Technical Report

XPS Analysis of Element Segregation at Surfaces and Interfaces

Takashi DOI*

Abstract

Fe- and Ni-based alloys are widely used as structural materials, where corrosion resistance is strongly influenced by surface and interface chemistry. However, the behavior of minor alloying elements at oxide/metal interfaces under service-relevant environments is not fully understood. In this study, angle-resolved hard X-ray photoelectron spectroscopy (HAXPES) was employed to non-destructively investigate elemental segregation and chemical states at reaction interfaces in Ni-based alloys exposed to a simulated synthesis-gas environment. The results demonstrate preferential enrichment of metallic Cu at the oxide/metal interface, with a higher interfacial Cu concentration observed in alloys exhibiting superior resistance to metal dusting corrosion. In addition, in-situ XPS reveals that Cu, Sn, and Sb segregate to Ni alloy surfaces under low oxygen potentials. These findings highlight the importance of controlled elemental segregation for corrosion-resistant alloy design and process optimization.

1. Introduction

Alloy materials primarily composed of Fe and Ni are widely used as structural materials where strength, formability, and reliability are paramount. Numerous alloying elements are added to impart the diverse properties required of these structural materials. During manufacturing processes or exposure to service environments, thermal histories can cause alloying elements and impurity elements to segregate to the surface. The driving force behind this phenomenon, known as surface segregation, is the reduction in surface free energy caused by segregation. Segregation behavior is influenced by the matrix phase, segregating elements, coexisting elements, and the atmosphere. Conversely, the material's response to the atmosphere and its oxidation resistance also change, making the segregation behavior observed in actual environments complex. Furthermore, surface segregation results in the alloy surface exhibiting properties different from its inherent composition, making it a critical phenomenon for material design.

Steel materials are alloys containing numerous added elements—such as C, Si, Mn, Cr, Ni, P, Cu, Sn, Sb, S, Al, B, and Ti—tailored to specific applications and purposes. Many of these alloying elements tend to segregate to the surface relative to Fe or Ni. Furthermore, since each element has different chemical properties from Fe or Ni, during the steel manufacturing process involving heat treatment under various oxygen partial pressure environments, they may form specific oxide layers on the surface or create subscales within the alloy. These surface properties significantly impact corrosion resistance and subsequent surface treatments.[1)] For example, it has been noted that carbon (C) segregation at the surface during annealing of cold-rolled steel sheets impairs subsequent chemical conversion treatment.[2)] Silicon (Si) promotes this C segregation, while manganese (Mn) suppresses it.

This paper introduces materials where segregation was utilized to enhance material properties, using surface segregation in Ni-based alloys as an example, along with analysis examples primarily employing XPS. Chapter 2 presents an analysis example[3)] of Cu segregation that functioned effectively in a Ni-Cr-Si-Cu alloy. Chapter 3 introduces the effects of environment[4, 5)] on the surface segregation behavior of candidate additive elements during the material development process introduced in Chapter 2.

2. Non-Destructive Analysis of Cu Segregation at the Oxide Layer/Base Metal Interface

This chapter introduces an example[3)] using hard X-ray photoemission spectroscopy (HAXPES) as a non-destructive analysis

* Ph.D. (Engineering), Senior Researcher, Materials Characterization Research Lab., Advanced Technology Research Laboratories
1-8 Fuso-Cho, Amagasaki City, Hyogo Pref. 660-0891

method for the oxide layer/base metal interface.

Recently, GTL[6] and DME[7], clean fuels derived from natural gas, have gained attention as new energy sources advantageous for reducing carbon dioxide emissions. However, during the production processes of GTL and DME, severe corrosion known as metal dusting corrosion[8] (hereafter abbreviated as MD) progresses.[9]

Conventional materials struggled with long-term operation in this corrosive environment, complicating the design of synthetic gas production equipment such as GTL plants. Addressing this challenge, it was discovered that Ni-based alloys containing Cr, Cu, and Si exhibit reduced corrosion progression even in this environment.[10] Based on research elucidating the mechanism, NEXAGE™696[11] was developed, incorporating a novel corrosion prevention concept.

