

# Redistribution Behavior of Trace Elements during Internal Oxidation of an Fe-6mol%Si Alloy at 1123 K

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SIMS and XPS have been applied to characterize the elemental distribution in the internal oxidation zone of an Fe-6mol% Si alloy. Internal oxidation behavior agrees well with predictions based on the thermodynamic data of oxidation. Redistribution of trace elements is deeply related to internal oxidation and interface segregation.

## 1. Introduction

External oxidation is observed when an oxide layer is formed on the alloy surface in which constituent elements similarly react with oxygen. On the other hand, internal oxidation may take place if oxygen penetrates into the alloy substrate and selectively reacts with a less-noble alloying element with mobility lower than oxygen.[1,2]

The Fe-Si alloy system is one of the most important systems in the application of electrical steel, the composition of which is nearly Fe-6mol%Si alloy. The internal oxidation behavior of cold rolled sheets of Fe-6mol%Si alloy is controlled by annealing atmosphere and temperature in a decarburization process.[3,4] A number of previous investigations [4-8] reported that the characteristic features of the external oxide layers formed on the surface of Fe-Si alloys strongly depended on the H<sub>2</sub>O / H<sub>2</sub> ratios in the annealing atmosphere. Morito and Ichida reported that small amount of Mn accelerated internal oxidation rate of Fe-Si alloy.[5] However, little attention has been paid to the point of redistribution behavior of trace elements during internal oxidation.

The aim of the present study is to characterize the elemental distribution in the internal oxidation zone of an Fe-6mol% Si alloy oxidized at 1123 K.

## 2. Experimental

A flat Fe-6mol%Si alloy sheet of 0.23 mm in thickness was produced through the process for grain-oriented silicon steel.[3] This sheet was fully decarburized and annealed to provide secondary recrystallization at 1473 K under dry hydrogen gas. The average grain size of this sheet was about 10 μm in diameter. The chemical composition of the sample is shown in Table I. They were subsequently oxidized by annealing at 1123 K for 300 s in 75%H<sub>2</sub>-25%N<sub>2</sub> atmosphere with H<sub>2</sub>O / H<sub>2</sub>=0.43 ratio. Heating and cooling rates were 5 K / s and 3 K / s, respectively.

Table I Chemical composition of the sample.

Elements	Si	Cr	Mn	Sn	Fe
mol%	6.10	0.03	0.08	0.06	bal.

The cross section of the oxidized samples was observed by scanning electron microscopy (SEM). The redistribution behavior of trace elements was detected by secondary ion mass spectrometry (SIMS). In SIMS, an incident beam of 10.0 keV Cs<sup>+</sup> ions was used for obtaining positive secondary ions and negative H<sup>-</sup> ions. The chemical state and composition of the oxide layers were analyzed by X-ray photoelectron spectroscopy (XPS), in which the

incident X-ray was monochromatized Al-K $\alpha$  and the analysis spot was about 200  $\mu\text{m}$  in diameter. XPS data were quantified using relative sensitive factors.

### 3. Results

Figure 1 shows a secondary electron image of the cross section of oxidized sample. The internal oxides show dark contrast and the thickness of internal oxidation zone (IOZ) is about 5  $\mu\text{m}$ . Fe layer without internal oxide exists between the surface and the IOZ. The IOZ is composed of plate-like oxides near the surface (zone 1) and fine spheroidal oxide in the middle (zone 2) and coarse oxides at the front of the IOZ (zone 3).

