PROTECTIVE Fe_2Al STRUCTURES ELECTRODEPOSITED ON 316L STAINLESS STEEL FROM A DEEP EUTECTIC SOLVENT

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Abstract

There is widespread attention to modification of 316 stainless steel for research development and application to advanced nuclear reactors. Here, a successful electrolytic plasma processing (EPP) technique has been developed for coating deposition of stainless steel 316L. The novelty consists in the use of an electrolyte based on a choline chloride-urea eutectic solution. The structural properties (morphology, composition and corrosion behaviour) were determined by SEM / EDS, XRD and potentiodynamic polarization curves. The results show that Fe2Al coating with a thickness of approximately 100 µm can be obtained on the stainless steel 316L by means of EPP for only 4 min. There is an obvious enhancement in corrosion resistance of stainless steel 316L after EPP treatment. The results demonstrate that the EPP technique can be successfully used to produce materials of nuclear interest intended for use in extreme conditions, specific to advanced nuclear reactors.

Keywords: *EPP, Stainless steel 316L, SEM/EDS, XRD, potentiodynamic polarization curves, Fe_2Al intermetallic compound*

Introduction

The materials used in the nuclear power plants are subjected to extreme conditions and for this reason, during operation, many problems arise that require solving. Research in the field of structural materials in order to improve their properties is of real interest and in continuous evolution, the development of environmentally friendly alternatives still representing a great challenge.

Aluminium (Al) and its alloys are excellent materials with good potential capability for various applications because of their excellent thermal properties, electric conductivity, light weight, and corrosion resistance [1, 2]. Al alloys are regarded as the preferred choice of coating material, they tending to develop a natural passive oxide layer on their surface during the contact with air, which makes them corrosion-resistant in different environments [3, 4]. Globally well-known companies such as Applied Materials or Raytheon employ electroplated aluminium to protect components in corrosive environments [1, 5].

Electroplating of Al offers certain advantages such as high purity deposits (≥ 99.99% Al), higher deposition rate compared to other vacuum deposition methods (ion vapor, chemical vapor, physical vapor), and allows for deposition of thick layers (up to 1000 µm) [6]. Electrodeposition is also a "non-line-of-sight" process and provides excellent coverage for small or complex geometries. Electroplating of Al finds application in aerospace and electrorefining. The versatility of electrodeposition lies in controlling the grain size and structure of the deposits with simple variation of the process parameters such as voltage, current density, and bath composition, which makes the electrodeposition method versatile relative to other coating methods where the substrate can be kept at a low temperature such as thermal spray coatings, physical, chemical vapor deposition, and roll binding [1].

Attempts have been made to use electrolytic plasma processing (EPP) as a relatively innovative means of surface treatment and coating for improving specific surface topographies and coating quality of metallic materials [7-14]. The formation of plasma on the surface of anodic or cathodic substrate, which depends on the polarity of applied voltage, gives the capability to carry out anodic or cathodic EPP for various surface engineering. The anodic EPP has been usually associated with surface passivation and coating, leading to oxidizing, carburizing, and/or nitriding of the electrode surface [7]. The cathodic EPP has been used for preparing metal nanoparticles or depositing metallic coating [15, 16]. Moreover, it has been realized that the cathodic EPP can both remove surface contaminants and boost filming kinetics, as it overcomes the issues of traditional methods [7].

Since Al has high negative reduction potential (−1.67 V vs. SHE), it cannot be electrodeposited from aqueous electrolyte media due to the occurrence of hydrogen evolution reaction prior to the Al metal or Al alloy reduction. Therefore, electrodeposition of Al /Al alloys needs to be performed in non-aqueous electrolytes [1].

A detailed review covering electrochemical deposition of Al and Al alloys using ionic liquids was recently provided in [17]. Over the past decades, Deep Eutectic Solvents (DES) have proved to be excellent alternatives to aqueous-based electroplating solutions for the electrodeposition of metals and alloys, since they have excellent properties. Among them, it can be highlighted that they are easy to prepare, have good ionic conductivity, have high thermal stability, large electrochemical windows, and the metal salts have good solubility in DES. Furthermore, DES are biodegradable and non-toxic, which make them excellent environmentally friendly alternatives to formulate electroplating solutions to overcome the environmental problems associated with the non-environmental wastewater produced by the industrial electrodeposition process based on aqueous electroplating solutions [18]. The most widely studied eutectic mixtures are based on a combination of organic salts, such as choline chloride, with hydrogen bond-donor compounds, such as either urea or ethylene glycol, in a molar ratio equal to 1:2 [17].

By employing DESs as an electrolyte media, electrodepositing Al and Al alloys (generally binary) with varying compositions that follow normal deposition behaviour can be achieved, allowing either primary metal or alloying metal rich in overall composition, which is dependent on the primary Al metal ion, binary metal ion (alloying metal ion) concentration and the deposition potential that is to be applied. Electrodeposition of aluminium on cathodes as copper, iron and especially glassy carbon, has been performed at temperatures between 80-95 °C with voltage from -1V to -2V and amperage stable at 80-95 mA, in two hours using choline chloride-urea eutectic solution [7].

A promising method for Al deposition was proposed by using AlCl3/[bmim]Cl (1-butyl-3-methylimidazolium chloride) ionic liquid as electrolyte [19].

Dense, bright and adherent aluminium coatings were obtained over a wide range of temperature (298–348 K) and current densities (8–44 mA/cm^2). Electrolytic plasma processing (EPP) has been successfully employed for both surface pretreatment and coating deposition of stainless steel 304 with Zn by controlling an applied potential to 150 V and 180V, respectively, for 60 s [7].

