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Characterization of Manganese Oxide-Enriched Surface Layers of Fe-Mn Alloys

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Abstract. Alloying elements are added to steel for improving surface properties such as corrosion resistance. The alloying elements exhibit different chemical characters, and they are often enriched to the surface of the alloys 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 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.

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 complicated morphology are formed on the surface of steel during annealing process and their morphology 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 oxide in the surface layer by annealing at high temperatures [1,2]. On the other hand, an 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]. For example, in hot dip galvanizing process of steel at high temperature under an oxygen partial pressure, reactive alloying elements are enriched to the surfaces. Since the alloying elements are oxidized, the oxide layer may prevent galvanizing. Therefore, characterization of the enrichment or oxidation of manganese 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 Fe-Mn surfaces by using techniques of low-angle incident X-ray diffractometry (XRD) and angle-resolved X-ray photoelectron spectroscopy (XPS), and the results showed that manganese were enriched to surface layers to form oxides [4]. 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 depth-resolved X-ray absorption spectroscopy (XAS).

Experimental

Sample preparation

An ingot of Fe-Mn binary alloy was prepared 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 mm thick sheets at 1273 K. Surfaces of sheet samples were mechanically polished and then cleaned with acetone in an 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 10^{-30} - 10^{-23} Pa in the temperature range. Under these annealing conditions, iron is not oxidized while manganese is oxidized, as shown in Fig. 1 [5]. 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.

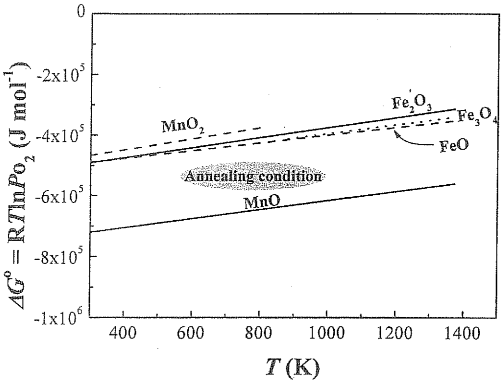

Fig. 1 Ellingham diagram for iron and manganese. Annealing conditions used in this work are denoted.

Measurements

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

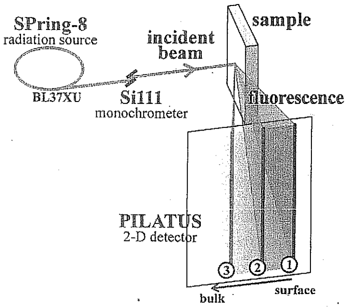

Fig. 2 Schematic view of geometry for the depth-resolved XAFS measurement.

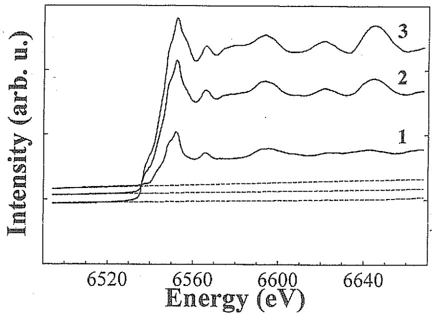

Fig. 3 XAFS spectra using the intensity detected at different pixels as a function of incident beam energy.

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 [6]), which was positioned in the direction parallel to the sample plane, was used to detect the emitted Mn 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 about 0.06 degree. 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 three-numbered pixel array, the array 1 includes the highest intensity ratio from surface to deeper layer 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. These profiles correspond to the X-ray absorbance spectra and their detection angles, 0.29, 3.26 and 5.54 degrees at arrays 1, 2 and 3, respectively. These raw data of the spectrum is represented in Fig. 3. The detected intensity includes background mainly due to elastic scattering. The intensity of Mn K fluorescence is obtained by deducting the background signal represented by broken lines in Fig. 3.

The surface morphology of annealed Fe-Mn alloy sample was observed by using a scanning electron microscope (SEM).

Results and Discussion

Fig. 4 shows the resultant normalized fluorescence intensity I_F profiles of as-prepared, annealed at 773 and 973 K samples. The spectra shown in this figure were selected data measured at 1st, 11th, 21st, 41st, 61st, 81st, 101st, 121st, 141st line of pixels. The intensity arising from deeper area becomes higher when the detection angle is increased. In case of the as-prepared sample, all spectra are allocated to bcc-metal as shown in Fig. 4(a). 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 detection angle dependence of Mn K fluorescence intensity in the data measured at certain