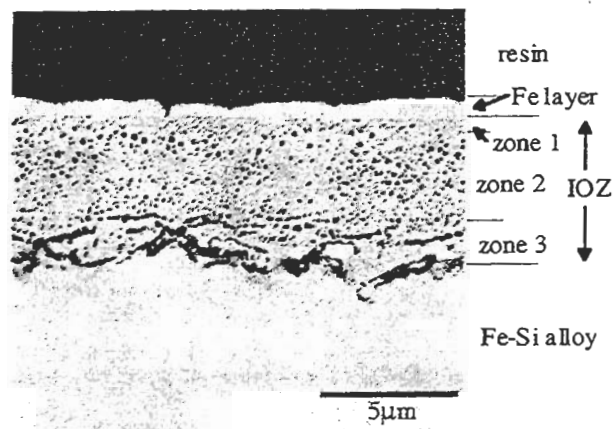


Figure 1 SEM image of the cross section of oxidized sample.

Figure 2 shows SIMS depth profiles of the oxidized sample. The secondary ion counts of Si<sup>+</sup> increase in the IOZ. The secondary ion counts of Cr<sup>+</sup> and Mn<sup>+</sup> heavily increase in zone 1. The SIMS profiles of H<sup>+</sup> and Sn<sup>+</sup> are similar to those of O<sup>+</sup> and Si<sup>+</sup>. The secondary ion counts of all elements become almost constant at the sputter-etching time greater than 6 ks as much as those of the sample before oxidation.

Figure 3 shows compositional profile and Fe 2p, O 1s, Si 2p, Cr 2p and Mn 2p XPS spectra of oxidized sample, which were in-depth measured by using argon ion sputtering.

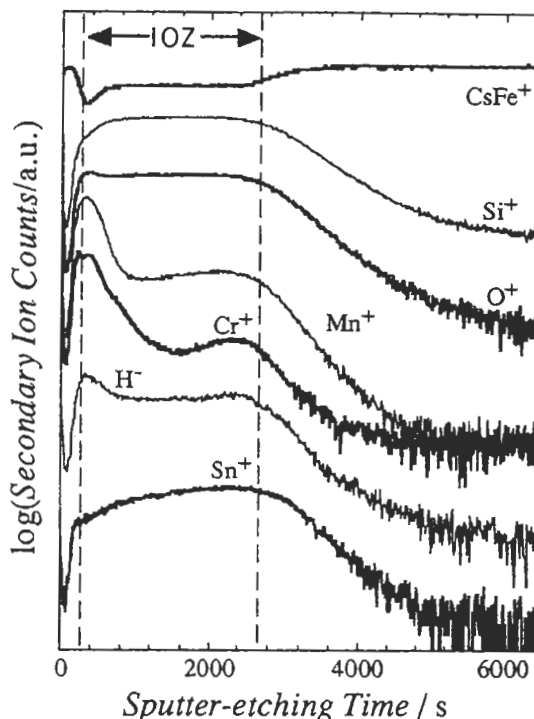


Figure 2 SIMS depth profiles of the oxidized sample.

The concentrations of Si in the IOZ and in the alloy substrate are quantified about 6 mol% and 5 mol%, respectively. Cr and Mn accumulate in zone 1. The concentrations of Cr and Mn are about 1.5 mol% in zone 1. On the other hand, it is impossible to detect enough intensity of Cr 2p and Mn 2p XPS spectra in zone 2 and 3, because of low concentrations.

The Fe 2p XPS spectra show that Fe exists in a metallic state in the IOZ. The O1s XPS spectra demonstrate a peak at about 532.5 eV in the IOZ, which are assigned to the binding energy of Si-O. The O1s XPS spectrum after 0.9 ks of sputtering is broad on the low energy side compared with the spectrum after 3 ks of sputtering. These spectra suggest that the IOZ is composed of SiO<sub>2</sub> and other oxide, such as Cr oxide and Mn oxide in zone 1 and SiO<sub>2</sub> in zone 2 and 3. The Si 2p XPS spectra demonstrate a peak at about 103.4 eV in the IOZ, which correspond to the binding energy of Si-O. After 0.9 ks of sputtering, oxide Cr 2p and Mn 2p XPS spectra are observed.

