

STUDY OF THE OXIDE LAYER FORMED ON THE ALLOY 182 IN A SIMULATED PRESSURIZED WATER REACTOR ENVIRONMENT¹

Renato de Mendonça²
Junhu Liu³
Rik-Wouter Bosch³
Milan J. Konstantinovic³
Steven Van Dyck³
Maximiliano D. Martins⁴
Waldemar A. A. Macedo⁴

Abstract

The present work describes a study of the oxide layer formed on the alloy 182 before and after exposure in simulated Pressurized Water Reactor (PWR) environment by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) equipped with an Energy Dispersive Spectroscopy (EDS), and Atomic Force Microscopy (AFM). Samples with two different surfaces treatment - with the surface mechanically and electrochemically polished - were exposed during four weeks in autoclave. We observed oxide layers with different thicknesses and chemical compositions in the depth profile obtained by XPS coupled with argon ion sputtering cycles. Furthermore, the morphologies of oxide layers formed on electrochemically and mechanically polished surfaces are different even though deposited particles seem to be present on both of them. The XPS analyses and AFM images of the samples before exposure showed that the electrochemical polishing stimulated the growth of an oxide layer relatively iron-depleted and chromium-rich.

Key words: Corrosion; Alloy 182; XPS.

ESTUDO DA CAMADA DE ÓXIDO FORMADA NA LIGA 182 EM AMBIENTE SIMULADO DE UM REATOR DE ÁGUA PRESSURIZADA

Resumo

O presente trabalho descreve um estudo da camada de óxido formada na liga 182 antes e depois da exposição da mesma a um ambiente simulado de um reator nuclear de água pressurizada (PWR). Amostras com dois tratamentos superficiais (com as superfícies mecanicamente e eletroquimicamente polidas) foram expostas durante quatro semanas ao ambiente PWR. Observaram-se camadas de óxido com diferentes espessuras e composições químicas no perfil de profundidade químico obtido por ciclos de erosão catódica com íons de argônio e medidas de espectroscopia de elétrons excitados por raios X (XPS). Adicionalmente, a morfologia da camada de óxido formada nas duas amostras é diferente, embora se observe em ambas, partículas depositadas. As medidas XPS e as imagens das amostras antes da exposição sugerem que a amostra polida eletroquimicamente possui uma camada de óxido relativamente deficiente em ferro e rica em cromo.

Palavras-chave: Corrosão; Liga 182; XPS.

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² MSc., PhD student, Universidade Federal de Ouro Preto – UFOP.

³ PhD, Researcher, Belgian Nuclear Research Centre – SCK•CEN.

⁴ PhD, Researcher, Centro de Desenvolvimento da Tecnologia Nuclear – CDTN.

1 INTRODUCTION

Nickel-base alloys are extensively applied in Pressurized Water Reactors (PWR) due to its thermal, mechanical and chemical properties.^[1] In general, these alloys have good toughness and stability at high temperatures what explains their use under severe conditions such as gas turbine and petrochemical systems.^[2,3] The corrosion resistance of these alloys in water, provided by a chromium-rich oxide layer is an important subject for research when we ponder the problems commonly related to safety and economy in nuclear industry.^[1,4]

The nickel-base weld metals, a particular group of these alloys, are of special interest in corrosion studies due to their intrinsic metallurgical heterogeneity which generates a sensitive region where the degradation is strong.^[5] Currently, the weld alloys commonly used are the alloys 182, 82, 152 and 52. Their standard chemical compositions are presented in table 01. As it can be noticed, several chemical elements are added to these alloys aiming to increase the mechanical and corrosive resistance.^[6] A comparative analysis of the Table 1 indicates the different characteristics in the weld alloys due to the presence of several alloy elements. The manganese is employed to provide these alloys a better weldability and the niobium, titanium and tantalum are used in order to give them good mechanical properties and better resistance to intergranular stress corrosion cracking (IGSCC), a crucial issue related to the materials used in nuclear power plants. Indeed, these elements can segregate preferably in the alloy forming carbides and intermetallic compounds, which avoid the growth of undesirable chromium carbides in the grain boundary and, consequently, the IGSCC.^[1,7,8]

Table 1. Standard chemical composition (wt%) of the Ni weld alloys applied in nuclear reactors^[4]

Alloy	C	S	Si	Cr	Fe	Mn	Nb+Ta	Ti
182	≤ 0.1	≤ 0.015	≤ 0.06	13-17	≤ 10	5-9.5	> 1.8	≤ 1.0
82	≤ 0.1	≤ 0.015	≤ 0.05	18-22	≤ 3	2.5-3.5	2-3	≤ 0.75
52	≤ 0.040	≤ 0.008	≤ 0.5	28-31	8-12	< 1.0	< 0.1	≤ 1.0
152	≤ 0.045	≤ 0.008	≤ 0.65	28-31.5	8-12	≤ 5.0	1.2-2.2	≤ 0.50

