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The PbO concentration influence on oxides films developed on Incoloy 800 in CANDU secondary circuit conditions

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Abstract. The presence of lead compounds in CANDU secondary water circuit contributes to the degradation of nickel alloys involved in critical equipments manufacturing, e.g. steam generator.

The pre-oxidated Incoloy 800 specimens (the steam generator tubes material) have been tested in autoclave, in secondary simulated water medium conditions: pH=9.5, at 5.1 MPa presssure and 260^0C temperature, in solutions containing 100, 200 and 300 mg/L PbO, the exposure time for each concentration being 10, 20 and 30 days.

The specimens evaluation after testing have been realised through ex-situ and in-situ methods: metalography, electrochemistry (potentiodynamic and impedance), gravimetry and scanning electron microscopy with energy dispersive spectroscopy.

It is investigated the influence of different PbO concentrations on tested specimens surface morphology (grain, layer thickness, layer composition) and on the corrosion susceptibility, resulting in increased corrosion tendency and loss of protective properties of films as the PbO concentration was higher.

Key words: Incoloy-800, PbO, oxide layer, secondary circuit, corrosion.

1. Introduction

The steam generator tubes from CANDU nuclear power centrals, made of Incoloy 800 (Ni alloy), is damaged by water corrosion at high temperature and stress corrosion cracking (SCC). The corrosion behaviour is strongly related to surface morphology and semiconductor properties of oxide film formed on the alloy. The oxide films formed at high temperatures on Ni alloys consist of an interior Cr enriched layer and an exterior Fe enriched layer. PbO has a negative

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effect on oxide films, the studies on Incoloy 600 alloys indicated occurence of SCC in the presence of 500-10000 ppm PbO, which simulates the crevice medium in secondary circuit water chemistry [1], [2]. The oxide layer on Incoloy 800 is very compact and it is Cr enriched compare to alloy mass Cr content, while the Ni content is lower than the alloy mass Ni content. The exterior layer is porous, having small oxides cristals of Cr-Ni-Fe [3].

Incoloy 800 is used for steam generators tubes manufacturing due to its SCC increased resistance compare to Inconnel 600 and to lower radioactive products release. The corrosion products are being accumulated and they concentrate the agressive species which can promote different corrosion forms: generalised, localised (pitting on Incoloy 800 tubes), crevice corrosion, stress corrosion cracking, etc. The corrosion cinetics for weight losses, corrsion rates, total corrosion formed products, adherent corrosion products and metal release rate at pH=7.5, pH=8.5 and pH=9.5 have a logarhitmic evolution, with the lowest values registered at pH=9.5 [4] ÷ [7].

The average thickness of oxides layers in secondary circuit conditions (pH =10.2 - 10.8, temperature 220-265^{0}C) after long exposure time (82-1290 days) varies between 0.14 μm and 0.7μm. The films have the conventional double layer structure, but after long exposure time the interior layer is masked by exterior layer development and/or deposits generated by the species from the cooling water. The photoelectronic X-ray spectroctroscopy highlighted the CrOOH, FeOOH and $Ni(OH)_2$ compounds. At metal/oxid interface layers, the metals ratios (Ni/Cr, Ni/Fe, Cr/Fe) are close to the base metal ones. The Ni/Cr ratio is over unity as it is in the double oxide layer also. There is a Ni enrichment in the exterior oxide layer. The Ni/Fe and Cr/Fe ratios increase in the following order: interior layer<base metal<exterior layer. The richer Ni and Cr compositions in the exterior layer compare to the base metal indicate a certain Fe quantity diffused outward [8].

