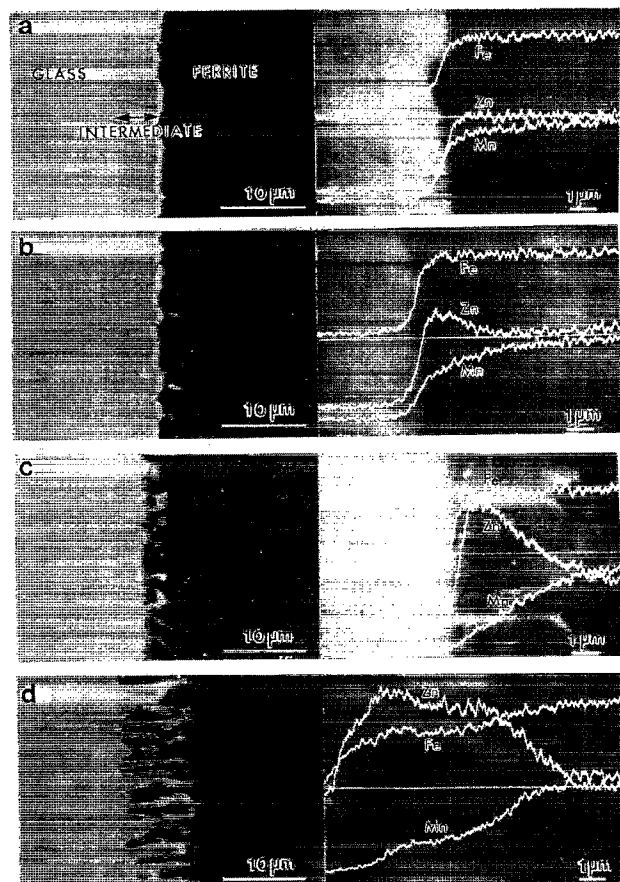

FIG. 1. SEM micrographs and lines traced by characteristic x rays of Fe, Zn, and Mn of interface between Mn-Zn ferrite single crystal and (a) 0Z, (b) 05Z, (c) 5Z, and (d) 12Z glasses heat treated at 900 °C for 1 h.

As shown in Fig. 1, the composition of Mn-Zn ferrite reacted with the glasses containing ZnO changes from inside to the interface. The Zn concentration near to the interface increases sharply, while the Mn concentration decreases symmetrically, and the Fe concentration decreases slightly. These anomalous concentration profiles, i.e., the hump of the Zn concentration at the ferrite adjacent to the interface appears even though the glass contains only 0.5 mol % ZnO. The height and width of the Zn hump increase with increase of the ZnO concentration in the glass.

Figure 2 shows x-ray diffraction patterns of the powder mixtures of Mn-Zn ferrite and 0, 05, 5, and 12Z glasses heat treated at 900 °C for 1 h. The intermediate phase in Fig. 1(a) is identified to be the same solid solution mixture, $[Pb_2(Mn,Fe)_2Si_2O_9$ and $Pb_8(Mn,Fe)Si_6O_{21}]$, as that of the previous study.[10] With increase of the ZnO concentration in the glass, the amount of these crystals decreases and they finally disappear. This result indicates that the Zn ions in the glass inhibit the formation of the intermediate phase at the interface. It is noticeable, however, that no second phase is formed but only spinel phase is detected even though the quantity of Zn ion increases at the ferrite adjacent to the interface, as shown in Fig. 1(d).

Figure 3 shows the effect of the ZnO concentration in the glass on the dissolution length of the Mn-Zn ferrite heat treated at 900 °C for 1 h. It decreases exponentially with increase of the ZnO concentration. The dissolution length of
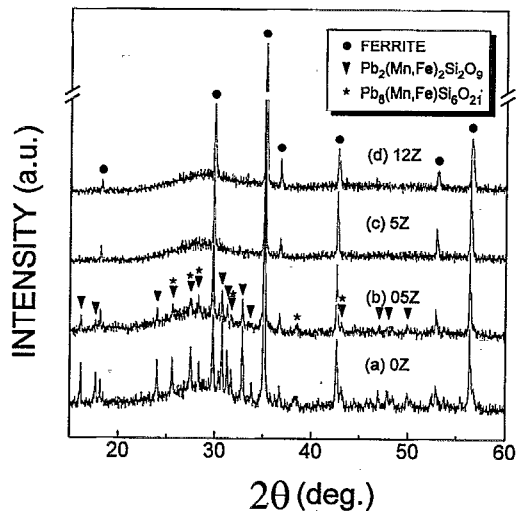
FIG. 2. X-ray diffraction patterns of powder mixtures of Mn-Zn ferrite and (a) 0Z, (b) 05Z, (c) 5Z, and (d) 12Z glasses heat treated at 900 °C for 1 h.

the ferrite reacted with the 0Z glass is about 27 μm whereas that with the 12Z glass is only 10 μm. This result indicates that the Zn ions in the glass suppress the dissolution of the ferrite.