Although the alloy 182 has been applied under several conditions, its behavior in simulated conditions of a nuclear power plant is not completely clear. The effects of alloy elements on the degradation are not reported in detail although empirical studies have showed that the alloys 52 and 152 present higher resistance to corrosion^[4]. The critical difference among these alloys is the concentration of chromium, manganese and niobium, which could influence the corrosive behavior. The effect of the manganese could be remarkable in the oxide formation on the alloy 182 since this element has high diffusivity and affinity with the oxygen.^[9] In other words, the manganese ions can segregate on the oxide surface of the alloy 182 forming manganese oxides, as observed in the other alloys in oxidation experiments.^[9,10]

Additionally, the effect of surface treatments on the alloy 182 in the corrosion process has been neglected. This surface treatment can be done through the electrochemical polishing, a technique in which the alloy is placed in acid solution at a specific voltage. This technique is generally used to remove the surface layers rich in defects such as dislocations and non-uniform oxide layer. The growth of the oxide layer often follows another path and a new oxide layer - chemically different - is formed.^[11-14] Experiments with Fe-Cr alloys indicate that in contrast to the air-formed passive films, those films grown in electrolyte accumulate a considerable amount of

Cr³⁺ on the surface. There is a common agreement that during the electrochemical treatment, the iron is preferentially dissolved in the prepassive and in the passive potential range applied and consequently chromium is stored within the passive layer.^[11]

Taking into account the issues illustrated above, we have motivation to study and discuss the chemical structure and the morphology of the oxide layer formed on the alloy 182 in PWR environment. We intend to understand about the behavior and influence of the critical elements during the growth of the oxide layer. Furthermore, we are aiming to observe the effect of the electrochemical polishing on the sample before and after the corrosion experiment. In order to carry out this work, the analyses of the two surfaces (mechanically and electrochemically polished) were performed with different techniques. We made a depth chemical composition profile using the data produced by X-ray photoelectron spectroscopy (XPS) coupled with argon ion sputtering and studied the morphology and chemical composition with a scanning electron microscopy (SEM) equipped with an energy dispersive spectrometer (EDS). In order to see more details in the morphology we also used an atomic force microscopy (AFM) to analyze the samples before exposure.

2 MATERIALS AND METHODS

The samples were cut from the tubes of the Nuclear Reactor of Lemoniz (Spain) and polished in two ways: mechanically, until grade 2400, and electrochemically in acid solution (330 ml of H₂O, 550 ml of H₃PO₄ and 120 ml of H₂SO₄ during 10 seconds). After the polishing, the samples were put in autoclave (water solution with 2 ppm of Li, 1000 ppm of B and 25 cc/Kg of H₂ at temperature of 300°C and pressure of 150 bar).

All samples were studied with XPS, ESCALAB 220i - XL Thermo VG Scientific, using a monochromatic source of Al K α . SEM images were obtained with a JEOL 6310 microscopy. AFM images were obtained of the samples after polishing and before exposures with a microscopy NT-MDT, NTEGRA.

3 RESULTS AND DISCUSSION

3.1 Samples Before Exposure

Figure 1 presents the SEM images and the EDS data obtained from the samples mechanically and electrochemically polished. It is possible to recognize the holes and the strikes of the polishing on the mechanically polished sample and segregated particles on the electropolished sample. The holes found on the mechanically polished sample are probably due to the polishing process that removed the intrinsic segregated particles.^[4] The EDS analyses in the region of the segregated particles (A) and far from the segregated ones (B) show that the particles are Nb-rich. It suggests that the Nb compounds do not dissolve while part of the surface is consumed by the acid solution during electrochemical polishing. This behavior may happen due to the different anodic dissolution of the particles and Ni substrate, as already pointed out by Huang et al. to Inconel 718.^[13]