In the developed material, while Cr and Si form protective oxide layers in MD corrosion environments, the role of Cu was less clear. However, we found that in Ni-Cu alloys, Cu segregates to the surface[12] and MD corrosion is significantly suppressed. These results indicate that in the developed material too, Cu likely segregates to the metal surface immediately beneath the protective oxide layer in high-temperature synthetic gas environments. For verification, it is essential to obtain information on the depth-dependent composition and chemical bonding state of specimens exposed to a simulated synthesis gas environment. After evaluating various methods, it was determined that non-destructive depth profiling using the HAXPES method, which employs hard X-rays as a source to excite high-kinetic-energy photoelectrons, would enable analysis of the distribution and existence state of alloy elements, including Cu, at the oxide layer/base metal interface. Unlike conventional XPS, XPS measurements using hard X-rays enable the acquisition of XPS spectra at depths of tens of nanometers, achieving an information depth more than ten times greater. Using this HAXPES, angle-resolved measurements were performed by tilting the sample relative to the photoelectron analyzer, as shown in **Fig. 1**. This provided information on the depth distribution and existence state of each element, including Cu.

Two types of samples, alloy1 and alloy2, were prepared. Alloy1 exhibits resistance to MD corrosion in a synthetic gas environment, whereas MD progresses in alloy2. Their compositions are: alloy1: Ni-22Cr-2Cu, alloy2: Ni-22Cr-1Cu. These were subjected to an oxidation test at 650°C for 600 seconds in a simulated synthesis gas environment (60%CO+26%H_2+11.5%CO_2+2.5%H_2O), then promptly removed and prepared for measurement.

HAXPES measurements were performed at SPring-8 BL47XU using 8 keV X-rays. Measurements were conducted using the angle-resolved method, with photoelectron take-off angles (TOA) set to 80°, 52°, 30°, and 15°.

Figure 2 shows representative spectra obtained from alloy1. The Cr $2p_{3/2}$ peak shown in Fig. 2(a) consists of a low-binding-energy component containing spectral information from the metallic component (labeled Met. Cr in the figure) and a high-binding-energy component containing spectral information from the oxide (labeled Cr-O in the figure). The Ni $2p_{3/2}$ spectrum shown in Fig. 2(b) and the Cu $2p_{3/2}$ spectrum shown in Fig. 2(c) both suggest that Ni and Cu primarily exist in a metallic state. Although not shown here, O 1s and C 1s spectra were also acquired. Among these, the C 1s spectrum contained two components: hydrocarbon (CH) and graphite (C).

After background correction using the Shirley method,[13] the Cr $2p_{3/2}$ and C 1s photoelectron peaks were separated into individual components by fitting with Voigt functions. The elemental concentrations obtained by integrating these peaks using theoretical photoionization cross-section values calculated by Yeh et al.[14] are shown in **Fig. 3**. The TOA dependence of the elemental concentrations constituting alloy1 and alloy2 can be broadly categorized into three groups. First, Ni, Cu, and Cr-Met. showed a tendency for their concentration ratios to decrease as the TOA became shallower. C and CH exhibited the opposite trend, with their concentration ratios in-

