APPLICATION OF ELECTROCHEMICAL PLASMA TECHNIQUES IN SURFACE ENGINEERING OF IRON BASED STRUCTURAL MATERIALS

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ABSTRACT

The surface of austenitic stainless steels 304L and 316L was modified by various complex surface treatments:
- plasma electrolytic carbo-nitriding by means of Plasma electrolytic saturation (PES); the saturation of cathodic surfaces with C, N was performed using suitable electrolytes (aqueous solutions of inorganic acids, appropriate salts containing the desired elements and certain organic compounds);
-electrodeposition of Al from ChCl based Ionic Liquid.

The coatings obtained in various experimental conditions have been investigated by means of electron spectroscopy, SEM, EDS, electrochemical techniques, and the properties of the thin films have been correlated with the microstructure and the composition of the surface layers which are strongly dependents of the different regimes of diffusion treatments.
The preliminary results on Electrochemical Plasma Technology (EPT) treatments demonstrate that we can select the processing parameters for essential improvement of corrosion behaviour in some aggressive medium and high values of microhardness.

Key words: (Electrochemical Plasma Technology, Ionic Liquid, Electrodeposition of Al)

Introduction

Alloy 316-L is an austenitic steel that has been used extensively in past sodium cooled fast reactors. From a cost and fabrication experience standpoint this material might be preferred for use for the vessel and other components of the LFR test demonstrator that are maintained at lower temperatures.
New surface treatments, including the alloying of steel surface with Al, are currently being investigated looking for better corrosion resistance properties of 316-L SS exposed in liquid Pb and relevant temperatures field for LFR condition.

A literature synthesis on the electrodeposition of nanostructured thin films, in order to obtain advanced materials, highlights the superiority of electrochemical deposition techniques in the synthesis of various nanomaterials , which showed improved characteristics compared to materials produced by conventional techniques, and describes their classification, routes of synthesis, properties and applications. Electrochemical Plasma Technology (EPT) is a patented, cutting edge surface engineering technique that has shown a great promise for its application on commercial scale for cleaning and coating of metal surfaces [1, 2]. EPT utilizes basic principles of electrochemical plasma, in which, D.C. potential is applied between two electrodes in an aqueous media.

EPT processing is a dynamic process that involves delivery of aqueous electrolyte into a confined chamber (EPT reactor) on the surface of the workpiece. The objective of this study is the improvement of iron based structural nuclear materials properties by Plasma Electrolysis techniques. Ability to form plasma on the surface of the work piece in liquid electrolyte gives the capability to carry out various treatments on metal surface (generally cathode). Ability to form plasma on the surface of the work piece in liquid electrolyte gives the capability to carry out various treatments on metal surface (generally cathode).

Furthermore, different chemical, electrical, mechanical and thermal interactions taking place on the metal surface in metal-plasma-electrolyte system provides the EPT processed surface with some unique characteristics [2, 3]. EPT has effectively removed oxide scale, lubricants, dirt, etc from metal surfaces [1, 4]. EPT cleaning is an environmentally friendly process that uses non-hazardous aqueous solutions as compared to acid pickling. Also, being an electrolytic process, it does not require safety measures as involved in case of grit blasting (dust) and acid pickling (air scrubbing). EPT has the ability to deposit metal and alloy coatings, such as Al, Ni, Zn-Ni, Ni-Cu, etc [1, 3]. EPT coatings exhibit excellent adhesion with the substrate and are deposited at significantly high deposition rates as compared to conventional electrolytic processes.

Experimental

The surface of austenitic stainless steels 304L and 316L was modified by various complex surface treatments:

I. plasma electrolytic carbo-nitriding and boro-carbo-nitriding by means of Plasma Electrolytic Saturation (PES); the saturation of anodic surfaces with C, N, B was performed using suitable electrolytes (aqueous solutions of inorganic acids, appropriate salts containing the desired elements and certain organic compounds). Experimental conditions of EPT treatments are presented in **Table 1**.