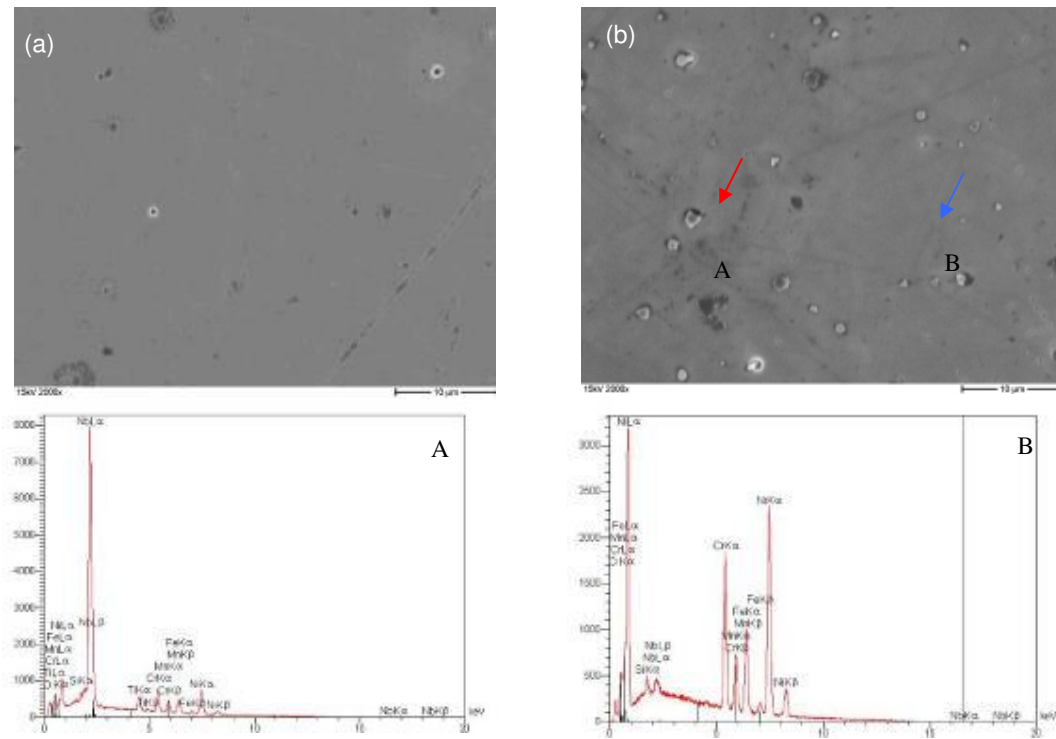


Figure 1. SEM images and ED spectra of the samples mechanically (a) and electrochemically (b) polished. The ED spectra indicate the presence of the Nb-rich particles on the electropolished surface.

The AFM images were obtained from these surfaces (Figure 2). The analysis of the images at low magnification (Figure 2(a,b)) presented similar characteristics of the SEM images. However, with the use of the program Nova-Image Analysis, it was possible to estimate the main size of the segregated particles in electrochemically polished sample which is around 0.8 µm. Surprisingly, this value perfectly agrees with the value described by Vaillant to niobium carbides in the alloy 182 [4]. Images with higher magnification were also taken (Figure 2(c,d)), and we observe two different morphologies on the surface of the samples. On the mechanically polished sample it can be seen that the surface has strikes from the polishing procedures whereas on the electrochemically polished sample, small particles could be easily noticed, which showed the formation of a new layer compounded of nanostructured grains.

The depth profile, Figure 3, obtained from the samples electrochemically and mechanically polished present the chemical composition of the alloy substrate, which shows that the concentration of nickel in the alloy is about 70% (a constant Ni concentration at low oxygen composition that could be used to recognize the interface oxide/alloy). The contaminant elements are practically removed during the sputtering process. We also observe that the sputter time to remove the oxygen from the electrochemically polished sample is longer than the cycle of the mechanically polished one. This result shows the presence of the oxide layer, whose morphology is observed in the AFM images.