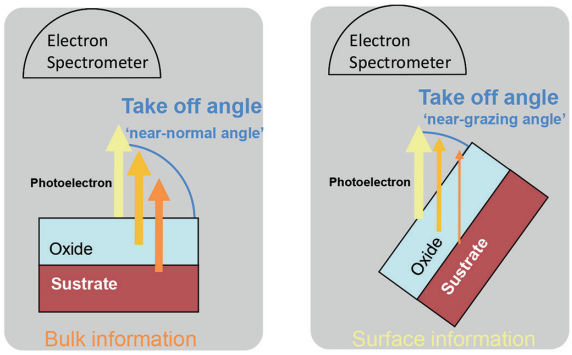

Fig. 1 Schematic diagram of angle-resolved XPS

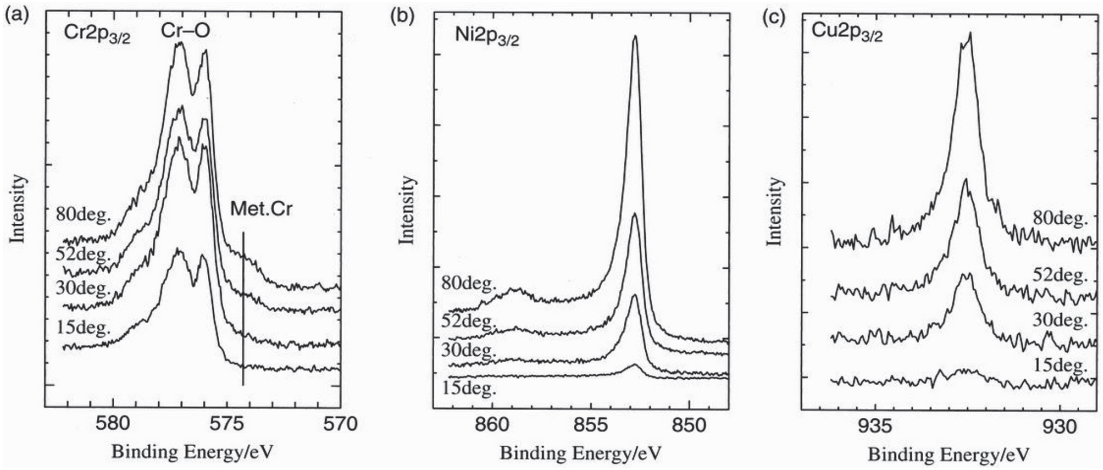

Fig. 2 Angle-resolved XPS spectra of each element in alloy1[3]
(a) Cr $2p_{3/2}$ spectrum. In the figure, Met.Cr indicates the metallic component and Cr-O the oxide component. (b) Ni $2p_{3/2}$ spectrum, (c) Cu $2p_{3/2}$ spectrum

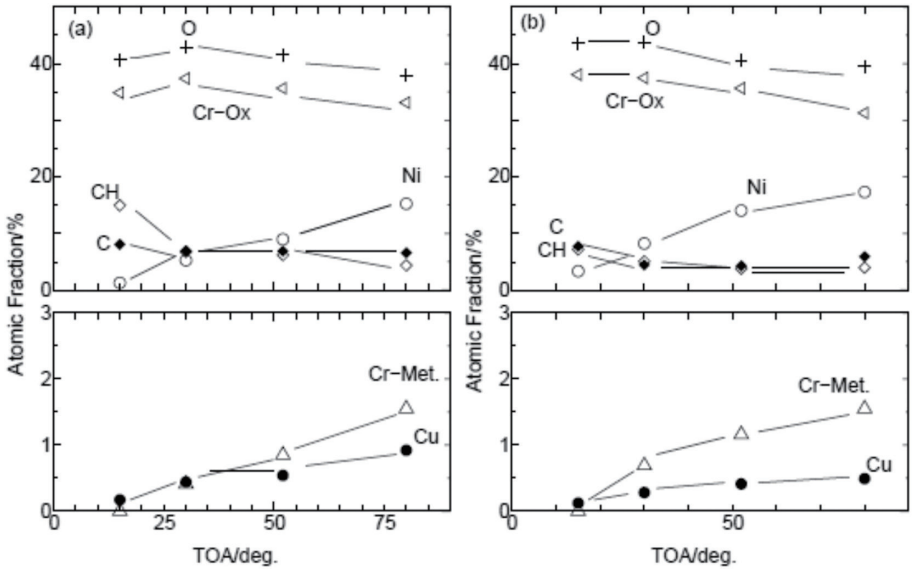

Fig. 3 Angular dependence of the quantitative values of each element on the take-off angle of photoelectron emission[3)]
(a) alloy1, (b) alloy2. In the figure, Cr-Met. is the Cr metal component, Cr-Ox is the Cr oxide component, and CH is the hydrocarbon component.