B. Effect of reaction temperature

Figure 4 shows SEM micrographs and the lines traced by WDX of the interface between the Mn-Zn ferrite single crystal and the 5Z glass heat treated at 700, 800, 900, and 1000 °C for 1 h. At 700 °C, the interface maintains the original flat morphology, which indicates that the ferrite hardly dissolves at this temperature. At 800 °C, a dendrite morphology appears. With increasing the reaction temperature, however, the interface has a planar morphology. As shown in Fig. 4, the hump of the Zn concentration at the ferrite adjacent to the interface appears clearly above 800 °C and stays at similar height above 900 °C. The width of the hump increases with increasing temperature.

SEM micrograph and the lines traced by WDX of the interface between the Mn-Zn ferrite and the 0Z glass heat
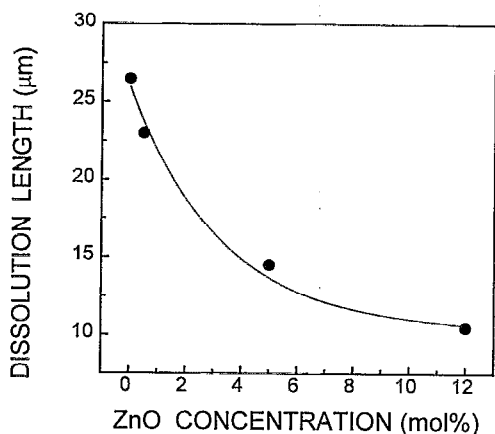

FIG. 3. Effect of ZnO concentration contained in glass on dissolution length of Mn-Zn ferrite heat treated at 900 °C for 1 h.
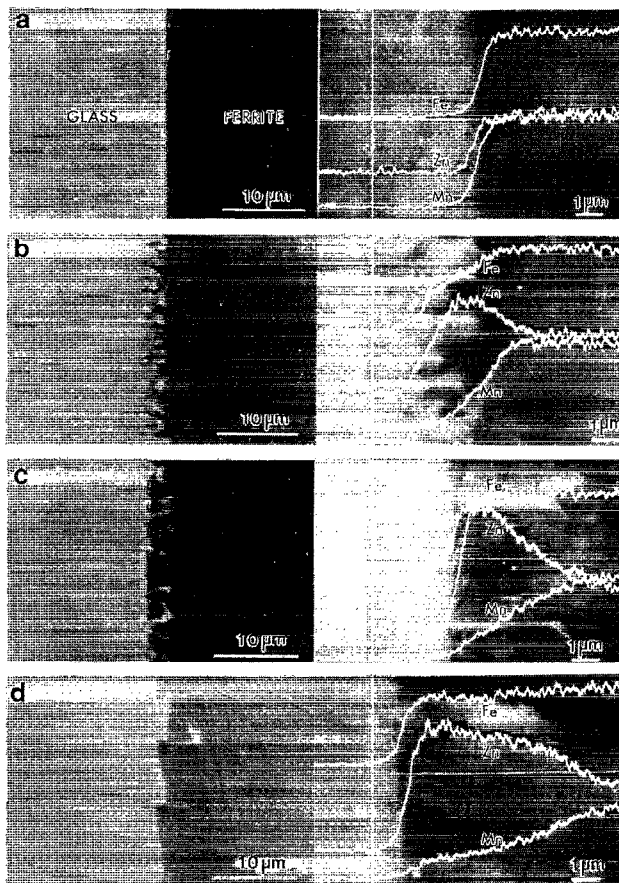

FIG. 4. SEM micrographs and lines traced by characteristic x rays of Fe, Zn, and Mn of interface between Mn-Zn ferrite crystal and 5Z glass heat treated at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C for 1 h.

treated at 1000 °C for 1 h are shown in Fig. 5. As compared with the result at 900 °C [Fig. 1(a)], the intermediate layer disappears, which coincides with the previous work.[10] It is noticeable that the Zn concentration at the ferrite adjacent to the interface increases very little and the Mn concentration decreases slightly. It indicates that the anomalous concentration profile appears in the case of the interface reaction between the Mn-Zn ferrite and the ZnO-free glass.

