

## Non-destructive analysis on oxidation states of Ti atoms in the passivation film formed on SUS321 using hard X-ray photoelectron spectroscopy

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An oxidation state of a small amount of Ti in the naturally formed passivation film on stainless steel (Fe-Cr alloy, SUS321) was non-destructively evaluated using angle resolved hard X-ray photoelectron spectroscopy (HX-PES) at BL46XU in SPring-8. The synchrotron radiation with photon energy of 7942.5 eV was used as an excitation source. The intensity of Cr 1s peak assigned to metallic state gradually increased with increasing of take-off angle  $\theta$  from 15° to 30°. It drastically increased at larger take-off angle region (30~80°). The results clearly suggest a formation of passivation film on SUS321 and enough large probing depth of HX-PES to evaluate the chemical states of elements placed below the passivation film. Ti 1s spectra collected at take-off angles from 15 to 80° revealed only Ti in tetravalent state. Taking an inelastic mean free path length of Ti 1s photoelectrons into account, it suggests that only Ti in tetravalent state exists in and below the passivation film.

Key words: Hard X-ray photoelectron spectroscopy, Passivation film, Stainless steel

### 1. INTRODUCTION

A conventional soft X-ray photoelectron spectroscopy (SX-PES) is widely applied to evaluate the oxidation states of elements in the materials. Al  $K\alpha$  and Mg  $K\alpha$  lines are generally used as an excitation source to emit photoelectrons. With these excitation sources, only photoelectrons emitted around shallow area can escape from materials into vacuum due to small kinetic energy. For this reason, it is known as a surface sensitive technique. It is, however, also desirable to the evaluation of elements placed in the buried interface or bulk. In some cases, Ar<sup>+</sup> sputter or chemical etching method has been used to removal of surface layers to make bare buried interface as a pretreatment technique, which is sure to give chemical alternation around the interface. Utilizing a photon in the hard X-ray region is the simple way to emit photoelectrons with enough high kinetic energy to escape from bulk or buried interface without destructive pretreatment, if some essential problems are solved. One of the most serious problems is rapid reduction of subshell photo-ionization cross-section as increasing of photon energy [1]. G. Beamsom et al. developed photoelectron spectrometer equipped with Cu  $K\alpha$  sealed tube and LiF(110) Johansson type monochromator [2]. According to them, several hours are required to obtain clear photoelectron spectrum. High brilliance synchrotron radiation beam is essential to use as an excitation source in order to achieve high throughput measurements or to evaluate a small amount of elements.

Recently, the hard X-ray photoelectron spectroscopy (HX-PES) using synchrotron radiation has been developed [3] and started to share for the industrial

usage at SPring-8 [4]. We applied it to evaluate the oxidation states of small amount of additional elements in stainless steel (Fe-Cr alloy) at BL46XU in SPring-8. Stainless steel is commonly used materials for industrial products due to its good property in corrosion resistance. Cr oxide film plays a role as the protective film to interrupt a progression of rust formation into the bulk. The small amount of additional elements such as Ti, Nb, Cu, Ni and so on are known to improve corrosion resistance property of passivation film [5, 6]. It is not, however, precisely known how such elements play a role in improvement of corrosion resistance yet. An estimation of chemical states of additional elements in the oxide film or at around buried interface between oxide film and substrate will help to understand a corrosion resistance mechanism. Thus, HX-PES is expected as a useful tool for evaluation of oxide film formed on steel.

### 2. EXPERIMENTAL

Naturally formed passivation film on SUS321 (Nilaco corporation) was used as a sample for the present study. SX-PES combined with Ar<sup>+</sup> sputter method was carried out by Quantera SXM photoelectron spectrometer (Ulvac-Phi, Inc.) in order to obtain depth profile of elemental composition of passivation film. Ar<sup>+</sup> beam with the energy of 1.0 keV was irradiated onto sample surface at an incidence angle of 45°. The sputter rate obtained by standard SiO<sub>2</sub> sample is 1.13 nm min<sup>-1</sup> under present condition. The photoelectrons emitted by monochromated Al  $K\alpha$  line (1486.7

eV) were detected at take-off angle  $\theta$  of  $45^\circ$  with respect to sample surface. The probing depth is roughly deduced to be less than 5 nm, in the present experimental condition.