creasing as the TOA became shallower. Cr-Ox and O showed a maximum value around a TOA of 30 degrees. This TOA dependence reflects the depth distribution of each component. For example, the behavior of C and CH components, where the concentration ratio increases as TOA becomes shallower, indicates their distribution toward the surface. Conversely, the opposite trend observed for Cr-Met., Ni, and Cu implies their distribution toward the subsurface. Based on their TOA dependence, the Cr-Ox and O components are distributed between the C, C-H group and the Cr-Met., Ni, Cu group. These Cr-Ox and O components form the protective oxide layer. Cr-Met., Ni, and Cu are the base material components beneath the oxide layer. C and CH are distributed at the very surface of the sample, most exposed to the environment. The distribution of C suggests that graphite was formed at the surface from CO components in the environment. For the CH components, it is unclear whether they originate from reaction products in the simulated synthesis gas or from surface contamination after sample removal.

The key points to clarify are the state of Cu and its depth distribution. Cu existed in a metallic state. Angle-resolved behavior suggests that it is distributed in the substrate just beneath the oxide layer, alongside Cr-Met. and Ni. To confirm whether there are differences in depth distribution among the three components Cr-Met., Ni, and Cu, their concentration ratios relative to the TOA were calculated using only these three components and are shown in **Fig. 4**. The Cr-Met. component ratio decreased as the angle relative to the TOA became lower. Conversely, the Ni and Cu ratios increased with lower angles. This TOA profile suggests that Ni and Cu were distributed more superficially than Cr-Met. Cr tends to be depleted at the oxide layer/base metal interface because it is consumed as an oxide. The angle-resolved HAXPES measurement results reflect this. To further clarify the difference in depth distribution between Ni and Cu, the Cu/Ni concentration ratio is shown in **Fig. 5**. Both alloy1 and alloy2 exhibit a tendency for Cu to be more abundant near the surface compared to Ni. This suggests that Cu tends to segregate at the oxide-metal interface. Figure 5 shows that the Cu concentration at this interface is higher in alloy1, which suppresses MD, than in alloy2. Further analysis of the results obtained by angle-resolved HAXPES allows quantitative information on the composition and thickness of each component to be obtained.[3)] The results showed that the Cu concentration at the interface was more than double that of alloy2 in alloy1. This difference in Cu concentration at the interface significantly contributed to suppressing carburization progression through defects in the protective oxide layer, determining the difference in MD resistance. Material surface composition is greatly influenced and altered by factors such as the atmosphere and temperature. It is essential to discern the nature of these changes.

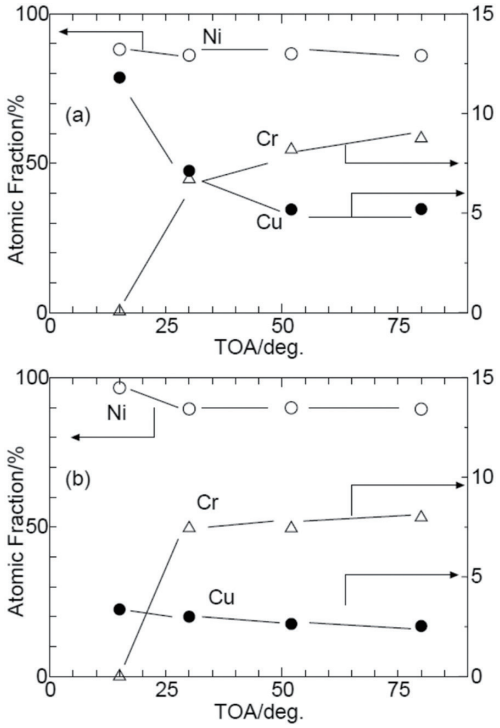

Fig. 4 Dependence of Cr metallic component, Cu and Ni concentrations on photoelectron take-off angle[3)] (a) alloy1, (b) alloy2