In order to thoroughly investigate the diffusion behaviors of the components of the Mn-Zn ferrite (ZnO, MnO, Fe_2O_3) at the interface during reaction, their concentrations in 0 and 5Z glasses were quantitatively analyzed by WDX before and after reaction at 1000 °C for 1 h. The analyzed zones were the inner parts of glass about 200 μm off the interface in Figs. 4(d) and 5. As shown in Table II, the concentrations of ferrite components in the glass increase after reaction due to the dissolution of the ferrite whether the glass contains Zn ion or not. It is noteworthy that the ZnO concentration in the 5Z glass increases slightly after reaction. This result indicates that the Zn ions in the ferrite dissolve into the glass during interface reaction even though the quantity of the Zn ion increases at the ferrite adjacent to the interface, which contradicts the previous work.[12]

Figure 6 shows x-ray diffraction patterns of the powder mixtures of the Mn-Zn ferrite and the 5Z glass heat treated at 700, 800, 900, and 1000 °C for 1 h. The mixture heat treated
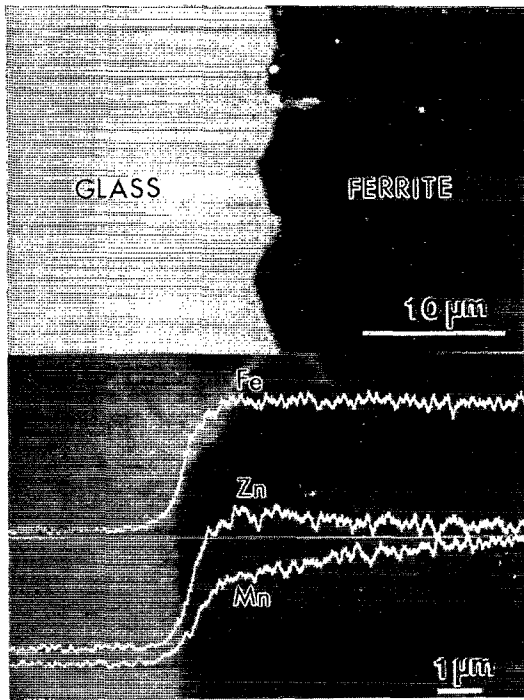
FIG. 5. SEM micrograph and lines traced by characteristic x rays of Fe, Zn, and Mn of interface between Mn-Zn ferrite crystal and 0Z glass heat treated at 1000 °C for 1 h.
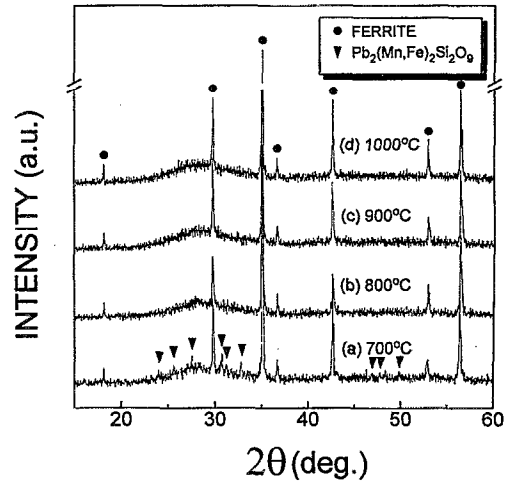

FIG. 6. X-ray diffraction patterns of powder mixtures of Mn-Zn ferrite and 5Z glass heat treated at (a) 700 °C, (b) 800 °C, (c) 900 °C, and (d) 1000 °C for 1 h.

C. Effect of reaction time

Figure 8 shows SEM micrograph and lines traced by WDX of the interface between the Mn-Zn ferrite single crystal and the 5Z glass heat treated at 900 °C for 10 h. The dendrite structure grows with increasing the reaction time due to the development of local corrosion of the ferrite. X-ray diffraction patterns of the powder mixtures of the ferrite and the 5Z glass heat-treated 900 °C for 1 and 10 h are shown in Fig. 9. It is also found that no second phase is formed even though the quantity of Zn ion increases at the ferrite adjacent to the interface.

The chemical composition of the undissolved ferrite adjacent to the interface indicated by A in Fig. 8 and of the inner ferrite that has no influence of the interface reactions are quantitatively analyzed by WDX and shown in Table III. It is found that the undissolved ferrite adjacent to the interface changes into a Zn-rich Mn-Zn ferrite, $Mn_{0.15}Zn_{0.85}Fe_2O_4$, which is the stoichiometric spinel (AB_2O_4) as a result of dissolving of the excess Fe ions. Even

at 700 °C has a small quantity of a second phase that is identified as $Pb_2(Mn,Fe)_2Si_2O_9$. This phase disappears and only spinel phase is detected above 800 °C.