Table 1 *Experimental conditions of EPT treatments*

Electrolyte	**Voltage range[V]**	**Duration range [s]**
Water, Glycerin, and NH_4Cl	80-120	50-120
Water, Glycerin, and NH_4Cl, Borax	80-120	50-120

II. EPT by cathodic polarization of 316-L SS in 0.5 M $AlCl_3$ in Deep Eutectic Solvent ChCl-ureea (1:2 molar ratio) in order to obtain ceramic–like surface structures containing Al; temperature was 60-70°C. During experiments was used a magnetic stirrer. Work parameters are presented in **Table 2**.

Table 2 *Work parameters in EPT cathodic polarization in 0.5 M $AlCl_3$ in Deep Eutectic Solvent ChCl-ureea (1:2 molar ratio)*

$U_{treatment}$ =125 V $t_{treatment}$ = 35 s;	$U_{stabilization}$ =170 V $t_{stabilization}$ = 80 s	$U_{heating}$ =210 V $t_{heating}$ = 90 s.

The coatings obtained in various experimental conditions have been investigated by means of optical microscopy, XPS (including "depth profiling" and "ball cratering depth profiling"), SEM and EIS. Microhardness measurements were performed and corrosion behavior of treated samples was investigated by electrochemical techniques.

Results and discussion

I. The coatings obtained of EPT treatments have been investigated by electrochemical techniques SEM and EDS. Typical microstructures induced by EPT treatments are presented in **Figures 1a-1b**.

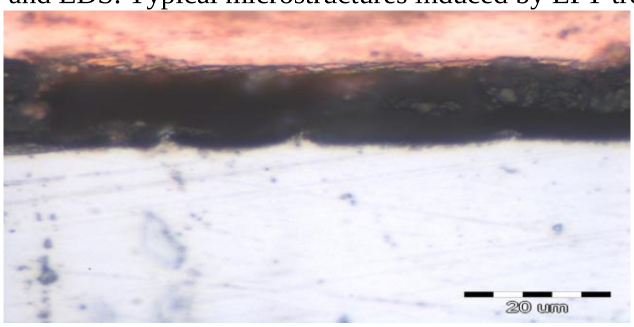


Figure 1a *316L SS sample microstructure after tratatament in Water, Glycerin, NH_4Cl, and Borax (boro-carbo-nitriding)*

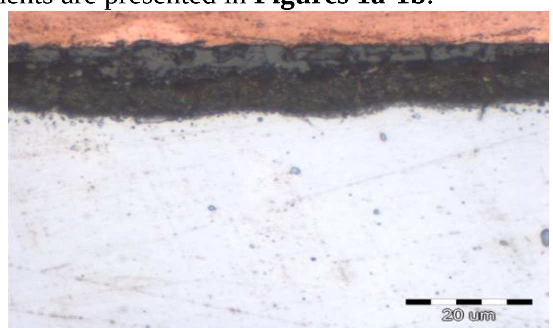


Figure 1b *304LSS sample microstructure after tratatament in Water, Glycerin, and NH_4Cl (carbo-nitriding)*

Typical results for microhardness measurements to reflect the variation with depth microhardness for evaluating the efficiency of EPT treatments performend are shown in **Figures 2a-2b**.

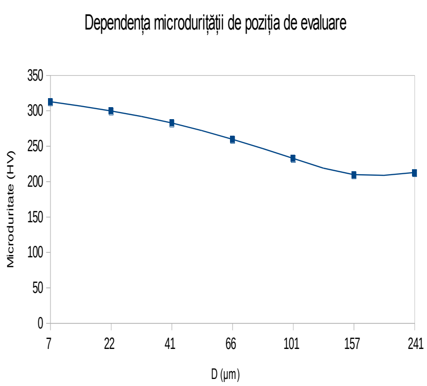


Figure 2a *Microhardness profile in depth for proper sample 304L SS treated in Water, Glycerin, and NH_4Cl*

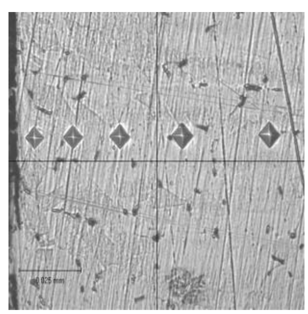


Figure 2b *Fingerprint images used in determining microhardness profil*

Developed surface structure of type 304L and 316L steel by EPT treatments were analyzed by XPS and "depth profiling", see **Figures 3a-3b**.