Low concentrations of Pb contained in cooling water promote SCC of Ni alloys. This is absorbed on the oxides and exposes the metal surface. Pb in concentrations up to 20% has been detected in the steam generator tube cracks peak. The Pb concentration in the feed water is lower than 10^{-5} mg/L and can accumulate up to $2x10^{-4}$ mg/L after recirculation [9]. The deposition process on tubes surface is complex and it has not been completely elucidated yet. There are two possible Pb transport modes toward the steam generator: as cation/dissolved complex or as adsorbed specie on the suspended solids from cooling water. The Pb (II) species are the dominating ones in water, as the dissolution or corrosion mechanisms occur through Pb^{2+} generation. In the presence of inorganic oxides, the Pb^{2+} in solutions have a strong adsorbing tendency on the surfaces, especially in alkaline operating conditions (pH>8). The Fe oxides which are generated and transported in CANDU secondary water systems are magnetite and hematite (in stable operating conditions) and lepidocrocite (at shutdown or after restart conditions). The corrosion products transportation studies showed that Pb is present in low concentrations, especially in new stations, apparently after maintenance shutdowns [10]. Tests on Incoloy 800, in solutions with 2 ppm LiOH, 500 ppm boric acid, 200 ppb Co^{2+}, added with 10, 20, 50 and 100 ppb PbO, autoclaved and oxidated for 100 h at 315^0C, highlighted morphological changes caused by PbO, demonstrated by scanning electron microscopy (SEM) analysis: changes in oxides particles dimensions and corrosion products appearance, as the PbO concentration increases. The PbO presence has an impact on oxidative properties of the Incoloy 800 film: the potentiodynamic polarisation tests registered a decrease of current densities for the samples with PbO addition and shifts of corrosion potentials toward more positive values up to 20 ppb PbO concentrations [11].

2. Experimental

The test specimens made by Incoloy 800 have been prelevated from 6000mm height tubes, exterior diameter of 15.9 mm, wall thickness 1.13 mm and cut on the diameter into 15 mm long pieces. The Incoly 800 specimens autoclaving static tests have been conducted in aqueous medium with pH=9.5 regulated with morpholine and ciclohexylamine, at 5.1 MPa pressure, 260^0C temperature, containing different PbO concentrations: 100, 200 and 300 mg/L PbO. The surface of exposed specimens has been pre-oxidated for 10 days. The testing times were defined at 240 h, 480 h and 720 h for each PbO concentration, at steam generator secondary circuit specific parameters 260^0C and 5.1 MPa.

The metalographic investigation (macrostructural aspect, oxide layer and corrosion products aspect) has been realised with metalographic microscope Olympus GX71, magnification factor x12.5-12000.

The electrochemical tests have been performed with electrochemical system PARSTAT 2273, consisting of potentiostat and electrochemical cell, the data being processed with Corrosion Model 352 and Power Sine software. The potentiodynamic tests have been perfomed on Incoloy 800 specimens having an operating history (as the initial state condition is not relevant), pre-oxidated for 10 days and exposed in the media with the three different PbO concentrations. The testing medium in the electrochemical cell was demineralised water with pH=9.5 (regulated with volatile amines) at 25^0C, the scanning rate being 1 mV/s. The impedance tests: Nyquist and Bode curves and phase angle curve have been conducted in 0.05 M/0.001M boric acid/sodium tetraborate solution.

By SEM and energy dispersive spectroscopy (EDS) analysis with electronic microscope TESCAN VEGA II LMU have been obtained images of specimens surfaces, the distribution maps of elements on certain analised areas and quantitative analisys of existing elements on a defined specimen area.

3. Results and discutions

3.1. The morphology and compositions of oxide films modificated by PbO

The figure 1(a,b,c) shows the macrostructural images of the specimens tested for 30 days at the three different concentrations of PbO: 100 mg/L, 200 mg/L and

300 mg/L respectively. In the presence of 100 mg/L PbO it is identified on the specimens surface a layer formed by a deposition which encapsulates corrosion products and Pb compunds from testing solution. The pre-formed oxid layer creates the conditions for a good adherence, but contributes in the same time to groove formation and even diffusion of some elements from base metal to the superficial layer and the backwards diffusion from solution to base metal, a complementary SEM and EDS analysis being necessary. At 200 mg/L PbO there is present a non-uniform layer, with initial magnetite next to base material. There are areas on the surface where only the initial pre-oxidation formed layer remain and areas with important aleatory depositions. As the PbO concentration increases at 300 mg/L, a strong non-uniformity of the layer is observed.

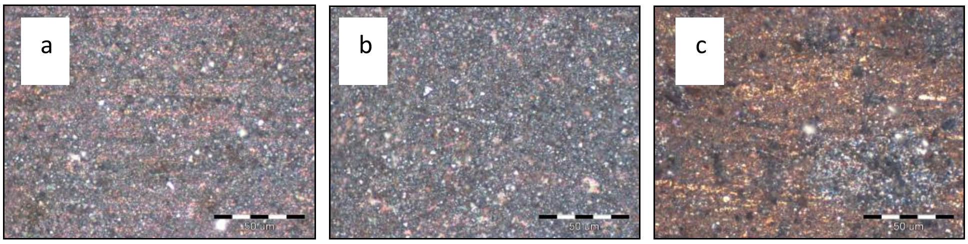

Fig. 1. The morphology of the oxides films on Incoloy 800, exposure time 30 days, t=260^{0}C, p=5.1 MPa, pH=9.5, in PbO presence: 100 mg/L (a), 200 mg/L (b) and 300 mg/L (c)