The effect of the reaction temperature on the dissolution length of the ferrite with various ZnO concentrations in the glass is shown in Fig. 7. With increasing the reaction temperature the dissolution lengths increase exponentially. When the reaction temperature is raised above 900 °C the dissolution lengths show a large difference upon the ZnO concentration. The dissolution length of the ferrite reacted with the 0Z glass at 1000 °C is about 72 μm and that with the 12Z glass is about 37 μm. These results mean that the effect of ZnO addition in the glass becomes evident with increasing the dissolution rate of the ferrite. The dissolution lengths of the ferrite in Fig. 7 are shorter than those of the previous study,[12,13] the reason of which is thought to be the difference in mass transport behavior between the polycrystalline and single-crystal ferrite. Generally, the polycrystalline ceramics would dissolve more rapidly into the glass melt than the single crystals due to the grain boundary diffusion.

TABLE II. Concentration of Mn-Zn ferrite components contained in 0Z and 5Z glasses before and after reaction at 1000 °C. (Analysis error: ±2% of the analyzed.)

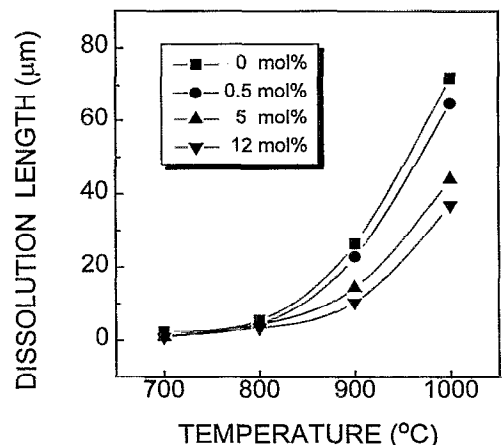| Z		ZnO (mol %)	MnO (mol %)	Fe$_2$O$_3$ (mol %)
0	Before	···	···	···
	After	1.54	2.24	3.90
5	Before	5.60	···	···
	After	6.19	1.71	3.01

FIG. 7. Effect of reaction temperature on dissolution length of ferrite with various ZnO concentrations in glass.
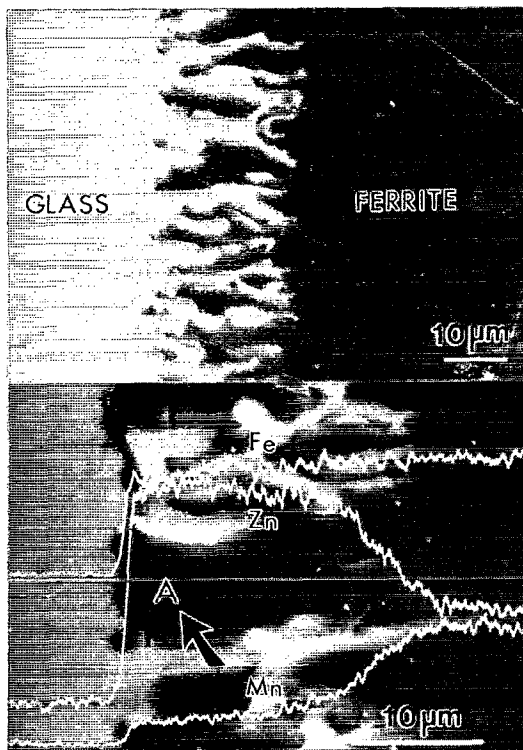
Je et al.

FIG. 8. SEM micrograph and lines traced by characteristic x rays of Fe, Zn, and Mn of interface between Mn-Zn ferrite crystal and 5Z glass heat treated at 900 °C for 10 h.

under the consideration of the analysis errors, it is obvious that the undissolved ferrite reacted with the 5Z glass changes from a Mn-rich to a Zn-rich Mn-Zn ferrite and near the stoichiometric spinel as result of dissolving of the excess Fe ions. As shown in Table III, Pb and Si ions in the glass hardly diffuse into the ferrite. This result indicates that the hump of Zn concentration is independent of the diffusion behaviors of them.
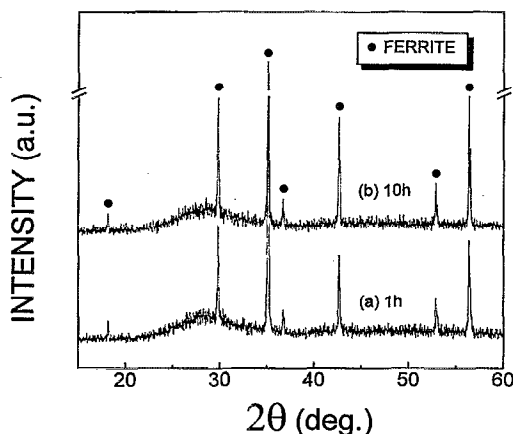

FIG. 9. X-ray diffraction patterns of powder mixtures of Mn-Zn ferrite and 5Z glass heat treated at 900 °C for (a) 1 h and (b) 10 h.

