

Nondestructive Depth Resolved Analysis by using Grazing Exit Fluorescence-Yield X-ray Absorption Spectroscopy

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Alloying elements added to steel for improving surface properties such as corrosion resistance exhibit different chemical characters, and they are often enriched to the surface of the alloys or oxidized there during annealing at high temperatures. In this study, depth-resolved X-ray absorption spectroscopy (XAS) measurements were carried out using a two-dimensional detector with geometrical arrangement of grazing exit in detection of fluorescence X-ray emitted from sample surface, in order to characterize the enrichment and oxidation of manganese on the surface layers of an Fe-Mn alloy annealed under low oxygen partial pressure. This technique facilitates non-destructive measurement for characterizing the compositional distribution and the oxidation state of manganese in the depth direction. The results showed that manganese was enriched to surface layers of the Fe-Mn alloys during annealing at high temperatures and formed as manganese oxide. The preferential oxidation of manganese by annealing under low oxygen partial pressure is considered the driving force for their enrichment on the alloy surface.

1. Introduction

Alloying elements such as Si, Mn and Cr are added to steel products to improve their mechanical and surface properties. Steel surfaces are exposed to various partial pressure of oxygen at high temperatures during production as well as in use. Oxide layers with various thickness, compositions and phases are formed on the surface of steel during annealing process and their forming process is strongly influenced by the chemical characteristic features of the alloying elements.

Although manganese is often added to steel for controlling not only the mechanical properties but also surface properties, manganese is formed as manganese monoxide, MnO in the surface layer by annealing at high temperatures [1,2]. On the other hand, a reactive element like manganese is known to be enriched to form an oxide in surface layers of iron-based alloys under low oxygen partial pressure, which alters the surface properties of the iron-based alloys [3]. Therefore, characterization of the enrichment or oxidation of alloying elements in the surface layers is very important for controlling the surface properties. Recently, the present authors have investigated the chemical state and the thickness of the oxide layer formed on the surface of Fe-Al alloys by using techniques of low-angle

incident X-ray diffractometry (XRD) for the phase identification, XPS for determination of the surface composition and obtaining the depth profile, and the results showed that behaviors of enrichment and oxidation of aluminum in the surface layers were different depending on the conditions of temperature and oxygen partial pressure [4]. Surface analysis for Fe-Mn alloys was also carried out and it was showed that manganese was enriched and formed oxide by annealing [5]. However, the formation mechanism of manganese oxides in the surface layers of Fe-Mn alloys during annealing is not understood well. Thus, the objective of this study is to clarify the formation process of surface oxide layers in Fe-Mn alloys annealed under low oxygen partial pressure through the analysis of compositional and chemical depth distribution by using take-off angle dependence of detected intensity of fluorescent X-ray and spectrum profile of X-ray absorption fine structure (XAFS).

2. Experimental

An ingot of Fe-Mn binary alloy was prepared as the sample for X-ray absorption spectroscopic measurement using vacuum induction melting. The chemical composition of the alloy was Fe - 3.72 mass % Mn. The ingot was hot-rolled to form 0.5

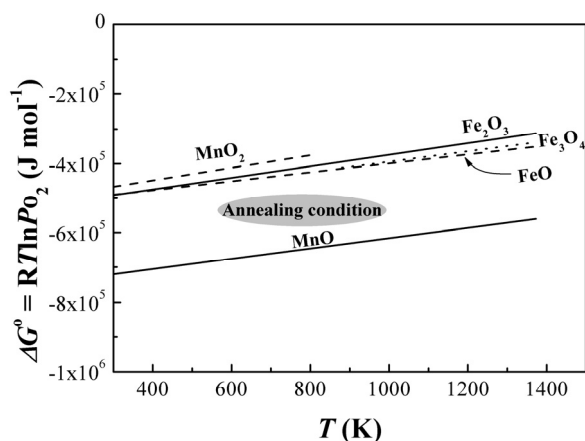


Fig. 1 Ellingham diagram for iron and manganese. Annealing conditions used in this work are denoted.

mm thick sheets at 1273 K. Surfaces of sheet samples were mechanically polished and then cleaned with acetone in the ultrasonic bath.