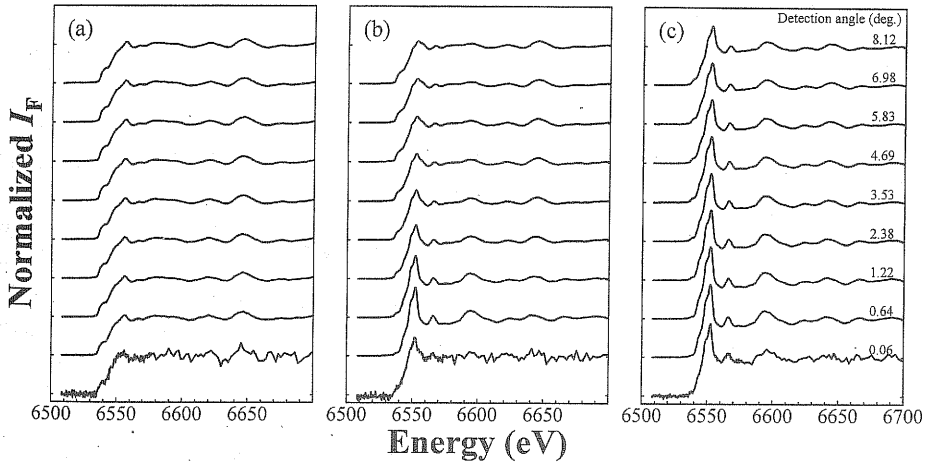

Fig. 4 Normalized fluorescence intensity profiles measured for samples of (a) as-prepared, and annealed at (b) 773 and (c) 973 K.

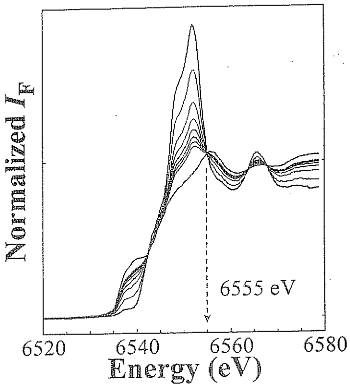

Fig. 5 Normalized fluorescence intensity profiles with different distribution of depth contribution in the near-edge region.

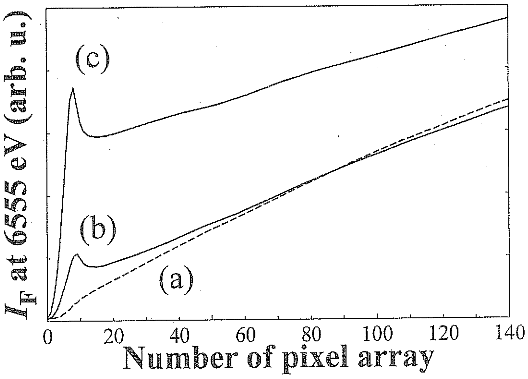

Fig. 6 Pixel array number (relating with detection angle) dependency of the intensity of Mn K fluorescence measured at 6555 eV for the samples of (a) as-prepared, and annealed at (b) 773 and (c) 973 K.

incident beam energy provides useful information. Some measured normalized XANES spectra with different weight distribution of contribution depending on depth from the surface are shown in Fig. 5. All spectra can be considered as summation of bcc-metallic and manganese monoxide (MnO) phases. Normalized intensities exhibit the same value at some absorbance 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 the energies indicating common absorbance is extracted and plotted as function of detection angle, it reflects the distribution of manganese at points deeper from the alloy surface. Fig. 6 shows the pixel array number dependency of Mn K fluorescence intensities of the three Fe-Mn alloy samples. The number of detection pixel array was counted from the position at zero detection angle. Therefore, the detection angle increases with increasing pixel array number. As shown in Fig. 6(a), the fluorescence intensity distribution of the as-prepared sample increased monotonically with the number of pixel array (detection angle). This is attributed to the fact that the fluorescence intensity detected at higher detection angle includes signals emitted from not only deeper area but also from shallower area. In comparison with this, the fluorescence signals were totally higher for samples treated at higher temperatures as represented in Fig. 6(b) and (c). This suggests the enrichment of manganese from deeper area to the surface area by diffusion. Furthermore, the gradient at the larger number of array corresponding to higher detection angle is slightly decreased for the sample annealed at higher temperature. This suggests that the concentration of manganese in deeper area was decreased due to depletion of manganese in the substrate alloy. On the other hand, the characteristic feature of the heat-treated samples is observed in the sharp peak of the fluorescence intensity profile at around 10th array corresponding to about 0.57 degree in the detection angle for both the samples. This is considered due to a quite low density at very shallow area, or may be due to presence of a thin layer with large deviance in density or manganese concentration at specific depth from the surface. This feature of the sharp peak cannot be explained by using a simple model of surface structure as a MnO layer with certain thickness formed on the surface of the iron alloy. The X-ray linear absorption coefficient μ at the energy of Mn K fluorescence calculated using the elemental composition along with the incident beam energy dependence of $\mu(E)$ obtained from the experimental XAFS spectra for MnO and Fe-Mn alloy sample is shown in Fig. 7. The linear absorption coefficient for incident X-ray beam energy such as 6555 eV, which is used to deal with the above discussion, is largely different in each other of MnO and Fe-Mn alloy. Considering the experimental geometry and path length of incident beam and emitted fluorescence, however, the feature of detected fluorescence intensity is affected