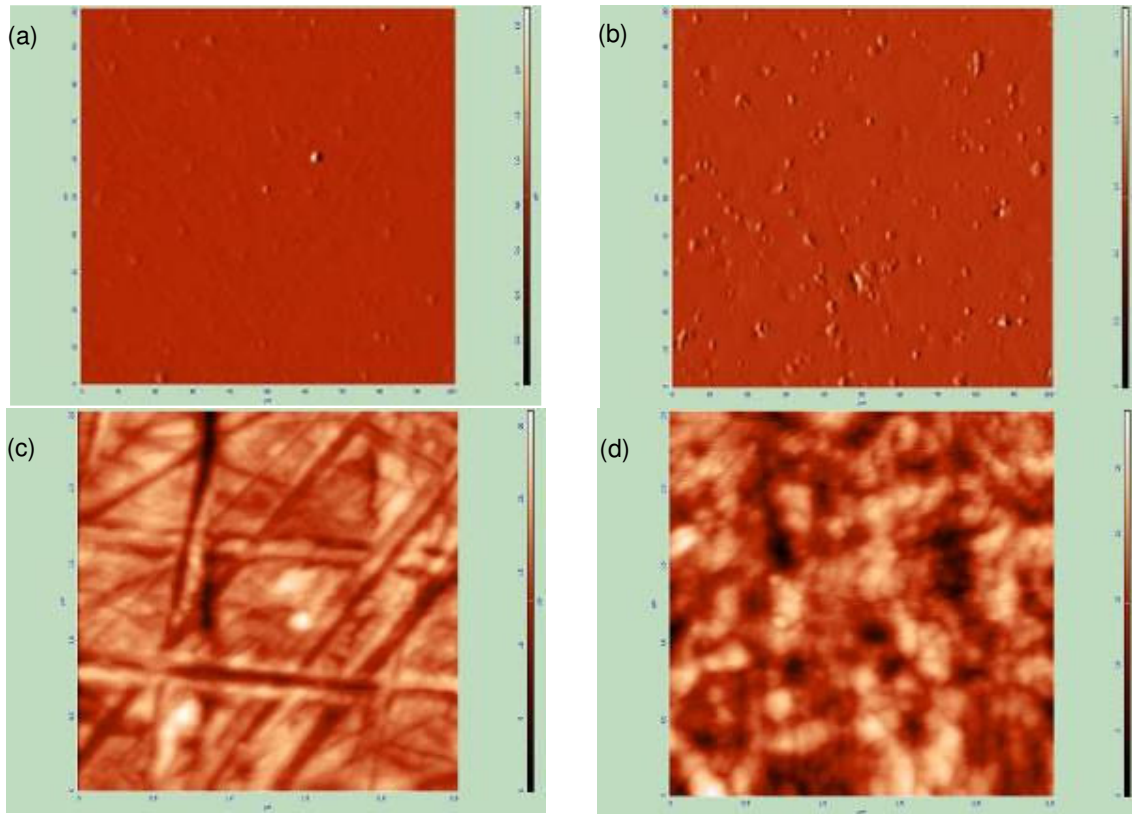


Figure 2. AFM images (100µm x 100µm) of the samples mechanically (a) and electrochemically (b) polished. Images (2.5 µm x 2.5 µm) of the samples mechanically (c) and electrochemically (d) polished. Images (c) and (d) illustrate the different aspects on the surfaces.

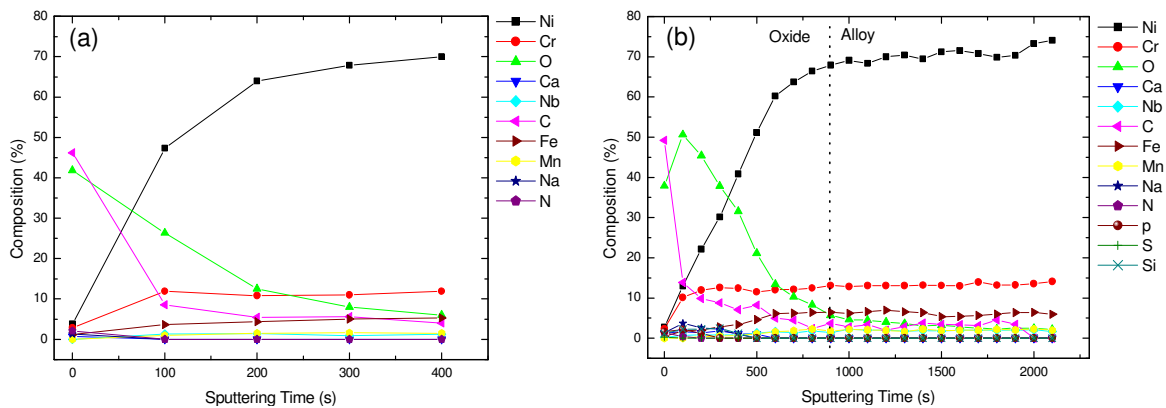


Figure 3. Depth profile obtained from the samples polished mechanically (a) and electrochemically (b).

It is possible to infer from the analysis of the depth profile that the Fe concentration in oxide layer is lower than in the substrate. We observe that, at 100s of sputter time, the Fe concentration is approximately 2.5% whereas, at 600s, the concentration of Fe is similar to the substrate, around 6.3%, as showed in Figure 3 (b). On the other hand, the chromium concentration is practically the same during the sputtering process, which suggests that the top oxide layer is chromium-rich. This result indicates that the dissolution of the elements in acid solution used is selective, and, because of that, the surface of the sample is relatively chromium-rich.

The XP spectra taken from both surfaces are showed in Figure 4. The mechanically polished sample reveals an oxide surface with some contaminants: calcium, aluminium and sodium. The origins of these elements are not clear, but they probably come from the weld process used in order to produce the alloy in the nuclear reactor plant.

