# Practical Characterization of Surface and Interface Phenomena in Iron and Steel

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Surface and interface phenomena play important roles in many properties of iron and steel. For instance, the surface of plain carbon steel is easily corroded in air with humidity. In order to improve the surface properties of steel, various kinds of coatings have been developed. Surface analytical techniques are used for characterizing the coatings and surface layers on steel. Typically, glow discharge optical emission spectrometry (GD-OES) is often used for rapidly evaluating the composition and thickness of the coatings. XPS, AES and SIMS are also applied to characterization of thin layers formed on the surface and interface of steel. These techniques provide essential information on enrichment of elements such as the surface segregation and grain boundary segregation. However, systematic experiments have shown that analyzed results are affected by microstructures of iron and steel. Therefore, the surface and interface phenomena should sometimes be investigated by different methods and from different viewpoints, in order to understand all the features of the phenomena. The present paper gives analyzed examples of these surface and interface phenomena analyzed by the surface analytical techniques and other techniques.

## 1. Introduction

Steel products are extensively used as structural and functional materials. However, normal carbon steels are easily corroded in wet air, and therefore steel products with a variety of kinds of coatings such as zinc, tin and chromium are manufactured. Surface analytical methods are often employed for evaluating the quality of these coatings. Typically, glow discharge optical emission spectrometry (GD-OES) is industrially applied to analysis of the composition and thickness of these coatings, because of its rapidness and its ability to quantify the analysis [1].

Characterization of microscopic chemical reaction and enrichment of elements in local areas of steel are also indispensable for clarifying the mechanism of the phenomena in iron and steel. For instance, surface analytical techniques such as XPS, AES and SIMS are often used for characterizing the surface and interface phenomena occurring in iron and steel [2,3]. Owing to the development of these surface analytical methods, small areas at the surface and interface have been analyzed. Although results obtained by the analytical methods may provide crucial information on the chemical composition and state of elements, much attention should be paid to interpreting the correlation between the properties and chemical characteristics of elements. This is because steel products consist of a variety of microstructures such as second phases, dislocations and grain boundaries, which are not fully characterized. Actually, results obtained by the microscopic analytical methods have shown that the chemical reaction and enrichment of elements heterogeneously occur on the surface and interface of polycrystalline steel [4,5].

Thus, in order to really understand many factors influencing the properties of iron and steel, steel products should be analyzed by different methods and microstructural effects on microscopic analyzed results should be taken into account. In the present paper, several examples of characteristic features of elements at the surface and interface obtained by surface analytical methods together with other techniques are described.

## 2. Coating analysis by GD-OES

GD-OES is used for evaluating the composition and thickness of coatings such as zinc-based alloys on galvanized and galvannealed steel sheets [1]. Rapid measurements are indispensable for analyzing these products with coatings, since they were produced industrially. GD-OES satisfies this condition, since it can conduct rapid analysis without ultra high vacuum (UHV) and give the average surface composition of coatings [6]. Fig.1 exemplifies GD-OES depth profiles of alloying processes of coated zinc with steel substrate, which demonstrate systematic changes of the zinc concentration in zinc coatings by annealing at high temperatures [7]. These compositional results suggest that a few alloy phases were formed on the surface of steel sheets with zinc coatings by annealing. However, a difference in their composition is relatively small, and their microstructures are complicated. Therefore, structural analyses by x-ray diffraction methods are performed, as shown in Fig.2.

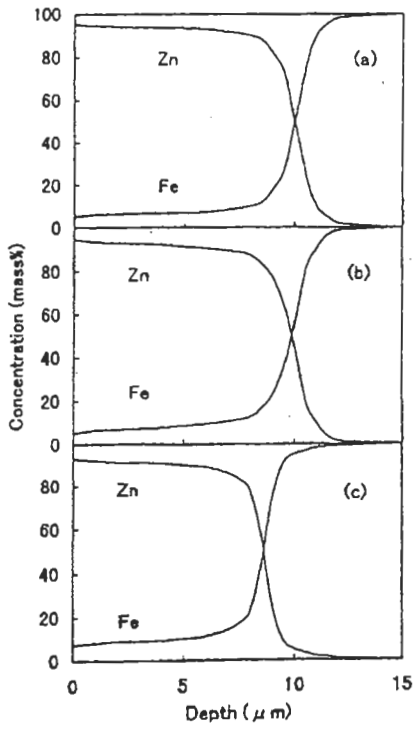


Fig.1 GD-OES depth profiles for zinc coated steel sheets annealed at 673 K for (a) 300 s, (b) 1000 s and (c) 3000 s.