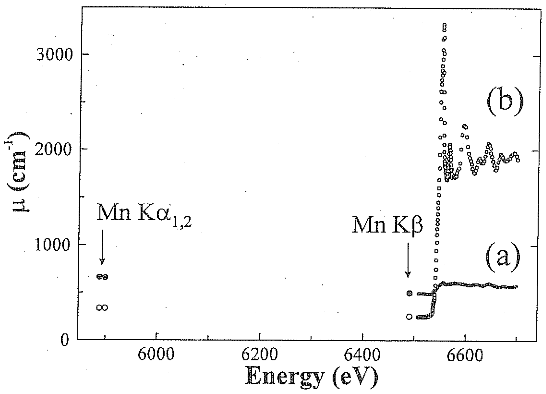

Fig. 7 Calculated linear absorption coefficient of (a) the Fe-3.74Mn alloy and (b) MnO.

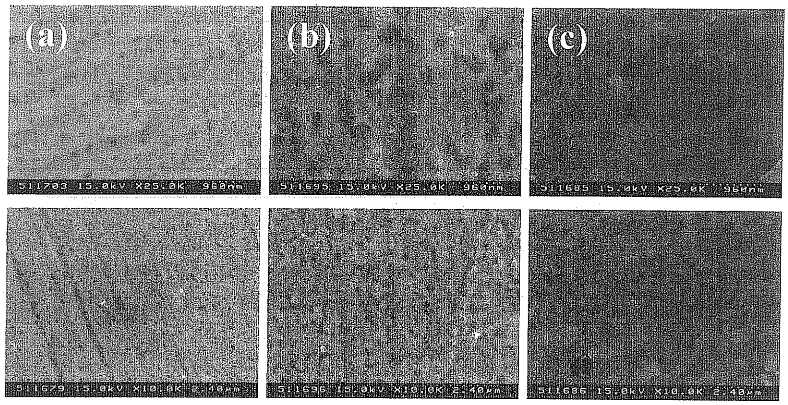

Fig. 8 SEM micrographs for the samples annealed at (a) 773, (b) 873 and (c) 973 K with high (upper) and low (lower) magnification.

not by this difference in absorbance of incident beam but by the difference of Mn K fluorescence or depth dependence in distribution of density. Fig. 8 shows the surface morphology of the samples annealed at 773, 873 and 973 K observed by using SEM. The roughness of the sample surfaces becomes larger with increasing the annealing temperature due to formation of manganese oxide and the grain growth at the surface. It is considered that the density decreased at the surface of the sample annealed at higher temperature. On the other hand, compositional distributions of the annealed Fe-Mn alloys were calculated from the XPS depth profiles by Ar ion sputtering, as shown in Fig. 9. The concentration of Mn increased to 35 and 50 % in the surface area of the samples annealed at 773 and 973 K, respectively. Considering the average concentration of Mn of 4 %, the results showed enrichment of manganese to the surface layer to form an oxide. The decrease in the density and compositional distribution in the surface layer are considered as important factors to investigate the distribution of density, composition and phase in surface area for understanding the mechanism of enrichment and oxidation of manganese.

Summary

The grazing exit fluorescence yield XAS method was used for analyzing depth-resolved manganese compositional distribution in the surface layer of as-prepared and annealed Fe-Mn alloys. The results of detection angle dependent XAFS profiles showed that manganese was present uniformly in metallic alloy phase in the as-prepared sample, while the formation of manganese

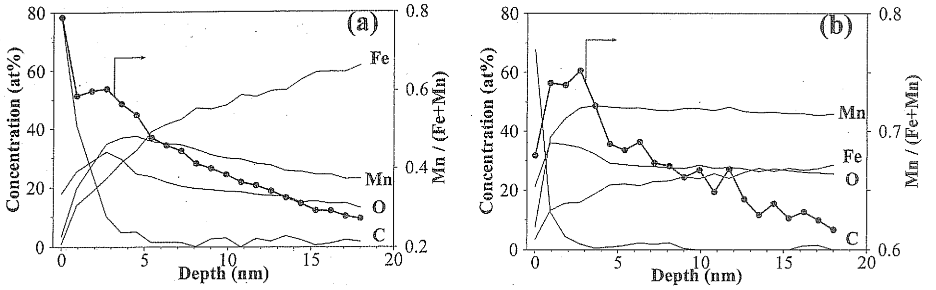

Fig. 9 XPS depth profiles of Fe-Mn alloys annealed at (a) 773K and (b) 973 K [4].

oxide was detected on the surface layer of annealed samples. The intensity of Mn K fluorescence emitted from the sample surface increased monotonically with detection angle for as-prepared sample, and showed the characteristic intense peak at low detection angle for annealed samples. Though it is difficult to explain this phenomenon completely, the surface morphology observed by using SEM and the compositional depth profile obtained by XPS measurements suggest the possible decrease of density at the surface layer or characteristic distribution of manganese in depth direction.

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. 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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