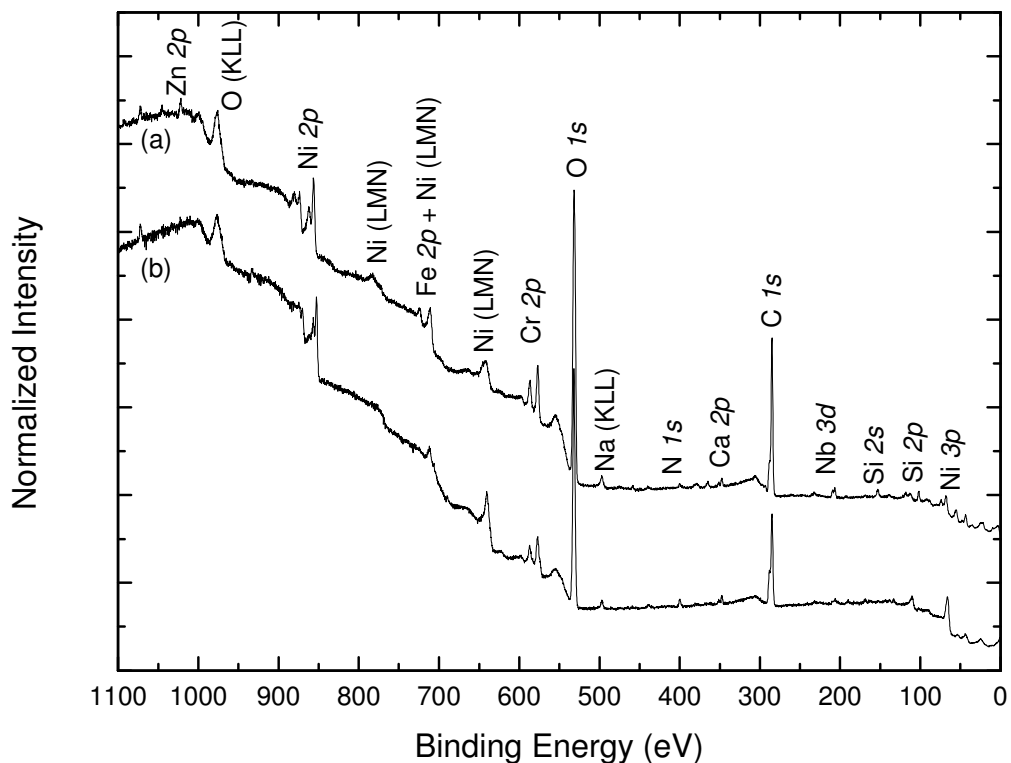


Figure 4. Survey XP spectra of the samples electrochemically (a) and mechanically (b) polished.

3.2 Four Weeks of Exposure

The morphology of the oxide formed on the samples exposed to autoclave during four weeks is presented in Figure 5. We observe a lot of deposited particles on the electropolished sample (Figure 5 a). ED spectra (Figure 5 g), in these particles reveals the strong presence of Fe and Nb. Iron oxides particles normally grow on sites rich in defects on samples that are exposed to water reactors. However it was also found Nb near these particles. It is therefore possible to think that the deposited particles are formed on the Nb-rich particles which were on the surface before autoclave exposures. The EDS result near the precipitated ones also shows presence of Ni, Ti, Cr, Mn, Si and O. The morphology of the oxide formed on the mechanically polished sample is different from the oxide formed on the electropolished one (Figure 5 (c,d,f)). It is possible to see detailed oxide grains on the mechanically polished sample after the exposure, however the same was not observed on the electropolished sample. It could be due to the thinner oxide layer formed on the electropolished surface, as will be noted in the sputtering time of the electropolished sample.