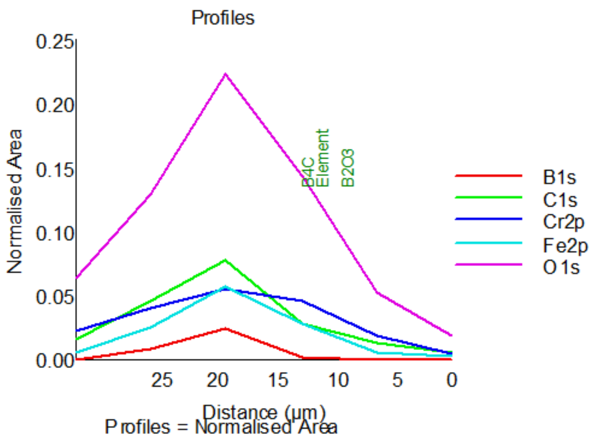


Figure 3a *General profile depth for boro-carbo-nitriding treated sample*

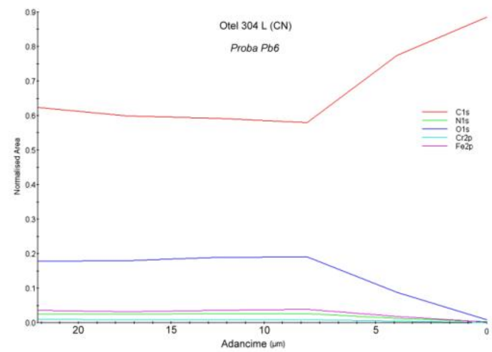


Figure 3b *General profile depth for carbo-nitriding treated sample*

II. Characterization of surface structures obtained by aluminisation treatment

Figures 4a-4c show the SEM images for Al containing structure obtained by described procedure.

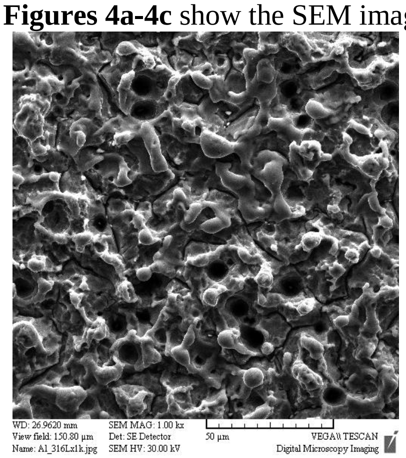


Figure 4a
SEM image for Al coatings

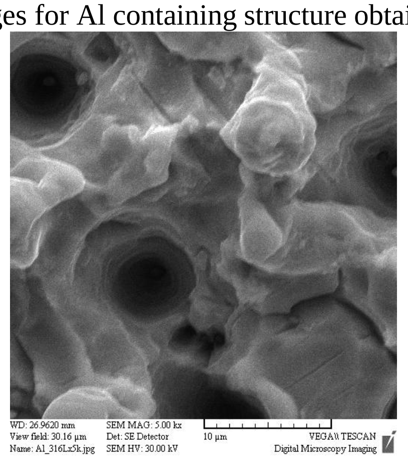


Figure 4b
SEM image for Al coatings - Details

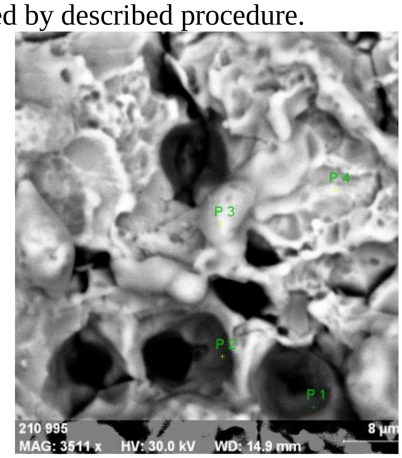


Figure 4c
Selected points on the SEM image for EDS analysis

SEM and EDS analysis show the synthesis of a nanostructured deposit with an average Al concentration on the surface structure of 2.19% (atomic percent), but the analysis in some selected points shows an Al concentration of ~21%, see **Table 3**.