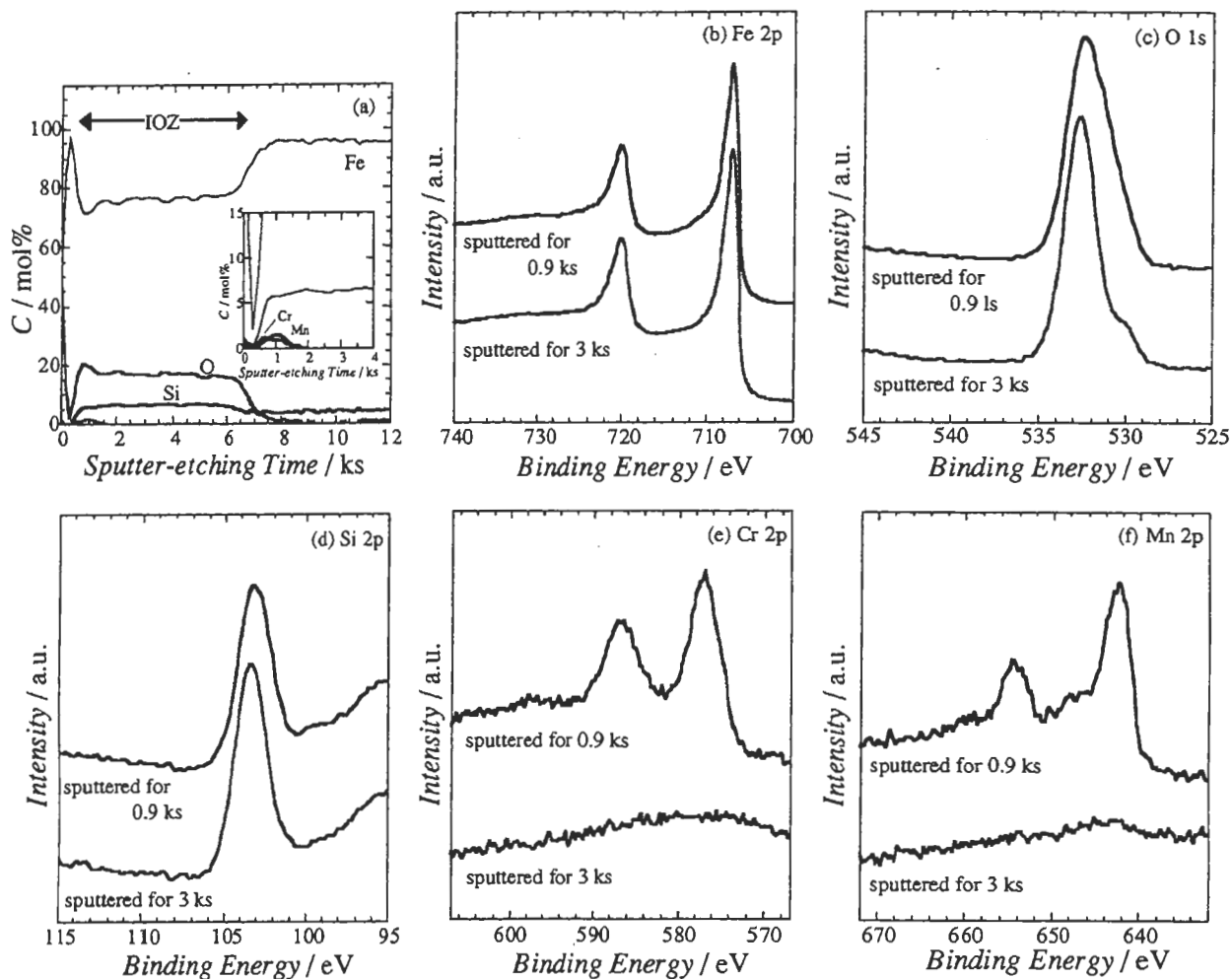


Figure 3 Compositional profile and Fe 2p, O 1s, Si 2p, Cr 2p and Mn 2p XPS spectra of oxidized sample.