The thickness of oxides layers formed after 30 testing days at the three different PbO concentrations is shown in figure 2(a,b,c). The thickness of the superficial layer varies from 2.8 μm in the presence of 100 mg/l PbO to 3.6 μm in the presence a 200 mg/L PbO. At 300 mg/l PbO the superficial layer has a thickness of 0.2-3.6 μm. The mixt layer composed by oxides, base material compounds and lead has a higher thickness, but it does not maintain its continuity. It is noticed that the initial formed layer influences the formation of non-uniform deposits, with non-uniform thickness and non-uniform compositions.

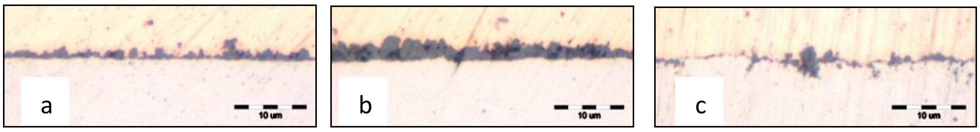

Fig. 2. The thickness of oxides layers on Incoly 800, exposure time 30 days, t=260^{0}C, p=5,1 MPa, pH=9,5, in the presence of PbO: 100 mg/l (a), 200 mg/l (b) and 300 mg/l (c)

The SEM analysis on Incoloy 800 specimens preoxidated for 10 days and tested for 30 days highlights the presence of several types of oxides particles: some of them are big and rare, with octaedric structure, others are frequent and smaller, with tethraedrical structure in the case of specimens tested in presence of 100 and 200 mg/L PbO (figure 3a and 3b), while the number of the big particles appears drastically reduced at 300 mg/L PbO , most of them are tetrahedrical, while scaly and needle particles appear (figure 3c). These morphological changes indicate, as PbO concentration increase, the dissapereance of spinnelic oxides and the formation scaly oxides in the corrosion process of Incoloy 800, so the increase of PbO concentration blocks the formation of stable and protective oxides on Incoloy 800.

The EDS spectrum and composition of Incoloy 800 specimen preoxidated for 10 days and tested for 30 days in the presence of 300 mg/L Pb O (figure 4) reveal the qualitative distribution of elements in the analysed area (Fe, Ni, Cr, Pb, O) and the quantitative composition of the layer Fe=38%, Ni=18%, Cr=18%, Pb=10% and O=8%. The lead from the test solution is found in the deposits formed on the specimen surface, indicating not only a simple adherence on the surface, but the formation of compounds with the other metals from the alloy: Fe, Ni, Cr, O. The presence of lead in the interior Cr enriched layer can promote the SCC of the Incoloy 800 material.

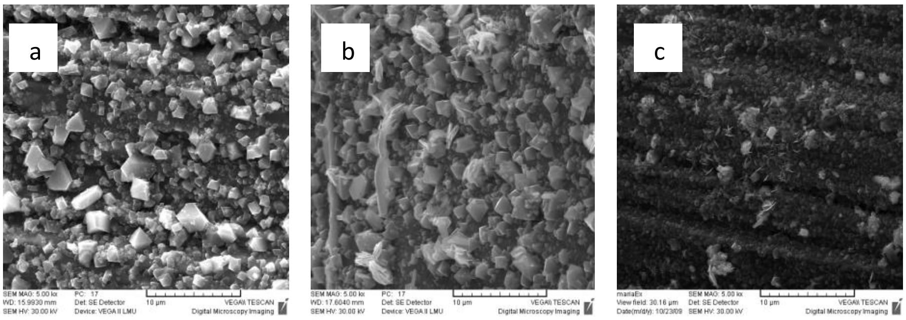

Fig. 3. The SEM morphology of the oxide films formed on Incoloy 800, exposure time 30 days, t=260^{0}C, p= 5.1 MPa, pH=9.5 in the presence of PbO: 100 mg/L (a), 200 mg/L (b) and 300 mg/L (c)