TABLE III. Chemical composition of Mn-Zn ferrite unreacted and reacted wth 5Z glass at 900 °C. (Analysis error: $\pm 1\%$ of the analyzed).

	ZnO (mol %)	MnO (mol %)	Fe_2O_3 (mol %)	PbO (mol %)	SiO_2 (mol %)
Unreacted	19.31	27.42	53.27	...	...
Reacted	42.17	7.47	49.62	0.74	...

IV. DISCUSSION

A. Phase formation

From Figs. 1(a) and 2 the intermediate phase is formed at the interface between the Mn-Zn ferrite and the ZnO-free glass heat treated at 900 °C for 1 h and identified to be the solid solution mixture, $[Pb_2(Mn,Fe)_2Si_2O_9$ and $Pb_8(Mn, Fe)Si_6O_{21}]$. As shown in Fig. 5, these crystals disappear when the temperature is raised to 1000 °C. These results are in good agreement with the previous work by Nitta et al.[10] However, the amount of these crystals decreases and finally disappears with the increase of ZnO concentration in the glass. It indicates that the Zn ions in the glass inhibit their formation. It is suggested that the Zn ions would diffuse into the intermediate crystals and make them a glass phase with the increase of ZnO concentration in the glass. As shown in Fig. 6, the powder mixture of Mn-Zn ferrite and 5Z glass heat treated at 700 °C has a small quantity of a second phase that is identified as $Pb_2(Mn,Fe)_2Si_2O_9$. However, it is not observed at the interface in Fig. 4(a), which means its thickness would be very thin. It is suggested that its formation is caused by the accumulation of the dissolved ferrite components near the interface that is resulted from the low diffusivities of them in the glass melt due to high viscosity of the melt. Therefore, it disappears with increasing the temperature above 800 °C.

According to the results of XRD analysis, it is found that no second phase is formed but only spinel phase is detected even though the quantity of Zn ion at the ferrite adjacent to the interface increases and that of Mn decreases. As shown in Table III, the chemical composition of the undissolved ferrite adjacent to the interface changes into a Zn-rich Mn-Zn ferrite, $Mn_{0.15}Zn_{0.85}Fe_2O_4$, after reaction with the 5Z glass at 900 °C. Mn-Zn ferrite is known to be a complete solid solution of Mn ferrite ($MnFe_2O_4$) and Zn ferrite ($ZnFe_2O_4$),[14] which means that Mn and Zn ions can be completely replaced by each other in the spinel structure. However, the increasing Zn ions would not go into the sites of dissolving Mn ions. Mn-Zn ferrite has an inverse spinel structure that the tetrahedral sites are occupied by Zn^{2+} and Fe^{3+} ions and the octahedral sites by Mn^{2+} and the rest of Fe^{3+} ions.[15] Therefore, it would be reasonable that the increasing Zn ions would go into the tetrahedral sites due to the preference for them over Fe^{3+} ions and the expelled Fe^{3+} ions on the tetrahedral sites would go into the octahedral sites of dissolving Mn ions. In conclusion, it is thought that the spinel structure is maintained by the rearrangement of Zn, and Fe ions at the

sites of the spinel structure even though a large quantity of Mn ions dissolves into the glass melt and the quantity of Zn ions increases at the undissolved ferrite adjacent to the interface.

B. Interface reaction mechanism

It is seen in Fig. 1 that the Zn concentration at the ferrite adjacent to the interface with the glasses containing ZnO is higher than that in the inside, while the Mn concentration is lower and the Fe concentration is slightly lower. These concentration profiles appear even though the glass contains only 0.5 mol % ZnO and more obviously with the increase of ZnO concentration in the glass. From a viewpoint that the concentration of ZnO in the Mn-Zn ferrite (about 19 mol %) is higher than that in the glass (at most 12 mol %), Zn ion in the ferrite would diffuse into the glass melt. On the contrary, however, it seems that Zn ion in the glass melt diffuses into the ferrite. At the previous work,[12] Nitta et al. have also observed the hump of Zn concentration at the ferrite adjacent to the interface after reactions with the glasses containing 1 and 5 mol % ZnO. They interpreted this anomalous Zn concentration profile as follows. When ZnO is added in PbO-SiO$_2$ glass the chemical potential of Zn ion in the glass might be higher than that in the Mn-Zn ferrite. Consequently, Zn ions in the glass would diffuse into the ferrite and thus the hump of Zn concentration at the ferrite adjacent to the interface has appeared. This interpretation means that Zn ions diffuse against the concentration profile of Zn because the concentration of Zn in the Mn-Zn ferrite is much higher than that in the glass. Namely, they have thought that the diffusion was caused not by the difference in concentration but by the difference in chemical potential. They have also interpreted the interface reactions between the Mn-Zn ferrite and the SiO$_2$-PbO-MnO glass melt[12] and between the Ni-Zn ferrite and the SiO$_2$-PbO-NiO glass melt[13] by the same mechanism. There was, however, no evidence that the chemical potential of a component in the glass with its lower concentration is higher than that in the ferrite with its higher concentration.