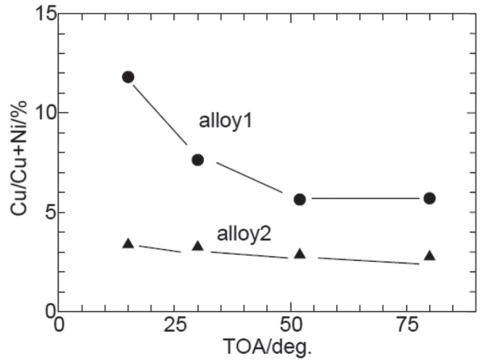

Fig. 5 Photoelectron emission take-off angle dependence of Cu and Ni ratios[3)]

3. In-situ Analysis of Surface Segregation and Oxidation Behavior of Ni-X Binary Alloys under Controlled Oxygen Potentials

The previous chapter introduced the role of Cu in suppressing MD corrosion in Ni-Cr-Si-Cu alloys. It was clarified that Cu segregation immediately beneath the oxide layer subsequently suppressed CO dissociative adsorption. In this MD environment, addition elements other than Cu that could potentially enhance corrosion resistance have been proposed.[15)] Among these, it was noted that Group 14 and 15 elements are highly likely to yield similar effects. Representing group 14 elements, Sn was selected, and representing group 15, Sb was chosen. Binary alloys with Ni were prepared for each.

Figure 6 shows XPS spectra (E0 = 1 486.8 eV)[4, 5)] acquired during heating from room temperature to 650°C under ultra-high vacuum for Ni-2Cu, Ni-0.5Sb, and Ni-0.5Sn samples (all in mass%). For each sample, the intensity of the main component Ni decreased during high-temperature heating, while the spectra of the added elements increased. That is, the added elements Cu, Sn, and Sb all segregated to the surface, covering Ni. This surface segregation is thought to proceed similarly in the reductive MD corrosion environment, which has an oxygen potential equivalent to or lower than that in ultra-high vacuum ($PO_2 = 4.6 \times 10^{-23}$ Pa). This result is consistent with the inference that MD was suppressed due to this surface segregation.[15)]

On the other hand, in oxidizing environments, these alloying elements do not function as strong inhibitors against Ni oxidation. While surface segregation onto Ni proceeds, both their own oxidation and Ni oxidation occur simultaneously.[4, 5)] Although research examples in oxidizing environments are scarce and definitive conclusions are difficult, it can be concluded that the effect of these elements on improving Ni's oxidation resistance is limited.

As stated at the outset, in steel materials containing numerous alloying elements, surface composition changes universally occur when exposed to high-temperature environments. During steel manufacturing processes and in service, heat treatment is applied under various conditions. In these processes, as observed here, changes in element surface concentrations may occur, potentially affecting material properties. Indeed, the elements Cu, Sn, and Sb presented here are well-known as tramp elements in steel and are also elements that promote red-hot brittleness in steel.[16–18)] It is necessary to investigate how the surface composition and reactivity of various steel materials change depending on the atmosphere and temperature under various gas environments and temperatures. We are developing analytical techniques to enable both experimental and theoretical examination.

4. Conclusion

Steel materials are alloys containing numerous added elements, such as C, Si, Mn, Cr, Ni, P, Cu, Sn, Sb, S, Al, B, and Ti, tailored to specific applications and purposes. To achieve the required material properties, they undergo diverse processes such as cold rolling, heat treatment, and surface conditioning before being introduced to the market. Many of these alloying elements tend to segregate to the surface relative to Fe and Ni. This surface segregation of elements with different chemical properties from Fe and Ni significantly alters their reactivity. In steel manufacturing processes involving heating under diverse conditions, this is expected to impact manufacturability and post-processing.