#### 4. Discussions

The present authors have reported that the oxidation behavior of an Fe-6mol% Si alloy agrees well with predictions based on thermodynamic data of oxidation of the elements [7]. Figure 4 shows the Ellingham-type diagram exhibiting oxygen potentials for metal / oxide pairs, in which the annealing conditions are plotted for the present study. Since the affinity of Fe with O is much smaller than that of Si, Cr and Mn, the internal oxidation of Si, Cr and Mn occurs selectively in the alloy.

Cs<sup>+</sup> ion beam decreases the emission efficiency of positive secondary ion, whereas O of the internal oxide increases it. Therefore, SIMS depth profiles shown in fig.2 should be different to concentration profiles. The secondary ion counts of Si<sup>+</sup> in the IOZ are

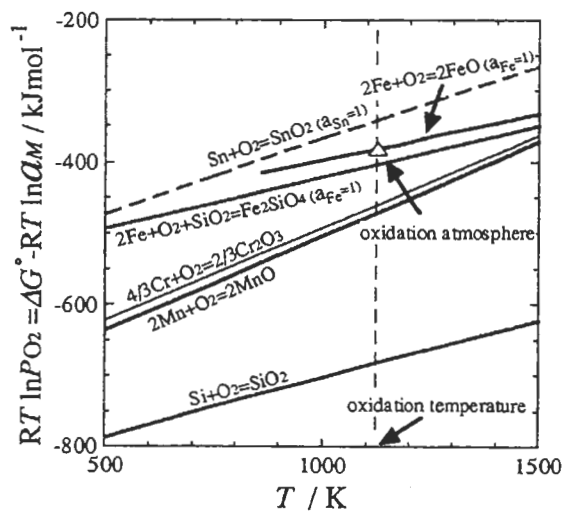


Figure 4 The Ellingham-type diagram.

higher by about three orders of magnitude than that in alloy substrate, although the Si concentrations are almost the same. Therefore, the secondary ion counts of Si increase mainly caused by matrix effect of SIMS analysis. In spite of the constant O concentration in the IOZ, the secondary ion counts of Cr and Mn heavily increase in zone 1. It, therefore, is reasonably considered that the accumulation of Cr and Mn increase the secondary ion counts in zone 1. Oxygen potential in zone 1 should be higher than that in zone 2 and 3. And the affinity of Cr and Mn with O is smaller than that of Si. Therefore, internal oxidation of Cr and Mn occurs only in the zone 1, whereas Si oxidizes in all of the IOZ (zone 1, 2 and 3).

The oxygen potential of the oxidation atmosphere in the present study is lower than that of the atmosphere in equilibrium with the Sn-SnO<sub>2</sub> system. Thus Sn may segregate at the internal oxide / alloy interface in a metallic state. In general, it is very difficult to obtain the solute H depth profiles in Fe alloys by SIMS because of the extremely high diffusivity of H in the alloys. Therefore, the H depth profile in Fig. 2 suggests that H may be present in the internal oxides and/or at the internal oxide / alloy interface.

## 5. Conclusions

SIMS and XPS have been applied to characterize the elemental distribution in the internal oxidation zone of an Fe-6mol% Si alloy oxidized at 1123 K in 75%H<sub>2</sub>-25%N<sub>2</sub> atmospheres with H<sub>2</sub>O / H<sub>2</sub>=0.43 ratio.

1. Internal oxidation of Si, Cr and Mn occurs in the alloy, which agrees well with predictions

based on the thermodynamic data of oxidation of the alloy.

2. The SIMS profiles of H<sup>-</sup> and Sn<sup>+</sup> are similar to those of O<sup>+</sup> and Si<sup>+</sup>. It, therefore, is reasonably considered that Sn segregates at the internal oxide / alloy interface in a metallic state and H may be present in the internal oxides and/or at the internal oxide / alloy interface.
3. Redistribution behavior of trace elements is deeply related to internal oxidation and interface segregation.

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