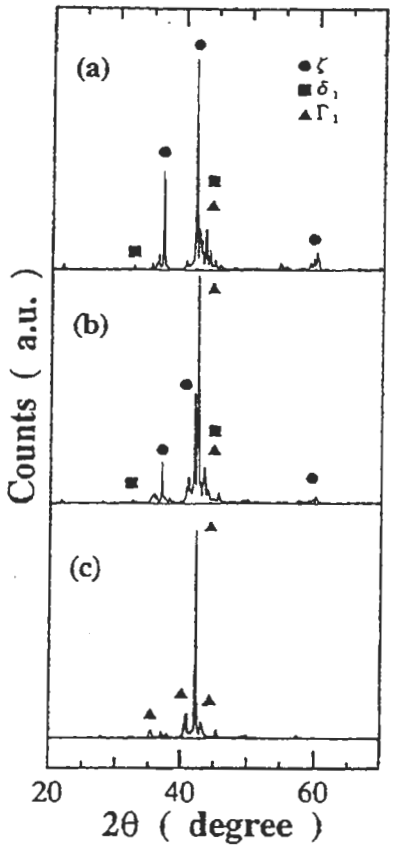


Fig.2 X-ray diffraction patterns obtained from zinc coated steel sheets annealed at 673 K for (a) 300 s, (b) 1000 s and (c) 3000 s. $\zeta$, $\delta_1$ and $\Gamma_1$ are Fe-Zn intermetallic phases formed during annealing.

## 3. Surface reaction analysis by XPS

XPS is a very effective method for analyzing the chemical composition and state of the surface of iron and steel [8], and its performance has been improved recently. Angle resolved (AR) XPS and microscopic XPS are non-destructive methods for conducting in-depth and two-dimensional analyses, respectively. Using a combination of these two methods, microscopic reaction products of oxides and oxyhydroxides have been observed on the surface of high-purity iron exposed to air at room temperature [4]. Fig.3 shows the surface composition measured by AR-XPS as a function of the take-off angle, which is the angle between the analyzer axis and the sample normal. These results suggest that a native oxide layer of thickness of a nanometer order of

magnitude is formed on the surface of high-purity iron, and an oxyhydroxide layer is formed on the native oxide layer formed on the high-purity iron. Moreover, observation of reaction products by micro-XPS imaging reveals that the fine reaction products, presumably oxyhydroxides, heterogeneously grow on the surface, as shown in Fig.4.

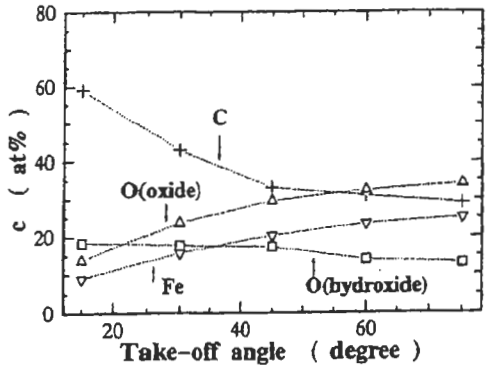


Fig.3 The concentration of iron, oxygen and carbon obtained by XPS versus take-off angle in a high-purity iron exposed to air. The oxygen components are divided into two components.