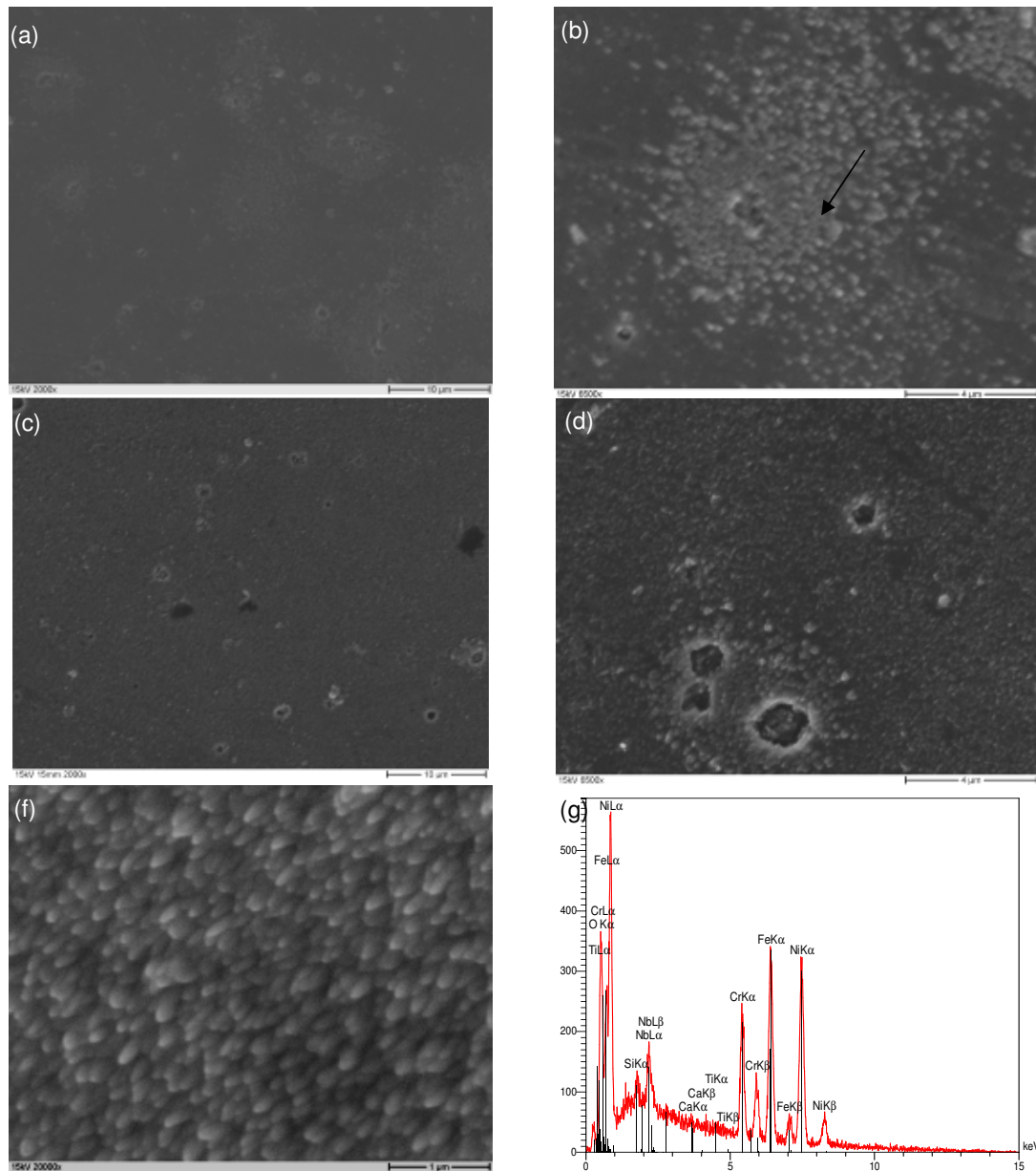


Figure 5. SEM images of the samples electrochemically (a,b) and mechanically polished (c,d,f) after 4 weeks in autoclave; (g) ED spectra of the point (deposited particle) indicated by the arrow.

The XPS results of the oxide layer present a lot of elements and a complex chemical composition, Figure 6. We observed that the elements B, Al, Ca, C and Zn disappear after some sputtering cycles. The presence of B is explained by the deposit of this element from the water solution while the Zn is a contamination from the cut process. Ca, Al and C were observed on the sample before the exposures. The XPS data did not show the presence of Mn on the top of the oxide layer; the depth profile showed that Mn composition increased near the interface oxide/alloy (indicated by the guide to the eyes) what suggests that the Mn ions did not diffuse fast into the oxide layer in the conditions of our experiment. The temperature was not high enough and the time was not sufficient for Mn enrichment in the oxide layer.

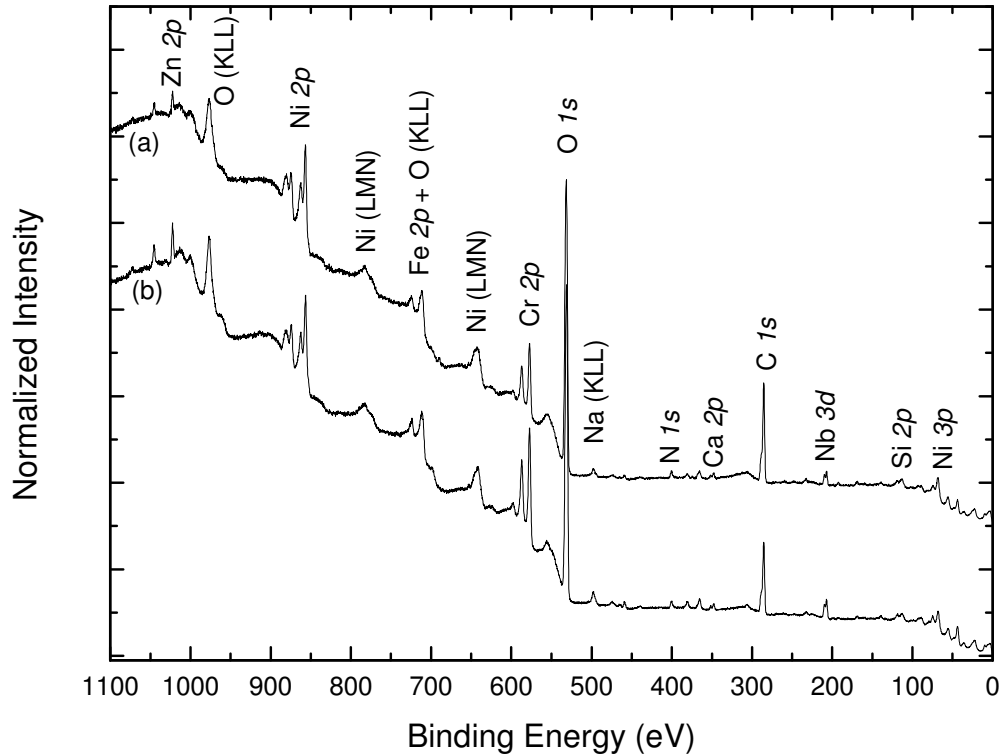


Figure 6. Survey XP spectra of the surfaces electrochemically (a) and (b) mechanically polished after exposure.