Table 3 *Quantification results(at%) of EDS analysis in selected points of SEM image*

Point	C	Al	Si	S	Cr	Mn	Fe	Ni
P1	20.34	1.83	2.61	11.45	12.05	2.90	39.76	9.05
P2	0.43	20.94	38.12	8.31	6.29	1.71	20.98	3.22
P3	8.49	1.98	2.69	4.84	15.13	3.35	53.86	9.66
P4	10.85	1.16	1.80	6.80	15.49	3.32	51.11	9.46

Figure 5 presents the results of analysis by EIS (Nyquist and Bode representations); in **Figure 6** one can see the modeling results by identifying the interfacial structure and in **Figure 7** calculation of equivalent electronic circuit circuit components.

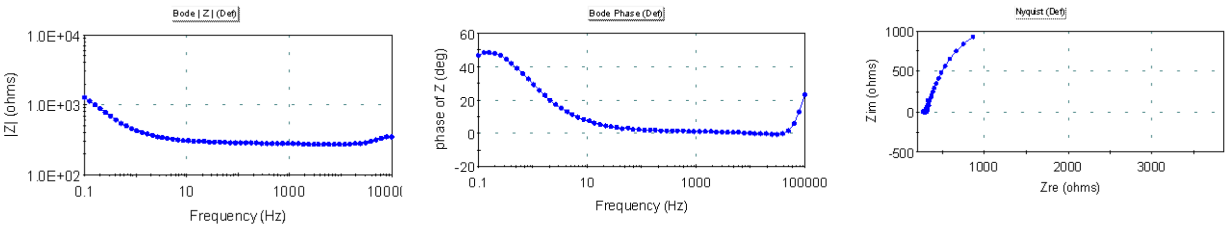


Figure 5 *EIS analysis: Bode and Nyquist Representations*

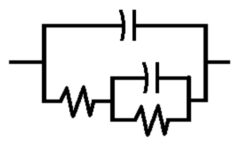
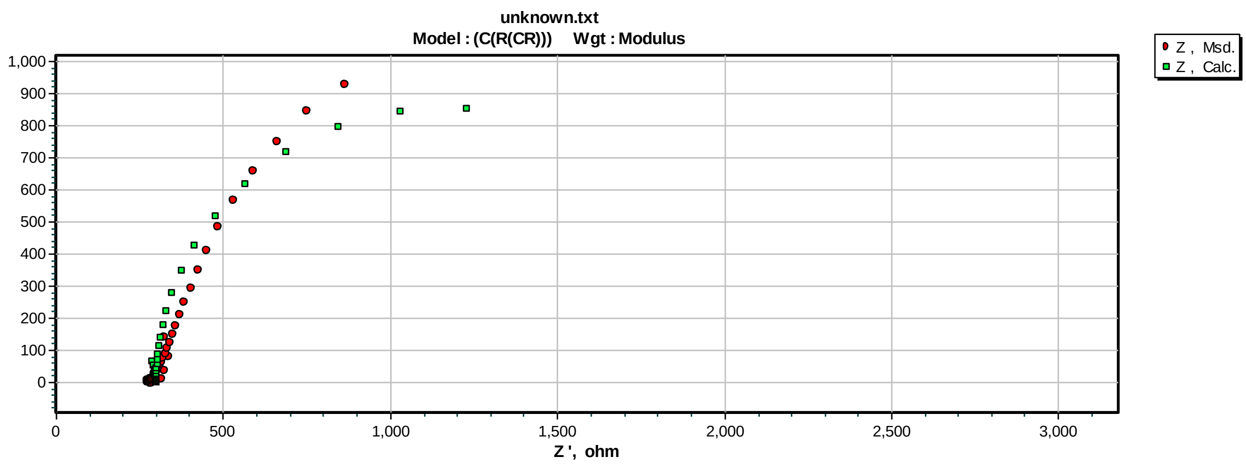
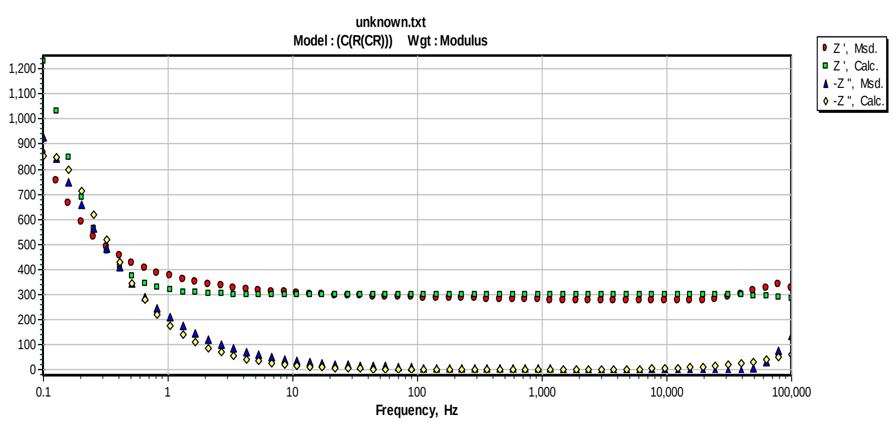