Recently, "carbon neutrality" has been touted as a common global challenge. To achieve this, it is important not only to make energy clean, but also to "decarbonize industry". Nippon Steel Corporation has also begun offering green steel, which significantly reduces CO_2 emissions compared to conventional steel manufacturing processes. The manufacture of steel products using electric furnaces

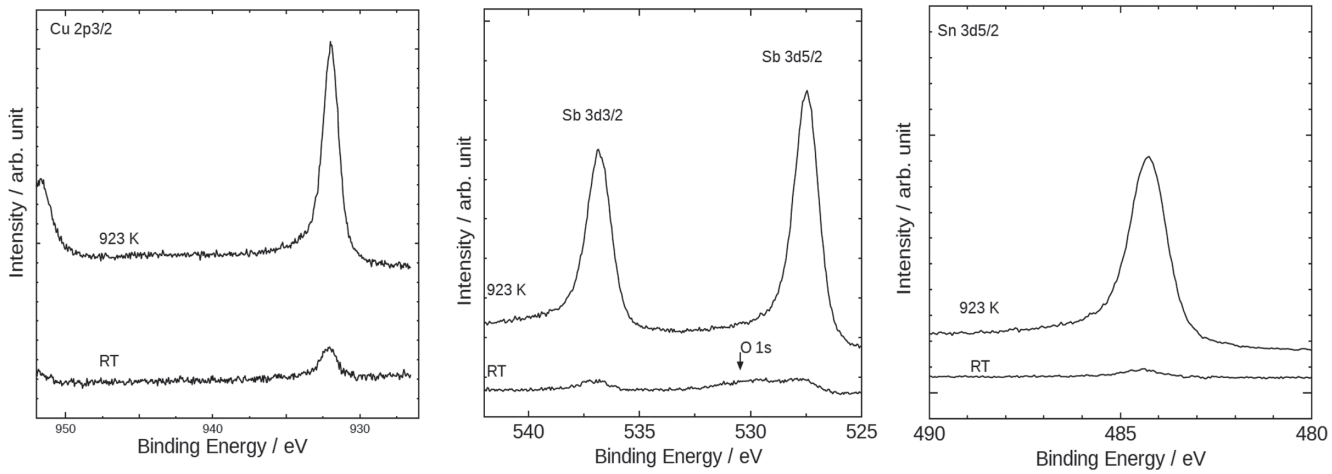

Fig. 6 In-situ surface composition analysis of Ni-X (X = Cu, Sb, Sn) alloys under ultra-high vacuum conditions, comparing room temperature and 932 K[4,5)] (a) Cu $2p_{3/2}$ spectrum of Ni-2Cu alloy, (b) Sb 3d and O 1s spectra of Ni-0.5Sb alloy, (c) Sn $3d_{5/2}$ spectrum of Ni-0.5Sn alloy

is also an important initiative for the production of this green steel. Although electric furnaces can significantly reduce CO_2 emissions, removing tramp elements is generally more difficult than in blast furnace production. Well-known tramp elements include Cu, Sn, and Ni. These elements affect material properties, leading to lower yields and surface quality degradation, which can make it difficult to produce high-quality steel sheets.

A thorough understanding of the composition and reactivity changes at the surface and reaction interfaces, influenced by thermal history and atmosphere, is now more critical than ever for steel materials containing diverse components and subjected to various heat treatments. Such knowledge facilitates improvements in degradation control, manufacturing yield, microstructure control, and surface property enhancement.

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Takashi DOI
Ph.D. (Engineering), Senior Researcher
Materials Characterization Research Lab.
Advanced Technology Research Laboratories
1-8 Fuso-Cho, Amagasaki City, Hyogo Pref. 660-0891