For the non-destructive analysis on oxidation state of elements in passivation film, HX-PES was performed using synchrotron radiation with the photon energy of 7942.5 eV at an undulator beamline BL46XU in SPring-8. The synchrotron radiation was monochromated by Si(111) double crystal monochromator. Two Rh-coated curved mirrors were placed at the most downstream of optics hutch for the elimination of higher harmonics and horizontal focusing. A Si(111) channel cut monochromator mounted between Si(111) double crystal monochromator and Rh-coated mirrors was used to reduce photon bandwidth for achievement of high resolution HX-PES. A vertical focusing mirror was mounted outside of optics hutch. The Gammadata-Sienta R-4000 electron energy analyzer was used with the input lens axis directed in the parallel direction to the polarization plane of synchrotron radiation beam. The photon energy and energy resolution were checked by Au  $4f_{7/2}$  core level spectrum and Fermi edge spectrum with analyzer pass energy of 200 eV. The full width at half maximum of Au  $4f_{7/2}$  was 470 meV. In order to changing probing depth, take-off angle  $\theta$  of emitted photoelectrons was varied from  $15^\circ$  to  $80^\circ$  with respect to sample surface by rotating sample.

The spectra were analyzed using standard least-squares-fitting with Voigt line shape after subtraction of background by Shirley method [7].

### 3. RESULTS AND DISCUSSION

#### 3-1 SX-PES combined with $\text{Ar}^+$ sputter

Fig. 1 shows depth profile of O, Fe, Cr, Ti, Ni of SUS321 as a function of  $\text{Ar}^+$  sputter time (min). The vertical axis represents atomic concentration (%) of elemental composition calculated from relative sensitivity factor, transmission function of spectrometer and peak area intensities of O 1s, Fe 2p, Cr 2p, Ti 2p, Ni 2p core level spectra. The depth profile shows formation of oxide layer (passivation film) on SUS321 surface. Ti atoms with the atomic concentration of less than 5.0% are uniformly distributed in depth direction. Here, we should note that core level spectra of each element were measured after destruction of surface by  $\text{Ar}^+$  sputter. Figs. 2 (a) and (b) show Cr 2p and Ti 2p spectra at each  $\text{Ar}^+$  sputter time, respectively. The Cr  $2p_{3/2}$  peaks suggest the existence of  $\text{Cr}^0$  and  $\text{Cr}^{3+}$ , which are placed at binding energy of 574.5 eV and 576.9 eV, respectively. The peak components originated from  $\text{Cr}^0$  grows at longer sputter time than 2.0 min. Ti 2p spectra suggest the existence of  $\text{Ti}^{4+}$ . The full width at half maximum (FWHM) of Ti  $2p_{3/2}$  become broader with increasing of  $\text{Ar}^+$  sputter time as shown in Fig 2(c), suggesting an appearance of Ti in lower oxidation states ( $\text{Ti}^{3+}$  or  $\text{Ti}^{2+}$ ). One may consider that it reflects

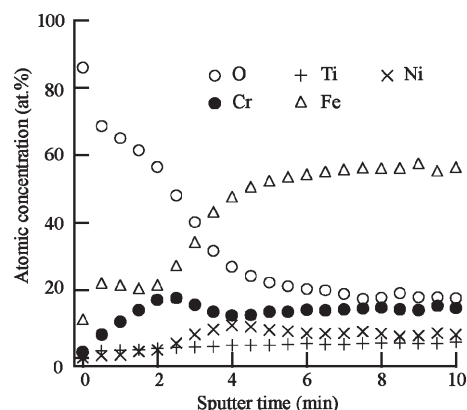


Fig. 1, Depth profile of O, Ti, Ni, Cr and Fe in SUS321 as a function of  $\text{Ar}^+$  sputter time (min)