The Fe-Mn alloy samples were annealed at 773 or 973 K for 1800 s in 9.8 % H_2 -Ar gas. The oxygen partial pressure was estimated to be approximately to 10^{-30} - 10^{-23} Pa in the annealing temperature range. Under these annealing conditions, iron is not oxidized while manganese is oxidized, as shown in

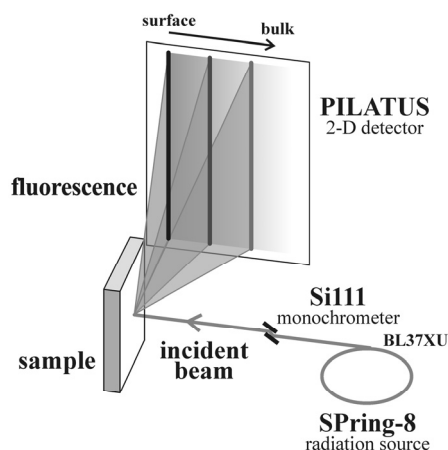


Fig. 2 Schematic view of geometry for the depth-resolved XAFS measurement.

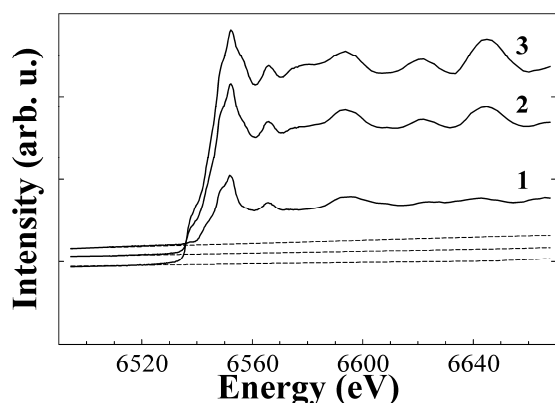


Fig. 3 XAFS spectra using the intensity detected at different pixels as function of incident beam energy.

Fig. 1 [6]. Thus, manganese is selectively oxidized in the surface layer of annealed samples. The alloy samples annealed under these conditions were cooled to room temperature, and then the surfaces of the samples were analyzed.

In this study, a grazing exit fluorescence yield XAS method was applied to analyze the depth-resolved atomic structure around Mn using XAFS spectra measured at Mn K absorption edge and the compositional distribution using the intensity of Mn fluorescence emitted from the surfaces of the alloys. The depth-resolved XAS experiments using synchrotron radiation were performed at the BL37XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2007B1454). Synchrotron X-ray beam monochromized by the Si111 double-crystal was irradiated perpendicularly on the sample surface after passing through the slit with 0.5 mm x 0.5 mm in size. The two-dimensional pixel array detector (PILATUS II [7]), which was positioned in the direction to parallel to the sample plane, was used to detect the emitted fluorescence. The distance between the irradiation point on the sample surface and the detector window was 172 mm. The detection angle resolution by one pixel array with 172 μm in width is 1 mrad. Fluorescence intensity detected at each pixel includes different weight of contribution from layers at different depths depending on the detection angle. The geometry for the depth-resolved XAS experiment is schematically shown in Fig. 2. Among the intensities detected at the three pixel array presented in the figure, the far left side array includes the largest contribution from surface region in total detected fluorescence. The intensities detected at each array for the Fe-Mn alloy sample annealed at 773 K are plotted against the incident beam energy in Fig. 3. Numbered 1, 2 and 3 profiles shown in this figure correspond to the X-ray absorbance spectra and their detection angles are 5, 55 and 97 mrad, respectively. The detected intensity includes background mainly due to elastic scattering as well as Mn K fluorescence. The intensity of Mn K fluorescence is extracted by deducting the background signal represented by broken lines in Fig. 3.

3. Results and Discussion

Fig. 4 shows the resultant normalized fluorescence intensity I_F profiles of as-prepared and annealed samples. The intensity arising from deeper area becomes higher when the detection angle (take-off angle) is increased. In case of the as-prepared sample, all spectra are allocated to