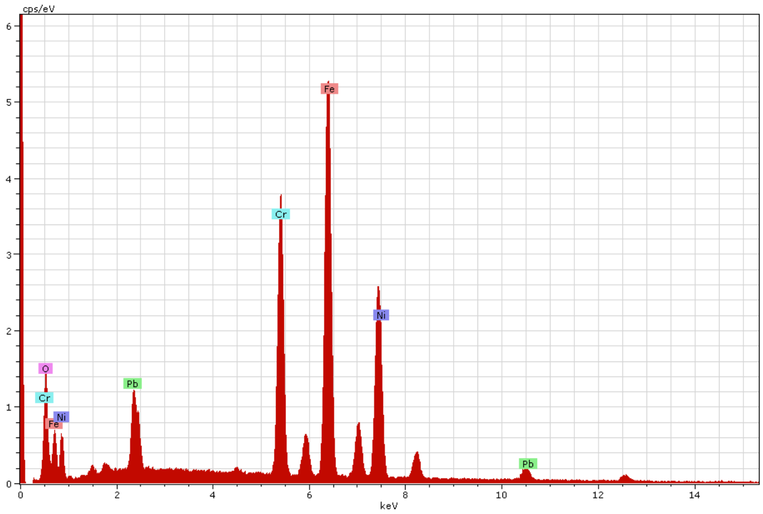

Fig. 4. The EDS spectrum and quantitative composition of the layer formed on Incoloy 800 , exposure time 30 days, t=260^{0}C, p= 5.1 MPa, pH=9.5 in the presence of 300 mg/L PbO

3.2. Electrochemical tests: potentiodynamic polarisation and impedance

Figure 5 presents the comparative potentiodynamic polarisation curves for the three different PbO concentrations (100, 200 and 300 mg/L) for each testing time (a-10 days, b-20 days and c-30 days). For the 10 days tested specimens the corrosion intensity does not proportionaly increase with the PbO concentration, due to the lead properties to react with the surfaces it comes into contact with or to remain in solution as solid or dissolved state. The 5b curves show higher current density and the decrease of corrosion potential as the PbO concentration increases, so the corrosion susceptibilty increases. The same corrosion behaviour is present for the 30 days tested specimens also (figure 5c), the corrosion being moderately accentuated when the PbO concentration increases too, the highest intensity being registered for 300 mg/L PbO.

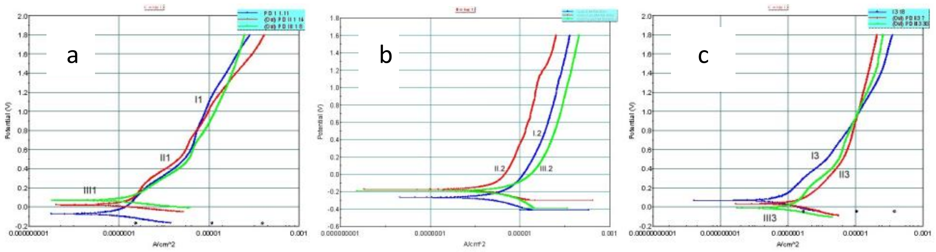

Fig. 5. Potentiodynamic polarisation graphs of the oxides films formed on Incoloy 800, t=260^{0}C, p= 5.1 MPa, pH=9.5 in the presence of PbO: 100 mg/L (a), 200 mg/L (b) and 300 mg/L (c), exposure times 10 days (a), 20 days (b) and 30 days (c)

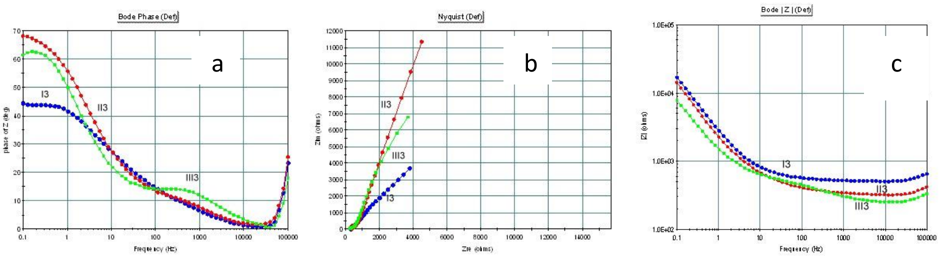

Fig. 6. Phase angle (a), Nyquist (b) and Bode (c) curves for Incoloy 800, t=260^{0}C, p= 5.1 MPa, pH=9.5 in the presence of PbO: 100 mg/L (I.3.), 200 mg/L (II.3) and 300 mg/L (III.3), exposure time 30 days