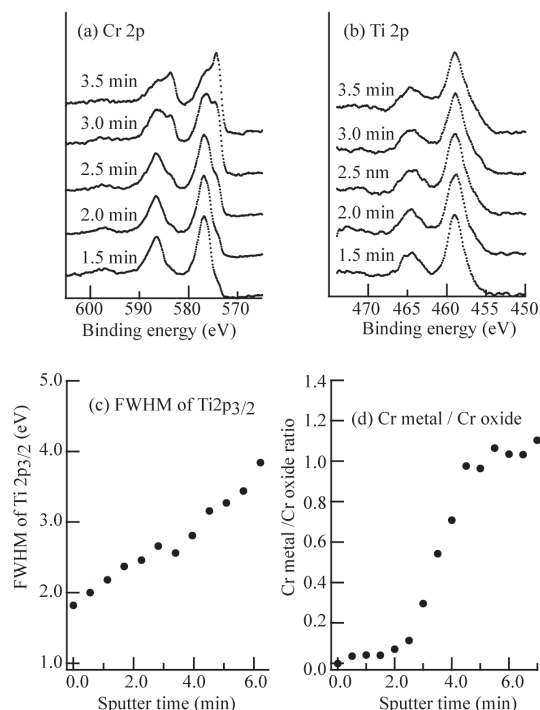


Fig.2, Cr 2p (a) and Ti 2p (b) spectra taken at each sputter time. FWHM of Ti  $2p_{3/2}$  (c) and Cr metal / Cr oxide ratio (d) as a function of sputter time, respectively.

realistic distribution of various oxidation states of Ti in depth direction. On the other hand, however, it is possible to speculate that the appearance of various oxidation states is result of reduction by  $\text{Ar}^+$  sputter.

Assuming that oxidation state of Cr oxide does not change by  $\text{Ar}^+$  sputter according to ref. [8], we obtain depth profile of peak area intensity ratio of  $\text{Cr}^0/\text{Cr}^{3+}$  by analysis of Cr  $2p_{3/2}$  peak as shown in Fig. 2 (d). The profile suggests constant distribution of Cr atoms in metallic state at sputter time region between 0.5 and 2.0 min. Here, we define an interface between passivation film

and substrate at sputter time of 3.5 min, where the  $\text{Cr}^0/\text{Cr}^{3+}$  ratio increases by a middle of maximum and minimum values.

### 3-2 Angle resolved HX-PES

Figs. 3 (a) and (b) show Cr 1s and Ti 1s spectra obtained using synchrotron radiation with the photon energy of 7942.5 eV at  $\theta$  of 15°, 30°, 55° and 80°, respectively. The horizontal axis of spectra represents in kinetic energy scale. We must pay attention that probing depth strongly depends on the kinetic energy of photoelectrons even at same  $\theta$ . The probing depth  $d$  is expressed by  $3\lambda\sin\theta$ , where  $\lambda$  is inelastic mean free path (IMFP) of photoelectrons. Approximately, kinetic energies of Cr 1s and Ti 1s photoelectrons are 1951 and 2974 eV, respectively. Assuming that passivation film consists of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , the calculated IMFPs of Cr 1s and Ti 1s using TPP-2M formula [9] are about 3.4 and 4.7 nm, respectively. The probing depth of Ti 1s is about 1.4 times larger than that of Cr 1s in the passivation film.

The Cr 1s spectra consist of two components at each  $\theta$ . The peak located at lower kinetic energy side is assigned to  $\text{Cr}^{3+}$ , while the other peak at higher kinetic energy side is assigned to Cr in metallic state. By analysis of line shape of Cr 1s spectra, we obtained relative peak area intensity ratio of  $\text{Cr}^0$  against  $\text{Cr}^{3+}$  ( $\text{Cr}^0/\text{Cr}^{3+}$ ) as a function of  $\sin\theta$  as shown in Fig. 3(c). The curve of intensity ratio shows slight increasing at small  $\sin\theta$  region and drastic increasing at larger  $\sin\theta$  region. The intensity ratio is expected to increase when a probing depth reaches around oxide/metal interface. Thus, the interface defined in Fig. 2 (d) may be placed at the region between  $\sin\theta = 0.50$  and 0.82 (calculated probing depth:  $3\lambda\sin\theta = 5.1$  nm and 8.2 nm) in the profile shown in Fig. 3(c). Although, it is difficult to determine definitely the oxide/metal interface due to less measurement points of  $\theta$ , the probing depth is enough large to reach interface. Here, we remind difficulty in obtaining depth profile accurately by analysis of angle resolved measurement due to heavy dependence on assumed structural model and the effects of surface roughness. Despite SX-PES combined with  $\text{Ar}^+$  sputter is destructive technique, it is useful to obtain an atomic concentration depth profile.

