

# $^{57}\text{Fe}$ conversion electron Mössbauer study of oxidized iron-nickel alloy pins

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**Abstract** Iron-nickel alloy pins were pretreated at 700°C and 500°C for 30 min in  $\text{H}_2$ , and additionally heat-treated at 600°C for 30 min in  $\text{N}_2$  atmosphere, respectively. The oxide layers of these samples were compared with that of a non-preheated sample. Thin iron oxide layers on all samples were observed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and  $^{57}\text{Fe}$  conversion electron Mössbauer (CEM) spectrometry. The iron products of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  were determined among various heated samples.

**Keywords** Iron-nickel alloy · Oxidation layers · Mössbauer spectrometry ·  $\text{Fe}_3\text{O}_4$  · Gamma- $\text{Fe}_2\text{O}_3$

## 1 Introduction

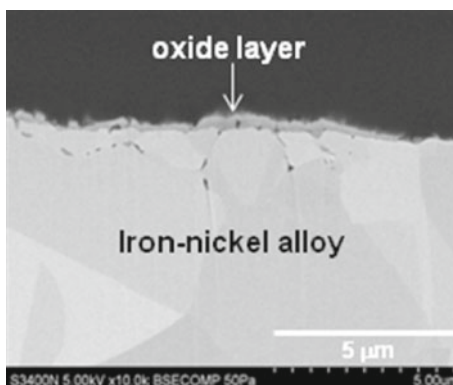
It is required in industry to realize glass-to-metal sealing contacts in microelectronic packages. Iron-nickel alloy is useful as the thermal expansion curve is accordant with that of hard borosilicate glass between 0–350°C [1]. But since iron-nickel alloy is not adhesive to the glass, hermetic sealing is realized by bonding of molten glass with an oxide films on the iron-nickel alloy [2, 3]. When glass contacts with oxides on iron-nickel alloy in the wetting process, it is reported that the oxides are dissolved into glass to form the reaction product  $\text{Fe}_2\text{SiO}_4$  [4]. It is believed that especially

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**Fig. 1** Cross-section SEM image of sample C after heat-treatment



$\text{Fe}^{2+}$  compounds contribute to glass-metal adhesion. When the iron-nickel alloy is heat-treated before contacting to glass, it is important to get sufficiently thick oxide layers containing  $\text{Fe}^{2+}$  for high bonding strength sealing. The purpose of this paper is to characterize the oxidized surface of iron-nickel alloy pins by conversion electron Mössbauer (CEM) spectrometry, scanning electron microscopes (SEM), and X-ray diffractions (XRD).

## 2 Experimental

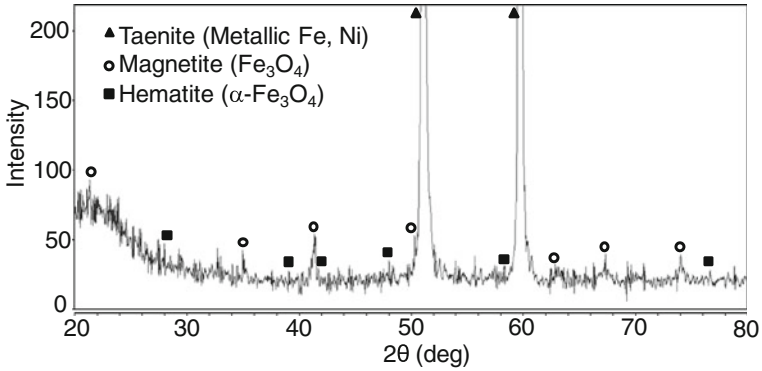
Iron-nickel alloy pins used in this study were 0.4 mm in length and 0.2 mm in diameter and the composition of the alloy is essentially 42 mass% nickel balanced with iron. The iron-nickel alloy pin samples A, B and C, were obtained by the following treatment. Iron-nickel alloy pins A and B were preheated at 700°C and 500°C for 30 min in  $\text{H}_2$  atmosphere, respectively, to reduce the oxides on the surface, and sample C was not preheated. All samples (A, B and C) were then additionally heat-treated at 600°C for 30 min in  $\text{N}_2$  atmosphere in order to form the uniform oxide surface.