In this study, Table II shows that the Zn concentration in 5Z glass increases after reaction with Mn-Zn ferrite even though the quantity of Zn ion increases at the ferrite adjacent to the interface. If the Zn ions in the glass diffuse into ferrite, the Zn concentration in the glass can not be increased. Therefore, the increase of Zn concentration in the glass after reaction means that Zn ions in the ferrite dissolve into the glass. In Fig. 5, moreover, the Zn concentration at the ferrite adjacent to the interface increases very slightly after the reaction between the Mn-Zn ferrite and the ZnO-free glass. In this case, it is impossible that the Zn ions in the glass diffuse into the ferrite. In conclusion, it is evident that the Zn ions in the glass do not diffuse into the ferrite but the Zn ions in the ferrite dissolve rather into the glass during interface reaction.

Then, what is the source of the hump of Zn concentration? Comparing the concentrations of the ferrite components [$C_{(Zn,Mn,Fe)_F}$ in at %] with those increasing in 0 and 5Z glasses after reaction [$\Delta C_{(Zn,Mn,Fe)_{0Z,5Z}}$ in at %] in Table II, the interesting results can be found as follows.

$$\frac{C_{(Mn)_F}}{C_{(Fe)_F}} = 0.26 \cong \frac{\Delta C_{(Mn)_{0Z}}}{\Delta C_{(Fe)_{0Z}}} = 0.29 \cong \frac{\Delta C_{(Mn)_{5Z}}}{\Delta C_{(Fe)_{5Z}}} = 0.28,$$

$$\frac{C_{(Mn)_F}}{C_{(Zn)_F}} = 1.49 \cong \frac{\Delta C_{(Mn)_{0Z}}}{\Delta C_{(Zn)_{0Z}}} = 1.46 < \frac{\Delta C_{(Mn)_{5Z}}}{\Delta C_{(Zn)_{5Z}}} = 2.90.$$

It is found that the concentrations of Mn, Fe, and Zn ion increasing in the ZnO-free glass melt after reaction [$\Delta C_{(Zn,Mn,Fe)_{0Z}}$] increase at the similar atomic ratio of those in the ferrite [$C_{(Zn,Mn,Fe)_F}$]. When 5 mol % ZnO is added in the glass, the concentrations of Mn and Fe [$\Delta C_{(Mn,Fe)_{5Z}}$] increase also at the similar ratio of those in the ferrite, but the Zn concentration [$\Delta C_{(Zn)_{5Z}}$] increases at the lower ratio than that in the ferrite. These results indicate that the Zn ions contained in the glass suppress the dissolution of Zn, resulting in suppression of dissolution of the ferrite as the results of Figs. 3 and 7. These interpretations from Table II are reasonable even under the consideration of the analysis errors because the concentrations of Mn, Fe, and Zn in the glasses were analyzed under the same conditions and compared relatively. It can be thought that if the diffusion rates of Zn, Mn, and Fe ions in the glass melt are same, the quantity of Mn ions dissolving into the glass melt would be larger by 2.9 times than that of Zn ions. Anyway, it is obvious that the Mn ions in the ferrite dissolve into the glass melt more than Zn ions because the dissolution of Zn ions in the ferrite is suppressed by Zn ions in the glass melt. Therefore, the source of the hump of Zn concentration is considered to be the undissolved, remaining Zn ions at the ferrite adjacent to the interface and the concentration profiles of Mn become symmetrical with those of Zn as shown in Figs. 1, 4, and 8. With the increase of ZnO concentration in the glass, the amount of remaining Zn ions at the ferrite adjacent to the interface would be increased due to the suppression of the dissolution of Zn ions in the ferrite, resulting in the increase of the height of the Zn hump as shown in Fig. 1.

On the assumption that the composition of undissolved ferrite at the interface after reaction with 5Z glass change into Mn$_{0.15}$Zn$_{0.85}$Fe$_2$O$_4$ and the quantity of Mn ions dissolving into the glass melt is larger by 2.9 times than that of Zn ions, a microscopic model of interface reaction between the Mn-Zn ferrite and the 5Z glass is suggested in Fig. 10. The quantity of dissolved Mn ion (a) and Zn ion (b) are calculated from the altered composition, Mn$_{0.15}$Zn$_{0.85}$Fe$_2$O$_4$. That of Fe ion (c) would be the sum of that of excess Fe ions (0.08) which become Fe^{2+} ions in spinel structure and 2 times of that of divalent ions (Mn^{2+},Zn^{2+},Fe^{2+}) for the conservation of the spinel stoichiometry (AB$_2$O$_4$). This model shows that the spinel structure can be maintained in the ferrite at the interface after reaction by the rearrangement of the remaining components at the sites of the spinel structure, resulting in only the compositional change from Mn-rich to Zn-rich Mn-Zn ferrite, i.e., the appearance of the hump of Zn concentration. In Nitta's mechanism[12] the dissolution of Mn-Zn ferrite into the glass has been neglected. In this model, however, the interface reaction is always accompanied by the dissolution of all

Je et al.