Ti 1s spectra show single core level peak at kinetic energy of 2973.6 eV and satellite structure at lower kinetic energy side. The difference in kinetic energy between Ti 1s peak and satellite structure is 13.4 eV. This is identical to the previous work on  $\text{TiO}_2$  powder using HX-PES by N. Moslemzader et al [10]. The satellite structure results from monopole charge transfer excitation. For this reason, we assigned that the Ti 1s peaks were originated from  $\text{Ti}^{4+}$ . Interestingly, the shape of spectra is independent to  $\theta$ , meaning a uniform distribution of  $\text{Ti}^{4+}$  in depth direction contrary to the result shown in Fig. 2. Thus, we concluded that the appearance of Ti in lower

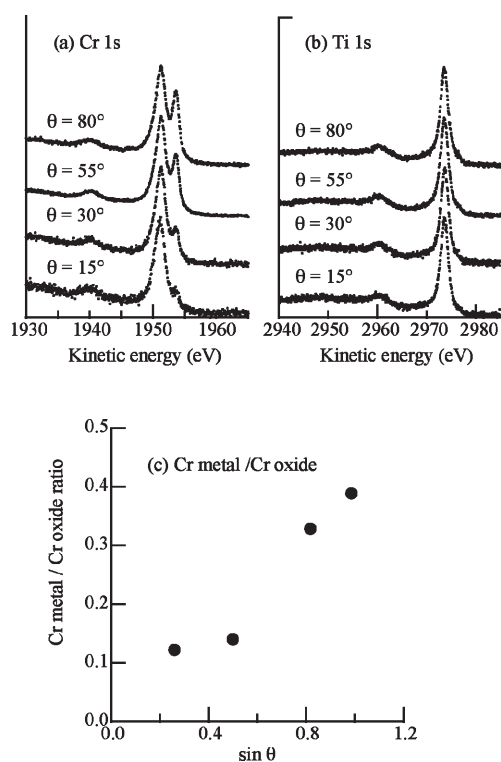


Fig. 3, Cr 1s (a) and Ti 1s (b) spectra taken at various take-off angle  $\theta$ , respectively. Relative peak area intensity ratio (c) of Cr metal against Cr oxide as a function of  $\sin\theta$ .

oxidation states found in the Ti 2p spectra obtained by SX-PES is results of the reduction of  $\text{Ti}^{4+}$  caused by  $\text{Ar}^+$  sputter. As mentioned above, the IMFP of Ti 1s photoelectrons is about 1.4 times larger than that of Cr 1s photoelectrons even at same take-off angles, i.e., the probing depth of Ti 1s photoelectrons collected at  $\theta$  of 55° or 80° crosses well over the  $\text{Cr}^0/\text{Cr}^{3+}$  interface. It means that Ti atoms placed even at below the interface are in the tetravalent state.

Previous studies on structural analysis of  $\text{FeOOH}$  particle, which is corrosion product of steel, precipitated from aqueous solution containing  $\text{Ti}^{4+}$  suggested that  $\text{Ti}^{4+}$  promotes the formation of  $\alpha$ - $\text{FeOOH}$  fine particles and inhibits the formation of unstable  $\beta$ - $\text{FeOOH}$  [5, 6]. It may produce similar effects on stainless steel surface. As a result, a dense passivation film consisting of Cr oxide and  $\alpha$ - $\text{FeOOH}$  fine particles forms on stainless steel surface, which prevents penetration of harmful elements into the steel substrate.

Our present result, that Ti is in tetravalent state even at below the passivation film, possibly suggests that oxidation of Ti occurs prior to form passivation film at surface. In that case, oxidation state of Ti is important in formation of dense passivation film on stainless steel.

#### 4. CONCLUSION

Oxidation states of Cr and Ti in the passivation film formed on SUS321 were non-destructively evaluated by HX-PES. The angle resolved Cr 1s spectra suggest that HX-PES provides enough large probing depth to evaluate oxidation states of elements around or under the interface between passivation film and stainless steel substrate without etching surface layer. As a result, we found that Ti atoms were in oxidized state ( $Ti^{4+}$ ) even at the deeper point than the interface. However, it is difficult to obtain depth profile accurately by angle resolved measurement. HX-PES with the assistance of SX-PES combined with  $Ar^+$  sputter method is realistic way to evaluate materials in depth direction.

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