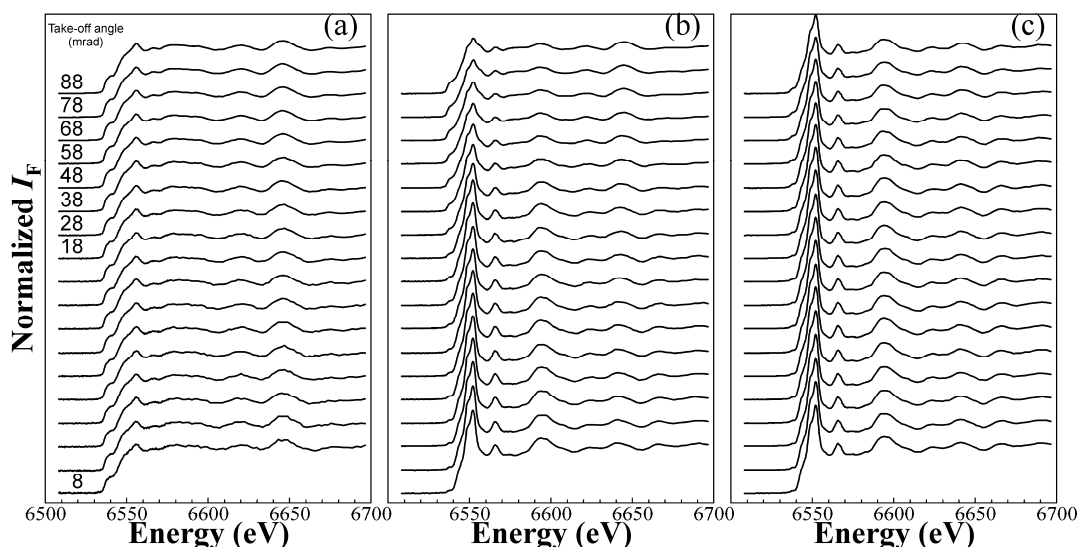


Fig. 4 Normalized fluorescence intensity profiles measured for samples of (a) as-prepared, and annealed at (b) 773 and (c) 973 K.

bcc-metal as shown in Fig. 4a. This indicates that manganese atoms occupy bcc Fe-Mn alloy lattice uniformly irrespective of the penetration depth from the surface. On the other hand, some features attributed to MnO appeared in the spectra of the two annealed samples. Furthermore, the enrichment of manganese in the oxide state was observed at deeper levels in the sample annealed at 973 K than in the sample annealed at 773 K.

The take-off angle dependency of I_F measured at certain incident beam energy provides useful information. Some measured normalized I_F intensity profiles in the near absorption edge region with different weight of contribution depending on depth from the surface are shown in Fig. 5. All spectra can be considered as summation of bcc-metallic and oxide (MnO) phases. Normalized I_F exhibit the same value at some energy points such as 6542, 6555, 6564 and 6568 eV in this figure. For example, when the intensity values at 6555 eV, which is one of such energies is extracted and plotted I_F as function of take-off angle, it reflects the distribution of manganese at points deeper from the alloy surface. Fig. 6 shows the take-off angle dependency of I_F for the three Fe-Mn alloy samples. In higher take-off angle region, the I_F increased monotonically with almost similar gradient to the take-off angle for all samples. Furthermore, the I_F of the sample annealed at 973 K was much higher than the one of other two samples. These are attributed to the fact that a thin layer with high concentration of Mn was formed in very shallow region due to outer diffusion and enrichment of Mn. On the other hand, the I_F decreased drastically at the region of take-off angle lower than 10 mrad. This indicates the influence of refraction under the critical angle [8].

The critical angle α_c of 9.1 mrad and the fluorescence escape depth of 2, 65 and 270 nm for the take-off angle below α_c , at 10 and 20 mrad, respectively, were obtained by calculation using the

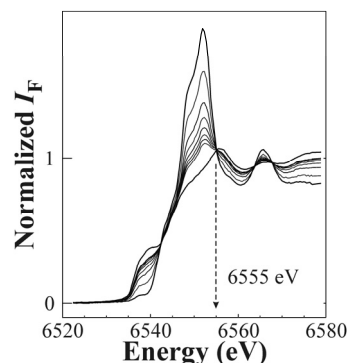


Fig. 5 Normalized fluorescence intensity profiles with different distribution of depth contribution in the near-edge region.