The crystalline oxides on the samples were measured by XRD, and the cross-section of the samples was studied by SEM.  $^{57}\text{Fe}$  CEM spectra were measured at room temperatures by a backscattering type of  $\text{He-CH}_4$  gas flow counter, and calibrated by using an  $\alpha\text{-Fe}$  foil, and fitted with Mosswin Software.

## 3 Results and discussion

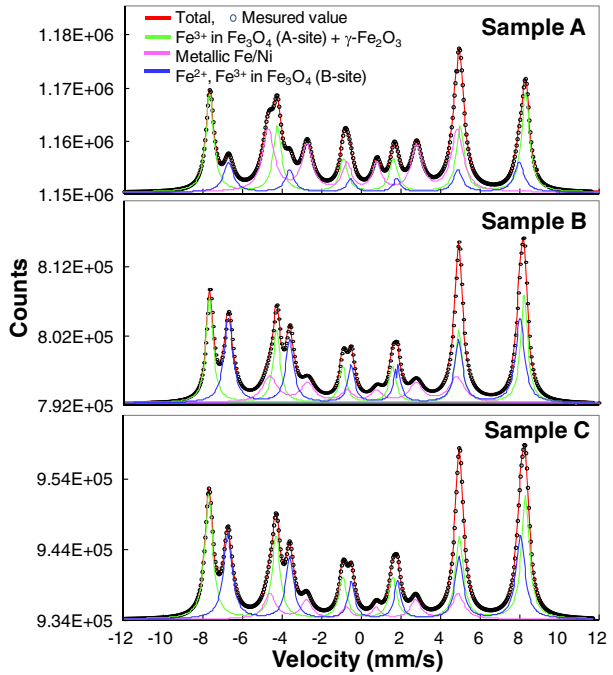
Figure 1 shows the cross-sectional SEM image after sample C was heat-treated at 600°C in  $\text{N}_2$  atmosphere. Thick oxide layers were observed around grains especially on uneven surfaces. It is found by SEM that the oxide layer was grown up to 2  $\mu\text{m}$  in thickness.

The XRD pattern of sample C is shown in Fig. 2. The detailed pattern of the oxide layer shows the trace diffraction peaks of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ) phases in addition to the diffraction peaks of Fe and Ni alloy, taenaite (Metallic Fe, Ni) phase. The taenaite phase is the original phase of Fe and Ni alloy. However, it



**Fig. 2** XRD pattern of sample C after heat-treatment

**Fig. 3**  $^{57}\text{Fe}$  Mössbauer spectra of heat-treated samples A, B and C



is difficult to compare the quantity of produced hematite and magnetite in samples A, B and C by XRD peaks.

Room temperature CEM spectra are deconvoluted into three sextets as shown in Fig. 3. The analyzed Mössbauer parameters are listed in Table 1. The hyperfine fields of three sextets are about 29T, 46T, and 49T, respectively. The sextet with  $B_{\text{hf}} = 29\text{T}$  corresponds to the metallic state because the isomer shift, IS, is close to 0 mm/s. It is considered to be due to the substrate alloy. The second sextet with  $B_{\text{hf}} = 46\text{T}$  shows the mixed valence states of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  because of the IS = 0.66 mm/s. This comes from  $\text{Fe}^{+2.5}$  in B site of magnetite ( $\text{Fe}_3\text{O}_4$ ). The third sextet with  $B_{\text{hf}} = 49.5\text{T}$  shows