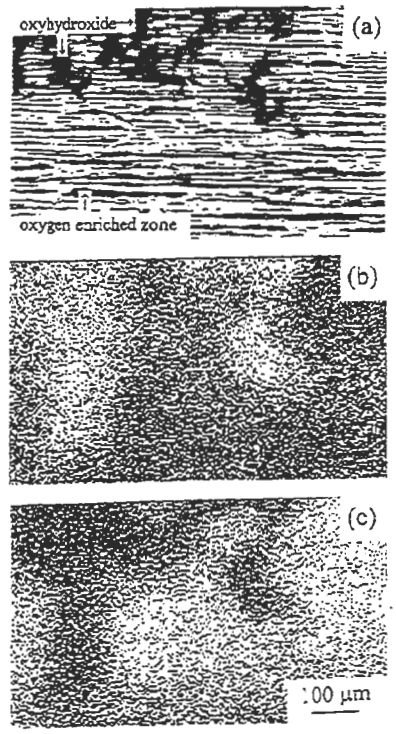


Fig.4 (a) Optical micrograph, (b) O 1s XPS image and (c) Fe 2p XPS image taken by micro-XPS for the surface of high-purity iron exposed to air.

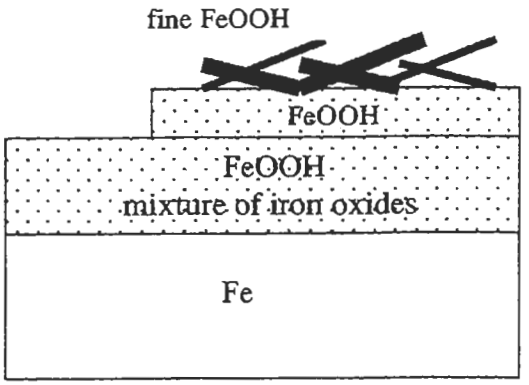


Fig.5 Schematic illustration of the layered structure consisting of oxide and oxyhydroxide formed on the surface of iron.

Besides oxyhydroxides, a native oxide layer is known to form on the iron surface [8]. Based on these results, the formation of layers of iron oxide, oxyhydroxide and fine reaction products on the surface may be summarized as shown in Fig.5.

## 4. Surface composition analysis by AES

AES is a microscopic method for analyzing the surface and interface using its small size of electron beams. In order to clarify the effect of the surface orientation of a polycrystaline sample on the results analyzed by AES, the electron channeling pattern (ECP) method has been used to determine the crystallographic orientation of the surface of the polycrystalline sample.

Using a combination of these methods, the dependence of the surface orientation on the surface composition was studied in an annealed Fe-18%Cr-8%Ni alloy [5]. Figs.6(a) and (b) exemplify AES spectra from two grains, with a large chromium peak and small chromium peaks, respectively. These results also indicate that chromium enrichment on the surface is correlated with nitrogen enrichment, and with regard to two surfaces, the surface with higher chromium and nitrogen is less oxidized. These results together with AES images show that the surface composition differs from grain to grain, and the degree of oxidation of the

grain surface depends on the surface orientation.

Figure 7 shows a plot of the Auger peak height ratio, N/O, in a stereo-triangle, which is used for denoting the surface orientation determined by ECP. The result of this determination indicates that the nitrogen or chromium enrichment is higher in low index planes such as (011) and (111), where oxide layers are relatively thin. This result also demonstrates the effect of a microstructure on surface phenomena.

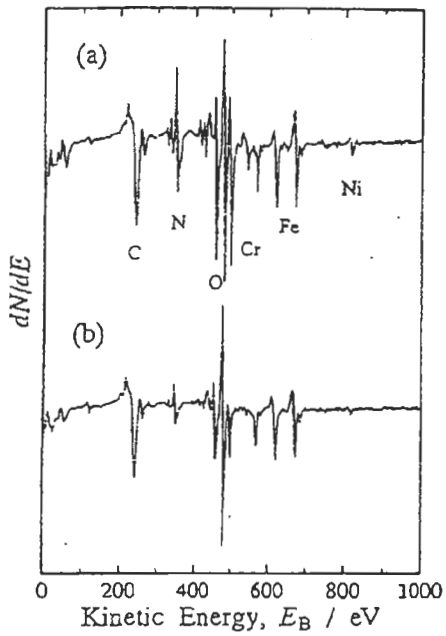


Fig.6 Auger spectra from two grain-surfaces with (a) a large chromium peak and (b) a small chromium peak in the stainless steel annealed at a high temperature.