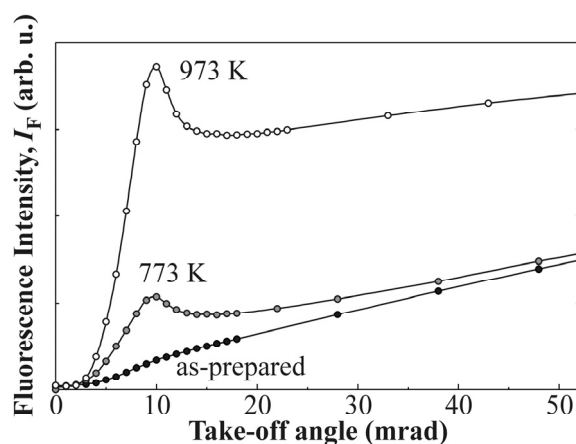


Fig. 6 Take-off angle dependency of the Mn K fluorescence intensity measured at 6555 eV for as-prepared and annealed samples.

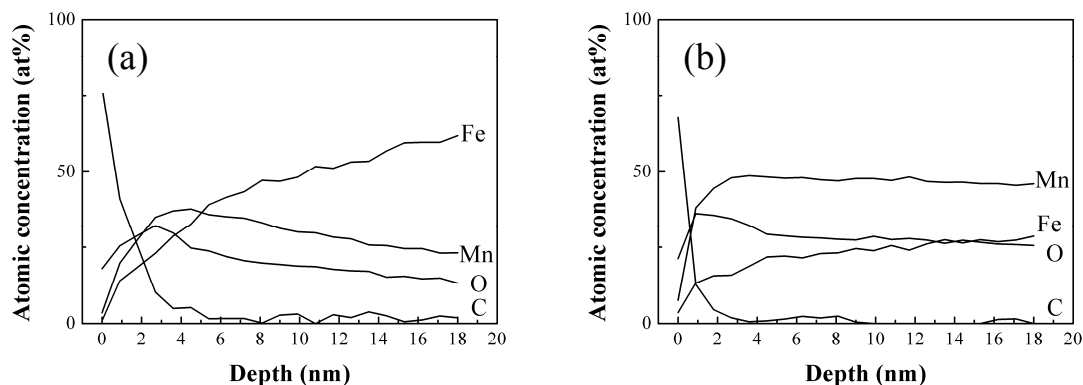


Fig. 7 XPS depth profiles of Fe-Mn alloys annealed at (a) 773K and (b) 973 K [5].

composition and the density of this alloy. Furthermore, in the two annealed samples the characteristic feature of sharp peak is observed in the I_F intensity profile at around 10 mrad of the detection angle. In case of a thin film laid on substrate, such a sharp peak is often observed at its critical angle [9]. The position of peak at 10 mrad in this case agreed with the value calculated under assumption that the surface of alloy is covered by thin MnO layer. This is considered due to forming thin oxide layer in the surface region. As shown in Fig. 4(b), the XAFS profiles measured at just above the critical angle of 9 mrad included partially the profile corresponding to the fcc metal alloy phase and the fraction of the metal phase increased with take-off angle in case of the sample annealed at 773 K. Considering the fluorescence escape depth, the thickness of oxide layer in the sample can be estimated within about 20 nm. On the other hand, in case of the sample annealed at 973 K the XAFS profiles include little fraction of metal phase even at high take-off angle as obviously shown in Fig. 4(c). This indicates that the oxide layer is more than 100 nm in thickness and it is much thicker than the sample annealed at 773 K. These results are confirmed by the compositional depth profiles of the annealed samples obtained from the XPS depth profiles by Ar ion sputtering shown in Fig. 7.

4. Summary

Grazing exit fluorescence yield XAS technique was used for depth-resolved analysis on as-prepared and annealed Fe-Mn alloys. The results of take-off angle dependent XAFS profiles showed that manganese was present uniformly in metallic alloy phase in the as-prepared sample, while the formation of manganese oxide was detected on the surface layer of annealed samples. The characteristic intense peak observed at 10 mrad of take-off angle corresponding to the critical angle of MnO for annealed samples and the increase of total

fluorescence intensity for the annealed sample indicate the enrichment of manganese and forming thin MnO layer in the surface of Fe-Mn alloys.

In this study, it was confirmed that the depth-resolved XAS is useful to analyze the change in local structure or compositional distribution and the mechanism of enrichment and oxidation of a specific element. The depth-resolved XAS is a nondestructive structural analyzing method in large depth range of single-nanometer to sub-micrometer order. This technique can be applied to in-situ measurement at high temperature in various conditions of atmospheric environmental around the samples.

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