X-RAY PHOTOELECTRON SPECTROSCOPY INVESTIGATION OF PLASMA MODIFIED 316L STAINLESS STEEL SURFACE

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Abstract

Although 316L stainless steel is widely used in the nuclear field as reactor pressure vessels cladding and piping systems due to its good mechanical and corrosion resistance properties, reported evidence shows the occurrence of stress corrosion cracking failures associated with high-temperature water applications. Additionally, water chemistry, dissolved oxygen and operating temperature can promote surface corrosion process by damaging the surface oxide layer. In this regard, an oxide coating developed on 316L stainless steel can enhance stress corrosion resistance under operating conditions. Therefore, the purpose of this paper is to investigate the effect of plasma electrolytic oxidation (PEO) coating on the surface chemistry behaviour of 316L stainless steel for primary water environment. By generating Aluminium oxide protective layers during electrochemical oxidation of metal surface in sodium aluminate electrolyte solution, the PEO technique can play an important role in 316L stainless steel protection. The assessed chemical species reveal the existence of a protective film of fully oxidized Aluminium (Al_2O_3) and Chromium oxide confined on the outermost surface layer, illustrating a surface passivating effect. In this work, we have demonstrated that Aluminium oxide coatings were prepared employing plasma electrolytic oxidation method. X-ray photoelectron spectroscopy was able to distinguish between mixed compounds, illustrating the occurrence of Aluminium oxide film accompanied by substrate-originated chromium oxide, confirming the existence of a protective surface layer.

Keywords: *PEO, 316L, XPS, Aluminium oxide, Chromium oxide*

Introduction

Previous studies have shown a successful and efficient application of 316L stainless steels in the nuclear field as reactor pressure vessels cladding and piping systems due to their good mechanical and corrosion resistance properties [1].

However, due to the extremely harsh environment inside the nuclear reactor, such as high oxygen and hydrogen content, water chemistry and high operating temperatures, 316L stainless steel corrodes in the presence of PWR primary water [1, 2]. Additionally, the corrosive environment, mechanical and thermal stress along with neutron bombardment led to the formation of surface cracking [3, 4]. This behaviour is a consequence of surface oxide film removal induced by in-reactor operation. Therefore, the oxide passivating film formed on 316L in high-temperature water environments is of crucial importance for enhanced surface corrosion resistance [4].

In this regard, promising results have been obtained in the literature towards generating protective coatings on steel, plasma electrolytic oxidation being a suitable method for providing ceramic-like oxide coatings by electrochemically oxidizing the metal substrate in an electrolytic solution [5].

Experimental set-up

Surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on PHI Quantera SXM equipment, with a base pressure in the analysis chamber of 10^{-7} Pa. The X-ray source was AlK_α radiation (1486.6 eV, monochromatized) and the overall energy resolution is estimated at 0.65 eV by the full width at half maximum (FWHM) of the $Au4f_{7/2}$ line.

In order to take into account the charging effect on the measured binding energies (BEs), the spectra were calibrated using the C1s line (BE = 284.8 eV, C-C (CH)n bondings) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure (e^- and Ar^+ ion beams) has been used to compensate the charging effect in insulating samples.

The atomic composition of surface was evaluated using Wagner sensitivity factors, specific for the instrument. The inelastic mean free path (IMFP) was calculated using the TPP-2M algorithm [6]. It is appropriate to note here that all the calculations were performed assuming that the samples were homogeneous within the XPS detected volume (<10 nm). We have to emphasize that the errors in our quantitative analysis (relative concentrations) were estimated in the range of ± 10 %, while the accuracy for binding energies (BEs) assignments was ± 0.2 eV.

Plasma electrolytic oxidation treatment of 316L stainless steel sample was performed using a DC unipolar power supply with 150 Hz frequency. The sample was prepared from a 316L steel sheet of 1 mm thickness and cut into a square shape of (2x2) cm.

The electrolytic solution contains 7g/l $NaAlO_2$ and 2g/l NaOH dissolved in distilled water. The PEO oxidation process was carried out for 3 min under a potentio-static regime at 350V.

Results and discussion

Due to its excellent surface characterization capabilities, the XPS technique illustrates the chemical species present on 316L surface after PEO oxidizing treatment for improved corrosion resistance.

The presence of the oxide protective layer formed by electrolytic oxidation was well-established from high resolution XPS spectra. The characterization method used explores the outermost surface layer (< 10 nm) for 316L stainless steel sample.

A close inspection of the XPS survey exhibits the presence of the coating elements, aluminium and chromium. Additionally, the occurrence of sodium characteristic fingerprints accompanied by aluminium transitions proves the existence of an increased content of the coating electrolytes. However, chromium was detected as rather slight amount (~0.9%) on the surface (see Table 1) due to an enhanced outermost surface contamination with carbon, as illustrated in Fig.1. This may suggest the coexistence of the both carbon sources, the adsorbed hydrocarbon and CO_2 on the surface from environment and the surface contamination during thin film deposition or sample handling. We have to emphasize that XPS method is surface sensitive (< 10 nm).