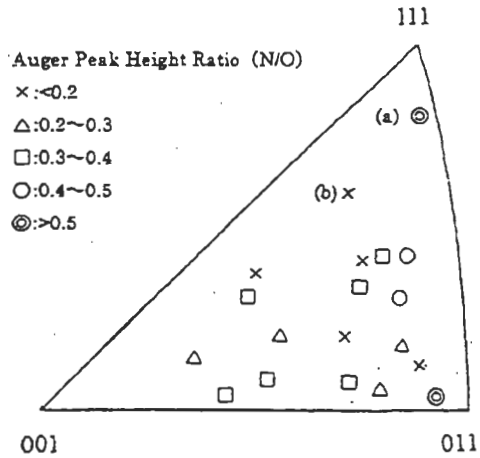


Fig.7 Plot of the Auger peak height ratio, N/O, in a stereo-triangle. The ratio range is given in the figure.

## 5. Grain boundary analysis by AES

In studies on grain boundary segregation of solute atoms [9-11], attention has also been focused on the effects of various microstructures, especially grain boundary structures. Since a grain boundary fractured plane of a polycrystal reveals a rough surface consisting of facets with a variety of orientations, the effect of these facets on AES analysis has been carried out. Fig.8 shows Auger peak height ratio, P/Fe, from two grain boundary fractured facets versus the angle between the plane normal and the analyzer axis in an Fe-P alloy. AES measurements were performed using cylindrical mirror analyzer (CMA). These results show that the values of P/Fe are almost independent of the geometry between the sample and CMA, which is consistent with a theoretical estimation [12]. This indicates that Auger spectra from grain boundary planes measured by CMA are almost insensitive to the measurement geometry.

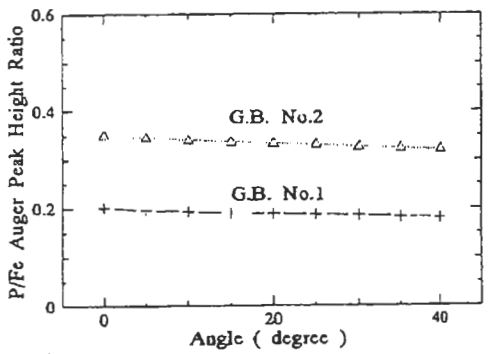


Fig.8 Auger peak height ratios, P/Fe, from two grain boundary fractured planes versus the angle between the plane normal and the axis of CMA.

Based on these fundamental data, the influence of a microstructure on grain boundary segregation has been investigated. In general, if grain boundary fractured planes of polycrystalline iron are analyzed using scanning AES, the segregated number of elements differs from boundary to boundary [11]. Fig.9 exemplifies the amount of sulfur versus that of carbon segregated on grain

boundary fractured planes in a polycrystalline Fe-S-C alloy. These results may arise from the fact that grain boundaries in polycrystalline materials are not composed of a specific well-defined structure, but instead various structures [11]. Thus, it has been pointed out that there are a number of types of grain boundaries with different structures of segregation in polycrystalline steel, as shown in Figs.10. Systematic studies of grain boundary segregation of solute atoms in Fe-Si bicrystals with various misorientations have also demonstrated that the grain boundary structure plays a crucial role in grain boundary segregation [11]. The grain boundary structure may be responsible for deviations of experimental data on grain segregation from values simply predicted by thermodynamic models.