(before) $Mn_{0.55}Zn_{0.37}Fe_{2.08}O_{4.04}$: Mn-rich

DISSOLUTION $\quad \downarrow a \quad \downarrow b \quad \downarrow c \quad \downarrow d$

(after) $Mn_{0.034}Zn_{0.192}Fe_{0.452}O_{0.904}$

$\Downarrow$

(spinel formula) $Mn_{0.15}Zn_{0.85}Fe_2O_4$: Zn-rich

$a = 2.9 \times b = 0.516$
$b = 0.178$
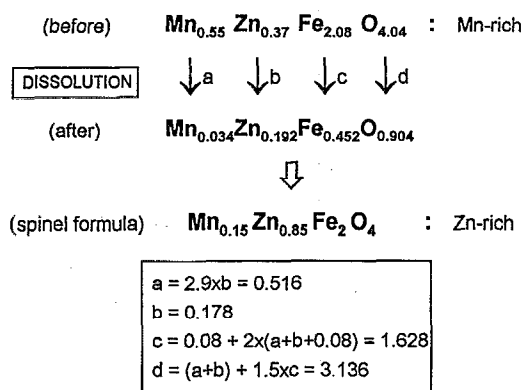$c = 0.08 + 2x(a+b+0.08) = 1.628$
$d = (a+b) + 1.5xc = 3.136$

FIG. 10. Model of interface reaction between Mn-Zn ferrite and 5Z glass on the assumption that the quantity of dissolving Mn ions (a) is larger by 2.9 times than that of Zn ions (b).

components of the ferrite, resulting in the dissolution of the ferrite as shown in Fig. 7.

It is found in Fig. 5 that the Zn concentration at the ferrite adjacent to the interface increases very slightly after reaction between the Mn-Zn ferrite and ZnO-free glass and the Mn concentration decreases slightly. This result is thought to be caused by the reason that Mn ions in the ferrite would dissolve into the glass melt slightly faster than Zn ions. In conclusion, in the case of an interface reaction between a liquid and a multicomponent solid, there are two cases that the concentration of a certain component at the solid adjacent to the interface can become higher than that in the inside except for the formation of an intermediate phase. The first is the case that the dissolution of a certain solid component is suppressed and the second is that the difference of the dissolution rates of the solid component is large. At the previous studies, the interface reactions between the SiO_2-PbO-MnO glass and the Mn-Zn ferrite[12] and between the SiO_2-PbO-NiO glass and the Ni-Zn ferrite[13] would be the first case and that between the SiO_2-PbO glass and the Ni-Zn ferrite[11] be the second case.

C. Interface morphology

It was reported that the grain boundary diffusion of the glass elements was dominant at the polycrystalline ferrite adjacent to the interface during the reaction.[7,8] It is, therefore, difficult to investigate the effect of interface reaction on the interface morphology during the reaction between the polycrystalline ferrite and glass. In this experiment, it can be thoroughly investigated using the Mn-Zn ferrite single crystal.

In 1990 Schmalzried[16] pointed out that a high transport capacity in the moving phase boundary tends to stabilize a planar morphology by rendering the interface to an equipotential surface. In this study, the interface morphology becomes a dendrite structure with the increase of ZnO concentration in the glass due to the suppression of the ferrite dissolution. The dendrite structure grows with increasing the reaction time due to the development of local corrosion of the ferrite. With increasing the reaction temperature, it becomes planar due to the rapid dissolution of the ferrite. These

results mean that the more soluble the ferrite is, the more planar the interface, which is in agreement with Schmalzried's suggestion.

V. CONCLUSION

The interface reactions between Mn-Zn ferrite single crystals and SiO_2-PbO-ZnO ternary systems were investigated and the microscopic model was suggested. The effect of the interface reactions on the interface morphology was also investigated. The intermediate phases, $Pb_2(Mn,Fe)_2Si_2O_9$ and $Pb_8(Mn,Fe)Si_6O_{21}$, were formed after interface reaction between the ferrite and the ZnO-free glass heat treated at 900 °C. With the increase of ZnO concentration in the glass, the amount of these phases decreased and finally they disappeared because Zn ions contained in the glass inhibited their formation. However, a small quantity of $Pb_2(Mn,Fe)_2Si_2O_9$ phase was formed at the interface between the ferrite and the 5Z glass heat treated at 700 °C. Its formation was caused by the accumulation of the dissolved ferrite components near the interface due to high viscosity of the glass melt. Therefore, it has disappeared with increasing the temperature above 800 °C.