The depth profile of the samples after exposures presented different aspects, Figure 7. The sputtering cycle applied to remove the oxide layer is longer for the mechanically polished sample. Thus the oxide layer is thicker in this sample. In comparison, it is noted, in electrochemically polished sample, that the Ni and Cr compositions at initial sputtering time, until 300s, are similar. Furthermore, the Fe composition is relatively low at same initial sputtering time at the electropolished surface, until 500s, which show the low Fe content in the oxide layer formed. Therefore, this sample seems to show a Fe-depleted top layer and a bottom layer relatively Fe-rich, basically with the same Fe composition of the alloy. The main difference of the oxide layer formed on the electropolished sample and mechanically polished one is the top layer due to the Fe composition which is almost constant in the depth profile of mechanically polished sample.

Additionally, we used the Fe/Cr and Fe/Ni ratios to understand the results, Figure 7(c). The electrochemically polished surface presented Fe/Cr ratios lower than the mechanically polished surface at the initial sputtering time. This data, commonly applied in corrosion studies,^[6,11,15] confirms the relative presence of the Fe-depleted layer. This Fe and Cr composition on the top layer could explain the difference in the nature of the morphology and thickness between the oxide layers on electrochemically and mechanically polished samples. The Fe/Ni ratios also show the contrast in the chemical composition of the oxide layers. It is noted faster decrease of Fe/Ni ratios to the electropolished sample which could also suggests the relatively Fe-depleted top layer.

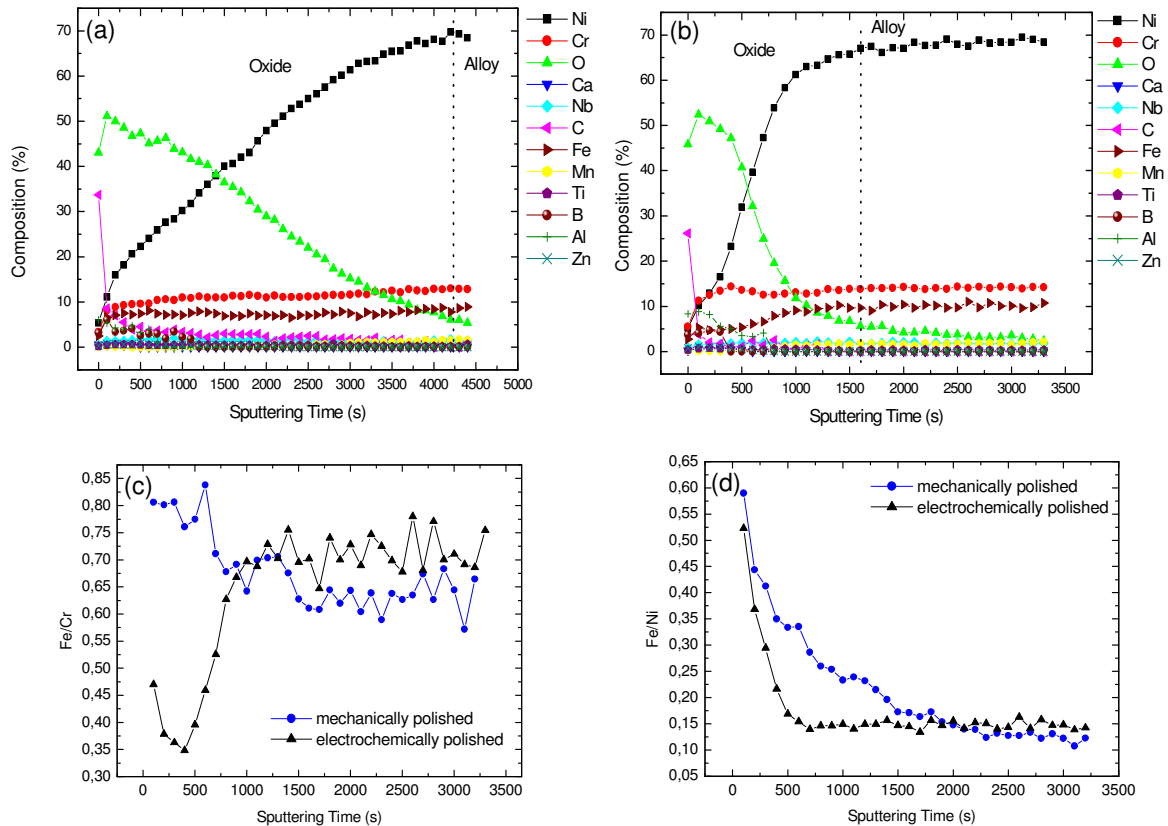


Figure 7. Depth profile of the oxide layers formed in 4 weeks of exposure in autoclave. (a) Mechanically polished sample; (b) electrochemically polished sample; (c) Fe/Cr and (d) Fe/Ni ratios showing the distinct Fe composition in the oxide layers.