**Table 1** Mössbauer parameters of sample A, B and C

Fe states	Parameter	Sample A	Sample B	Sample C
$\text{Fe}^{3+}$ in $\text{Fe}_3\text{O}_4$ (A-site)+ $\gamma$ - $\text{Fe}_2\text{O}_3$ or $(\text{Fe}^{3+})_A[\text{Fe}_{1-3x}^{2+}\text{Fe}_{1+2x}^{3+}\square_x]_B\text{O}_4$	Area (%)	43.3%	48.4%	40.0%
	$\delta$ (mm/s)	0.34	0.31	0.31
	$B_{\text{HF}}$ (T)	49.5	49.5	49.3
	$\Delta$ (mm/s)	-0.05	-0.03	-0.04
	$\Gamma$ (mm/s)	0.48	0.48	0.42
	Metallic Fe/Ni alloy	Area (%)	40.6%	14.6%
$\delta$ (mm/s)		0.04	0.07	0.07
$B_{\text{HF}}$ (T)		29.6	29.4	29.3
$\Delta$ (mm/s)		0.05	0.15	0.08
$\Gamma$ (mm/s)		0.72	0.7	0.91
$\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ in $\text{Fe}_3\text{O}_4$ (B-site)		Area (%)	16.1%	37.0%
	$\delta$ (mm/s)	0.62	0.66	0.66
	$B_{\text{HF}}$ (T)	45.6	45.7	45.7
	$\Delta$ (mm/s)	0.01	-0.01	0.01
	$\Gamma$ (mm/s)	0.59	0.54	0.53

the valence state of  $\text{Fe}^{3+}$  because of the IS = 0.34 mm/s. The third sextet originates from two  $\text{Fe}^{3+}$  species, the A site of  $\text{Fe}_3\text{O}_4$  and maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ) because it is hard to distinguish both sextets of  $\gamma$ - $\text{Fe}_2\text{O}_3$  and A site of  $\text{Fe}_3\text{O}_4$ . The doublet of FeO was not detected, and the sextet of hematite with  $B_{\text{hf}} = 51\text{T}$  was not clearly observed although the trace peaks were recognized in XRD patterns.

The area intensity ratio of A-site and B-site of  $\text{Fe}_3\text{O}_4$  was assumed to be 1/2. As a result, we derive that the sample A, B and C contain 24.4%, 55.5% and 59.1% of  $\text{Fe}_3\text{O}_4$ , respectively.

On the other hand, the component of  $\gamma$ - $\text{Fe}_2\text{O}_3$  estimated in this study may be one of magnetite components if the magnetite does not have the constant intensity ratio of 1/2 for A site/ B site, that is magnetite with oxygen defects [6]. In this case, the formula can be written as  $(\text{Fe}^{3+})_A[\text{Fe}_{1-3x}^{2+}\text{Fe}_{1+2x}^{3+}\square_x]_B\text{O}_4$  ( $0 < x < 0.33$ ). However, in order to estimate the iron states, the area intensity ratio of  $\gamma$ - $\text{Fe}_2\text{O}_3$  was calculated by subtracting the area intensity ratio of 1/2 of B-site from the area intensity ratio of the sextet with the largest magnetic field. As the results, the sample A, B and C contain 35.2%, 29.9% and 20.3% of  $\gamma$ - $\text{Fe}_2\text{O}_3$ , respectively.

In the wetting process, a chemical reaction occurs between oxides and  $\text{SiO}_2$  in the glass drop as follows [4]:  $2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 = 3\text{Fe}_2\text{SiO}_4 + \text{O}_2$ . A sufficient thickness of oxide on the metal surface is required for sealing with high bonding strength [5]. If magnetite with large contents of  $\text{Fe}^{2+}$  were effective for contact between glass and alloy, it would be not necessary to preheat in  $\text{H}_2$  atmosphere before heating at  $600^\circ\text{C}$  in  $\text{N}_2$  atmosphere.

## 4 Summary

In order to study thin iron oxide layers on Fe-Ni alloy, we have prepared samples by preheating in  $\text{H}_2$  at  $700^\circ\text{C}$  and  $500^\circ\text{C}$  and heat-treatments at  $600^\circ\text{C}$  in  $\text{N}_2$  atmosphere, and characterized by SEM, XRD, and CEMS. It is found that the iron oxide layers produced on Fe-Ni alloy consist of  $\text{Fe}_3\text{O}_4$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$ , but not FeO and  $\alpha$ - $\text{Fe}_2\text{O}_3$ . The product ratios of  $\text{Fe}_3\text{O}_4$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$  were estimated by CEMS. It is concluded

that preheating in H<sub>2</sub> atmosphere is not necessary, and that only heating at 600°C in N<sub>2</sub> atmosphere is practically useful for glass-metal contact because of the large amount of Fe<sub>3</sub>O<sub>4</sub> produced.

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