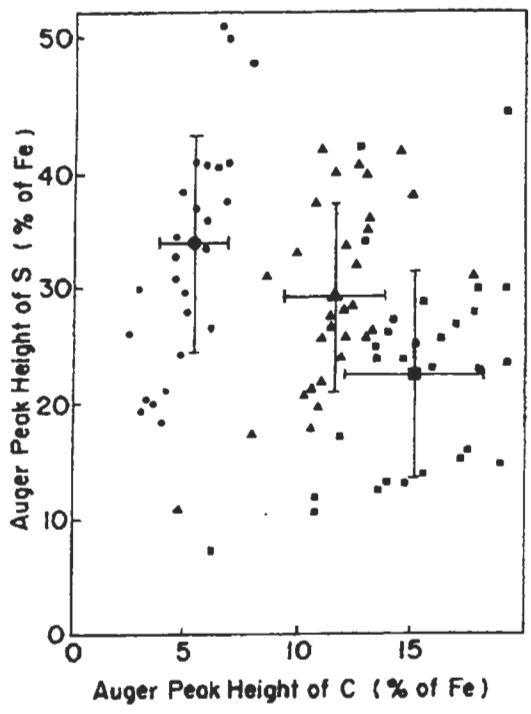


Fig.9 Auger peak height ratio of S/Fe versus C/Fe in grain boundary fractured planes for Fe - 100ppmS - 12ppmC(●), 40ppmS(▲) and 75ppmC(■) alloys. Each small point was taken at one grain boundary plane, and the large points attached with error bars represent the average value of segregation in each sample with the standard deviation.

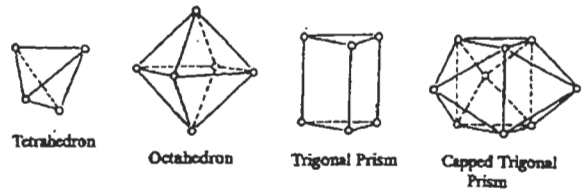


Fig.10 Compact polyhedra of atoms found in grain boundaries.

## 6. Interface analysis by SIMS

SIMS analysis is sometimes performed, in order to investigate the segregation behavior of a small number of elements in steel products. If a SIMS depth profile is measured in a sample with a flat surface, an elemental enrichment is efficiently detected in the depth profiles.

Figure 11 shows SIMS depth profiles for several elements in a flat and smooth Fe-3%Si alloy sheet covered with a silicon oxide layer, which was formed during annealing at a high temperature [13]. Sputter-etching time in SIMS depth profiles was converted to the distance from the surface using a reference $SiO_2$ film, while it is difficult to quantify the composition from secondary ion counts. Nevertheless, the depth profiles of Fig.11 show that a uniform $SiO_2$ layer of 10nm in thickness was formed on the surface. Drastic changes in the depth profiles are found at the $SiO_2$/alloy interface. These profiles indicate that phosphorus and sulfur are considerably segregated at the $SiO_2$/alloy interface. It is also found in this result that surface-active elements such as phosphorus and sulfur are easily segregated at the interface. Although other surface analytical methods such as XPS and AES are also employed to depth profiling of silicon steel [14], these methods are less sensitive than SIMS. Thus, the importance of SIMS has been demonstrated, when a small number of elements at the surface and interface are detected by surface analytical methods.

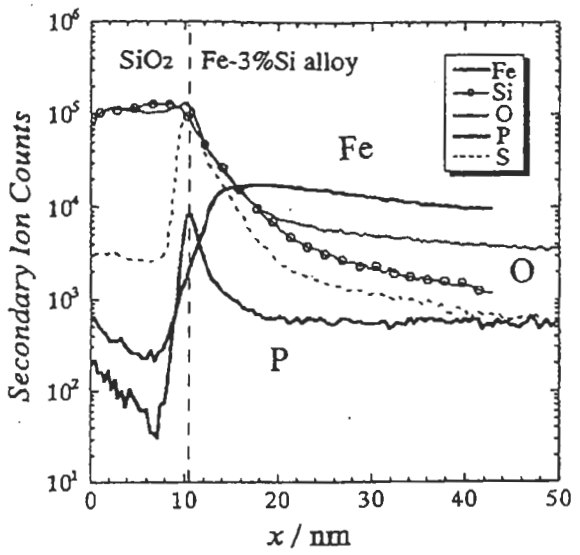


Fig.12 SIMS depth profiles of an external oxide layer formed on the surface of an Fe-Si alloy.

## 7. Concluding remarks

Surface analytical methods have contributed to not only analysis of steel products but also characterization of the mechanism of surface and interface phenomena occurring in iron and steel. Several examples of characteristic features of elements at the surface and interface obtained by surface analytical methods were described in this paper. Emphasis should be placed on microscopic heterogeneous processes of chemical reactions and influences of microstructure on elemental segregation, because the size of steel products is generally large and these products consist of various microstructures. This large size and microstructural and compositional variation may make it too difficult to understand the experimental results. Thus, although characteristic features of these phenomena depend on the kind process condition of materials, information obtained from microstructural viewpoint is very useful in developing advanced materials.

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