4 CONCLUSIONS

The oxide layer formed on alloy 182 under simulated condition of a nuclear reactor was studied by X-Ray Photoelectron Spectroscopy, Scanning Electron Microscopy and Atomic Force Microscopy in two different conditions. The results showed that the superficial treatment affects the corrosion process. Our data indicated that the electropolished sample has oxide layer relatively rich in Cr and depleted in Fe, what provide remarkably changes in the oxide layer formed on the alloy 182 in PWR environment. The oxide layer formed on sample electropolished after 4 weeks of exposure in autoclave conditions has chemical and morphology characteristics different from the oxide layer formed on the mechanically polished sample. The influence of the manganese in the growth of the oxide layer was not observed in our experiment because manganese was only found near the interface oxide/alloy.

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REFERENCES

- 1 SCOTT, P. M.; COMBRADE, P. Corrosion in pressurized water reactors. In: *Metals Handbook*. vol. Corrosion in specific industries. ASTM international, 2007. p. 362-383.
- 2 WANG, J.D. GAN, D. Effects of the grain boundary carbides on the mechanical properties of Inconel 600. *Materials Chemistry and Physics*, v. 70, p. 124-128, 2001.
- 3 CHOUDHURY, I.A. AND EL-BARADIE, M.A. Machinability of nickel-base super alloys: a general review. *Journal of Materials Processing Technology*, v. 77, p. 278 – 284, May 1998.
- 4 VAILLANT, F.; BOURNIER, J.M.; AMZALLAG, C.; BIBOLLET C.; PONS S. Environmental behavior and weldability of Ni-base weld metals in PWRs. *Les Matériaux Dans Le Nucléaire*. RGN N 6, p. 62-71, December 2007.
- 5 TSAI, T.W. YU, C.L. LEE, J.I. Effect of heat treatment on the sensitization on alloy 182 weld. *Scripta Materialia*, v. 53, p. 505-509, September 2005.
- 6 DELAUNAY, F. BERTHIER, C. LENGLET, M. LAMEILLE, J.M. SEM-EDS and XPS studies of high temperature oxidation behavior of inconel 718. *Mikrochimica Acta*, v. 132, p. 337-343, April 2000.
- 7 FERGUSON, J.B.; LOPEZ, H.F. Oxidation products of inconel alloys 600 and 690 in pressurized water reactor environments and their role in intergranular stress corrosion cracking. *Metallurgical and Materials Transactions A*, v. 37A, p. 2471-2479, August 2006.
- 8 GANG, B. YAMAMOTO, M. SHINOZAKI, K. Precipitation and Cr depletion profiles of Inconel 182 during heat treatments and laser surface melting. *Journal of Materials Processing Technology*, v. 209, p. 416-425, January 2009.
- 9 SABIONI, A.C.S.; HUNTZ, A.M.; BORGES, L.C.; JOMARD, F. First study of manganese diffusion in Cr₂O₃ polycrystals and thin films by SIMS. *Philosophical Magazine*, v. 87, p. 921-1937, April 2007.
- 10 MACHET, A.; GALTAYRIES, A.; ZANNA, S.; KLEIN, L.; MAURICE, V.; JOLIVET, P.; FOUCAULT, M.; COMBRADE, P.; SCOTT, P.; MARCUS, P. XPS and STM study of the growth and structure of passive films in the high temperature water on a nickel-base alloy. *Electrochimica Acta* 49, p. 3957-3964, September 2004.
- 11 KELLER, P. STREHBLow, H.H. XPS investigations of electrochemically formed passive layers on Fe/Cr - alloys in 0.5 M H₂SO₄. *Corrosion Science*, v. 46, p. 1939 - 1952, August 2004.
- 12 SHIH, C.C.; SHIH, C.M.; SU, Y.Y.; SU, L.H.J.; CHANG, M.S.; LIN, S.J. Effect of surface oxide properties on corrosion resistance of 316L stainless steel for biomedical applications. v. 46, p. 427-441, February 2004.
- 13 HUANG, C.A. CHEN, Y. C. and CHANG J.H. The electrochemical polishing behavior of the Inconel 718 alloy in perchloric-acetic mixed acids. *Corrosion Science*, v. 50, p. 480-489, February 2008.
- 14 LANDOLT, D. Fundamentals aspects of electropolishing. *Electrochimica Acta*, v. 32, p.1-11, 1987.
- 15 GRAHAM, M.J. 2003 W.R. Whitney Award Lecture: Application of surface techniques in understanding corrosion phenomena and oxide growth mechanism. *Corrosion Science Section*, v. 59, p. 475-488, June 2003.