The behaviour of the superficial layers formed on Incoloy 800 investigated by electrochemical impedance method is presented in figure 6. The 44^0 phase angle value (figure 6a) for the specimen tested with 100 mg/L PbO suggests the low capacitive behaviour of the layer, therefore the existence of a porous exterior layer, having less protective properties. The PbO concentration increase from 200 to 300 mg/l does not allow the surface repassivation, the phase angle value decreases from 68^0 to 62^0. The same increasing tendency for the corrosion susceptibilty when the PbO concentration increase to 300 mg/L is noticed from the Nyquist (figure 6b) and Bode (figure 6c) curves also.

3.3. Gravimetric tests

The corrosion rates calculated by the gavimetric method are graphically presented in the figure 7. The generalised corrosion rate constantly increases with the exposure time, the oxides films formed in the presence of PbO does not succeed to provide the anticorrosive protection, the highest corrosion rates being registered for the specimens tested in the solution with 200 mg/L PbO.

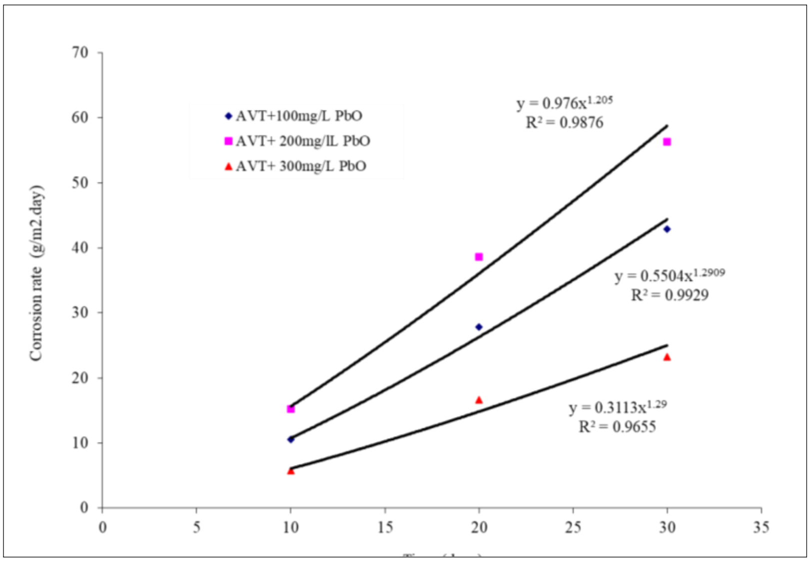

Fig. 7. Corrosion rate of Iy-800 tested in presence of PbO: 100 mg/L, 200 mg/l and 300 mg/L

As a qualitative assessment, it can be appreciated that the scales (oxides and corrosion products films) developed on the Iy-800 surfaces have a low porosity and high hardness, these playing the role of a barrier offerring a relative protection, especially for short periods of exposure, in very aggressive solutions by not allowing the diffusion of lead to the interface, which determines the protection for short term of the metal surface against corrosive attack in case of higher concentration of the impurities. This may be an explanation for the fact that at a concentration of 300mg/L PbO, the corrosion rate is lower compared to the corrosion rate obtained for a concentration of 200mg / L PbO.

4. Conclusions

It has been investigated the corrosion behaviour of the oxides films formed in CANDU secondary circuit conditions on Incoloy 800 in the presence of PbO concentrations of 100, 200 si 300 mg/L, which can appear in the steam generators through impurities and corrosion products concentration and transport.

The presence of PbO in concentrations of 100, 200 si 300 mg/L has a big influence on the specimens surface, the protective layer becomes non-uniform, even strongly non-uniform, both from the thickness and composition point of view. These morphological changes indicate the corrosion tendency on Incoloy 800, through stable and protective oxides formation blocking when the PbO concentration increases.

The electrochemical tests confirm the intensification of corrosion tendency: the increase of the current intensities and the shifts of the corrosion potentials toward more electronegative values when the PbO concentration and the testing time increase. Also, the impedance tests confirm the morphological changes in the case of higher PbO concentration through the decrease of protective qualities of the oxides films formed in the presence of 300 mg/L PbO.

The corrosion kinetics determined by gravimetrical method gave a constantly increase of the generalised corrosion rate during the exposure time, with the highest corrosion rates for the specimens tested in solution with 200 mg/L PbO.

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