Table 1. Element relative concentrations (at %)

C1s	Na1s	O1s	Al2p	Cr2p	Fe2p
43.1	2.3	38.0	11.5	0.9	4.2

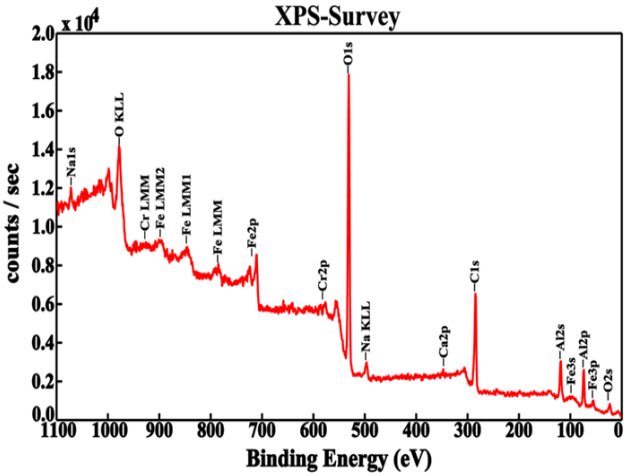


Fig. 1. XPS general spectrum (survey) for 316L sample after PEO process

To get a better understanding of carbon surface chemical behaviour and to assess the associated carbon chemical species, C1s photoelectron line was deconvoluted, as shown in Fig. 2. Therefore, besides C-C/(CH)n located at 284.8 eV used as internal standard, C-O, C=O and O=C-O chemical bondings occur [7, 8], in agreement with carbon and oxygen relative concentrations (see Table 1). The high carbon relative concentration (~ 40 %) suggests that the surface is contaminated.

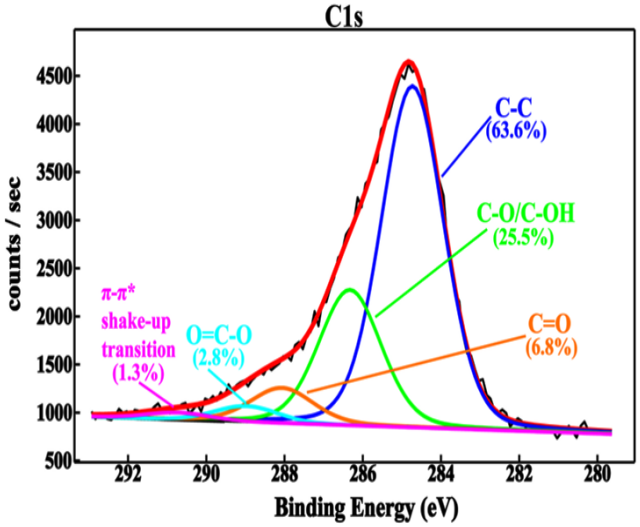


Fig. 2. C1s XPS deconvoluted spectrum for 316L sample after PEO process

Oxygen was monitored by acquiring O1s photoelectron peak in order to study the surface chemical modifications. Oxygen chemistry exhibits three features: oxygen bonded into the lattice (O^{2-}), OH groups and H_2O (moisture) [7, 8] adsorbed on the outermost layer of the sample surface (see Fig. 3). Table 1 shows a rather high oxygen concentration (~38.0 %), as well as OH groups and H_2O (see in Fig. 3). Moreover, carbon chemistry shown in Fig. 2 displays an enhanced oxidized contribution in agreement with carbon and oxygen relative concentrations given in Table 1.

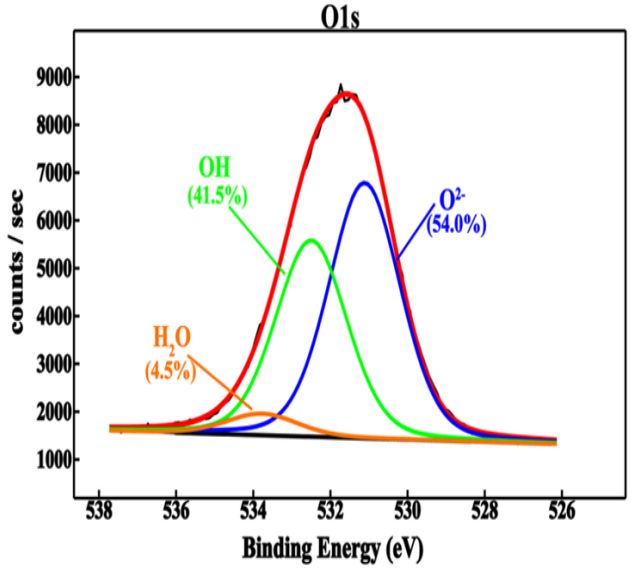


Fig. 3. O1s XPS deconvoluted spectrum for 316L sample after PEO process

Fig. 4 shows the aluminium surface chemistry occurring as Al_2O_3; it can be identified by its fingerprints on binding energy scale at 74.3 eV and reliable databases [7, 8]. It can be concluded that anticorrosion coating was formed.