The composition of the Mn-Zn ferrite reacted with the glasses containing ZnO changed from inside to the interface. The Zn concentrations at the ferrite adjacent to the interface increased sharply, while the Mn concentrations decreased symmetrically. These anomalous concentration profiles appeared even though the glass contained only 0.5 mol % ZnO, and more obviously with the increase of ZnO concentration in the glass. It was found that the Zn ion has dissolved from the ferrite into the glass melt during reaction between the ferrite and the 5Z glass even though the quantity of Zn ion increased at the ferrite adjacent to the interface. It was also found that Mn ion in the ferrite has dissolved into the glass melt more than Zn ion because the dissolution of Zn ion in the ferrite was suppressed by Zn ion contained in the glass melt. Therefore, the source of the hump of Zn concentration is considered to be the undissolved, remaining Zn ions at the ferrite adjacent to the interface. Although a large quantity of Mn ions dissolved into the glass melt and the quantity of Zn ions increased at the undissolved ferrite adjacent to the interface, no second phase was formed and the spinel structure was maintained, which was thought by the rearrangement of Mn, Zn, and Fe ions at the sites of the spinel structure. The undissolved ferrite reacted with 5Z glass was changed into a Zn-rich Mn-Zn ferrite, $Mn_{0.15}Zn_{0.85}Fe_2O_4$.

A microscopic model of interface reaction between the Mn-Zn ferrite and the 5Z glass was suggested in this study. The interface reaction in this model was always accompanied by the dissolution of all components of the ferrite, resulting in the dissolution of the ferrite.

The interface morphology became a dendrite structure with the increase of the ZnO concentration in the glass due to the suppression of the ferrite dissolution and with increasing the reaction time due to the development of local corrosion of ferrite. With increasing the reaction temperature, the interface morphology became planar due to the rapid dissolution of the ferrite.

[1] M. Sugimoto, in *Crystals for Magnetic Application*, edited by C. J. M. Rooijmans, Crystals: Growth, Properties, and Applications Vol. 1 (Springer, Berlin, 1978), pp. 125–139.

[2] K. Kugimiya, Ceram. Bull. **69**, 696 (1990).

[3] K. Kugimiya and K. Hirota, in *Advance in Ferrites*, edited by C. M. Srivastava and M. J. Patni, Proceedings of the 5th International Conference on Ferrites (Oxford & IBH, India, 1989), pp. 853–60.

[4] S. Kawahara and S. Toyota, Sumitomo Tokusha Kinzoku Giho **9**, 57 (1987).

[5] H. Tanigawa, T. Ueno, and K. Fukushima, Bull. Gov. Ind. Res. Inst. Osaka **25**, 142 (1974).

[6] H. Tanigawa, T. Ueno, and Y. Nishida, Bull. Gov. Ind. Res. Inst. Osaka **27**, 68 (1976).

[7] M. Mino and H. Watanabe, J. Jpn. Soc. Precis. Eng. **44**, 685 (1978).

[8] W. O. Freitag, P. Mee, and R. Petersen, IEEE Trans. Magn. **MAG-15**, 876 (1980).

[9] A. Nitta, T. Miura, T. Komatsu, and K. Matusita, J. Am. Ceram. Soc. **72**, 163 (1989).

[10] A. Nitta, H. Nakamura, T. Komatsu, and K. Matusita, J. Am. Ceram. Soc. **72**, 1351 (1989).

[11] A. Nitta, H. Nakamura, T. Komatsu, and K. Matusita, J. Mater. Sci. **25**, 2857 (1990).

[12] A. Nitta, H. Nakamura, T. Komatsu, and K. Matusita, J. Appl. Phys. **71**, 1992 (1992).

[13] A. Nitta, T. Ono, T. Komatsu, and K. Matusita, J. Mater. Sci. **29**, 2629 (1994).

[14] Th. J. Berben and D. J. Perduijn, in *Ferrites*, edited by H. Watanabe, S. Iida, and M. Sugimoto, Proceedings of the 3rd International Conference on Ferrites (Center for Academic Publication, Japan, 1981), pp. 722–25.

[15] A. Goldman, *Modern Ferrite Technology* (Van Nostrand Reinhold, New York, 1990), pp. 21–34.

[16] H. Schmalzried, Reactiv. Solids **8**, 247 (1990).