Figure 6 *Modeling interface by selecting an equivalent circuit and setting the components*





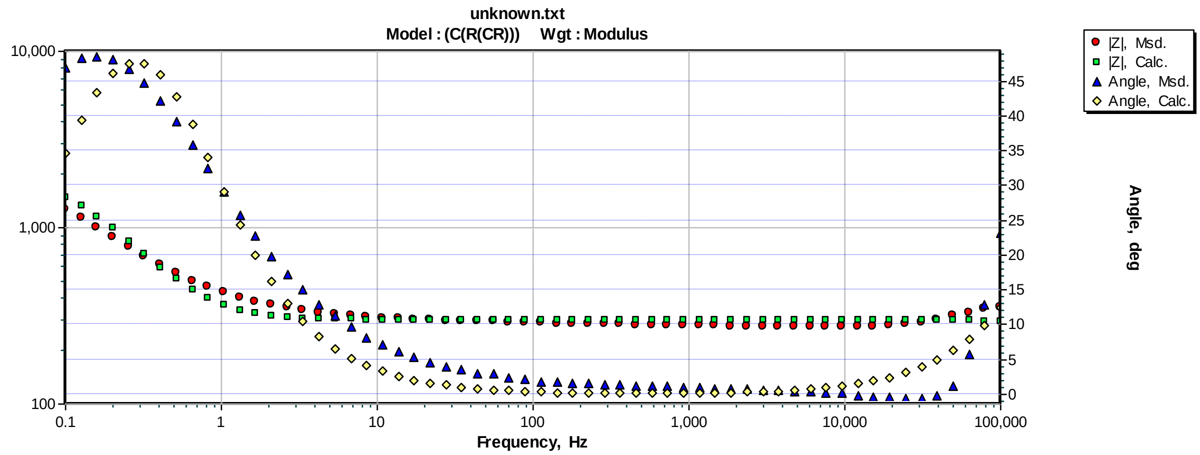


Figure 7 *Comparison between the experimental and calculated values of impedance data model*

Conclusions

1. The cathodic polarizations in carburizing, nitriding, nitro-carburizing, boro-nitriding and boro-nitro-carburizing processes avoid the substrate oxidation and are preferred in the nanostructured coatings synthesis.
2. Carbonitriding and boro-nitro-carburizing treatments under cathodic electrolysis in plasma assisted conditions (EPT) have been performed.
3. The structures obtained by EPT have been characterized metalographycally, by XPS, XPS-depth profiling and SEM-EDS.
4. The formation of a surface layer enriched in C and N and the presence of B in the structure of the sample obtained by boro-nitro-carburizing process was evidenced.
5. Successful experiments of Al electrodepositions on OL 316L steel in plasma assisted conditions with cathodic polarization by EPT, using $AlCl_3$ dissolved in choline chloride : urea = 1:2 were performed.
6. SEM and EDS analysis show the synthesis of a nanostructured deposit with an average Al concentration on the surface structure of 2.19% (atomic percent), but the analysis in some selected points shows an Al concentration of ~21%.

References

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