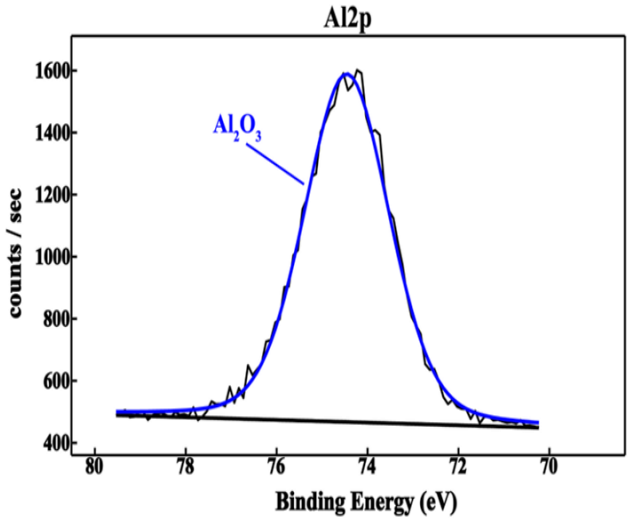


Fig. 4. Al2p XPS deconvoluted spectrum for 316L sample after PEO process

In order to establish a reliable surface chemistry, chromium spectra of CrO_3 and Cr_2O_3 standard samples were recorded and plotted in Fig. 5. The noisy Cr2p (~0.9%) XPS superimposed spectra show a mixture of CrO_3 and Cr_2O_3 chemical states, the latter feature being enhanced. CrO_3 minor chemical contribution was assign due to additional oxidation of Cr_2O_3 responsible for the anticorrosion effect [7, 8].

To reveal the surface chemistry of iron, Fe2p XPS signal was collected indicating a mixture of Fe_2O_3 and FeO/FeOOH [7, 8] assigned from the binding energy of the 2p doublet as well as from the line profile including the presence of characteristic satellites associated to the main doublet lines confined on top of the surface due to the presence of OH groups (Fig. 6).

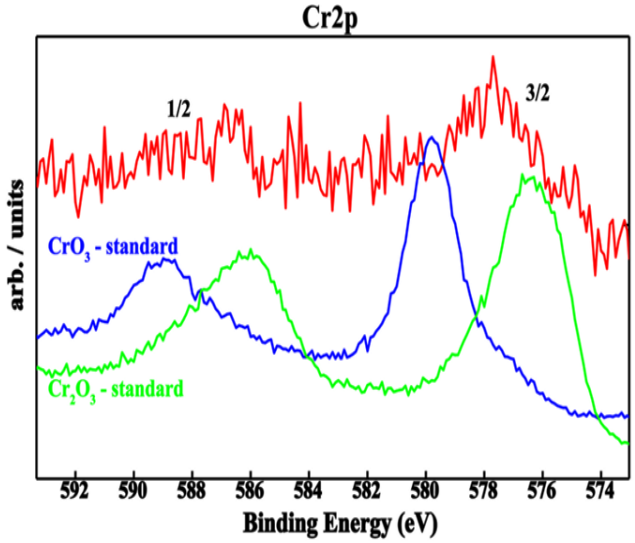


Fig. 5. Cr2p XPS superimposed spectra

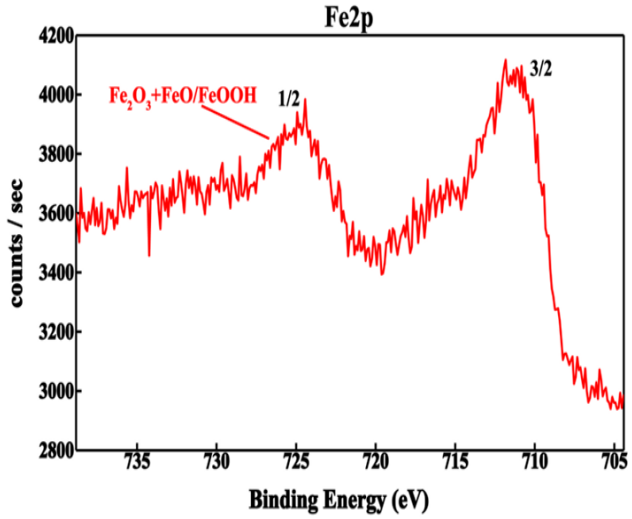


Fig. 6. Fe2p XPS spectrum for 316L sample after PEO process

Conclusions

The work presented in this study demonstrated a plasma electrolytic oxidation-deposition of aluminum-based coatings on 316L steel prepared in sodium aluminate electrolyte solution.

Surface chemistry was assessed using X-ray photoelectron spectroscopy measurements.

It was found that a protective film of aluminum oxide (Al_2O_3) forms on 316L stainless steel during electrolysis process. In addition, a thin layer of chromium oxide originating from the substrate occurs on the surface, reinforcing the protective role of aluminum coating.

Both fully oxidized aluminum and chromium are confined on the outermost surface layer, illustrating the passivating effect of the surface.

References

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