However, the use of DES for aluminium electrodeposition on 316L stainless steel has not been reported previously. In this work, electrolysis plasma processing (EPP) is extended to deposit Al – Fe structures on 316L from the choline chloride-urea eutectic solution containing $AlCl_3$.

Experimental details

Samples of stainless steel 316L were cut into pieces of 30×20×1mm in size. The configuration plasma electrolysis set-up used for EPP tests on the stainless steel 316L is presented in Fig. 1. The electrolyser consisted of a silica glass container. The sample of 316L stainless steel was used as a cathode and the anode supply was connected to a cylindrical plate, 20 times larger than the cathode and made of stainless steel 316L, which surrounded the sample. The power supply provided a constant voltage, U=200 V, with an accuracy of approximately ± 1% of the desired value and the processing time was 4 minutes.

Electrolyte (choline chloride / urea / $AlCl_3$) was prepared as follows: Choline Chloride and urea were mixed in a specific molar ratio and heated to 90 °C by an oil bath; aluminium chloride was dissolved slowly in Choline Chloride/Urea mixture, with stirring. The temperature of the electrolyte was maintained in the range 90-95 °C. After electroplating, the cathode was washed with deionized water and finally dried.

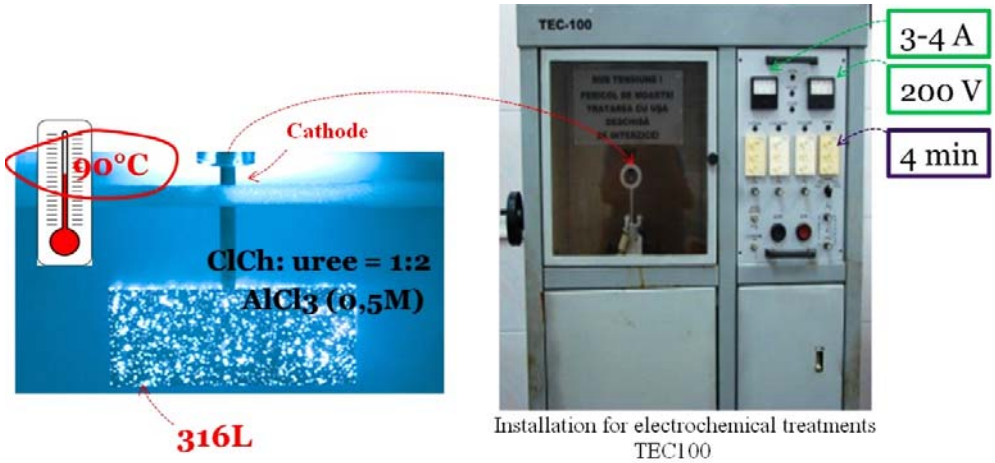


Fig. 1. The configuration plasma electrolysis set-up used for EPP tests on stainless steel 316L

The characterization techniques used were:

- *Metallography;*
- *Scanning Electron Microscopy – SEM,* performed with a *TESCAN VEGA II LMU* microscope;
- *Energy-Dispersive X-ray Spectroscopy – EDS* for chemical characterization of sample surface;
- *X-ray diffraction – XRD,* performed on *a Rigaku Ultima IV diffractometer*. *X-ray* diffraction patterns were recorded with CuK_α radiation. Qualitative phase analysis was performed using the software package PDXL 2.4 (Integrated X-ray powder diffraction software X) and the ICDD PDF4 + database (2015). For surface structure determinations grazing incident angle geometry was used.

- *Electrochemical techniques*: The equipment used to study the electrochemical behaviour consisted of a conventional three-electrode electrochemical cell connected to *the Parstat 2273* potentiostat (Fig. 2). Potentiodynamic polarization experiments were performed in NaCl 0.5 M aqueous solution, using the *Power Suite* software package. The working temperature was 30 °C. The area of the working sample exposed to the electrolyte was set to 1 cm^2. After stabilization of the electrochemical system (20 – 30 minutes), the polarization curve was recorded using a scan rate of 2 mV/s, starting from -0.25 V vs. open circuit and going up to +0.25 V vs. open circuit.

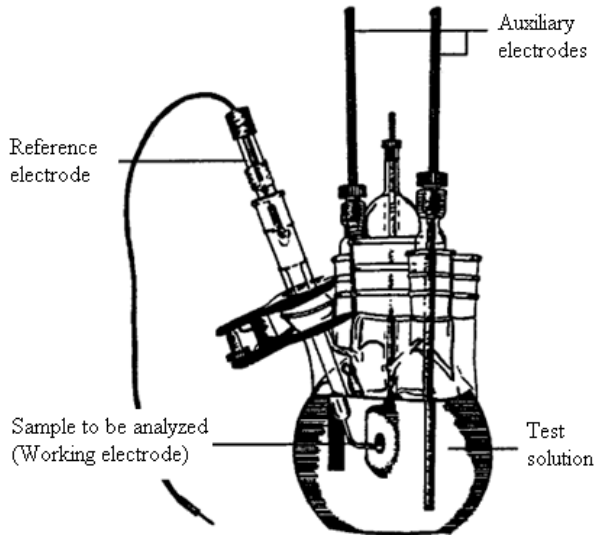


Fig.2. Electrochemical cell used in potentiodynamic polarization tests

Results analysis

Metallographic microscopy

Fig. 3 shows a metallographic microscopy image of the coating section for the EPP treated SS 316L sample. It can be clearly seen a layered structure formed. The thickness of the coating is ≈ 100 μm, which consists of a porous layer on the top and a denser one below.

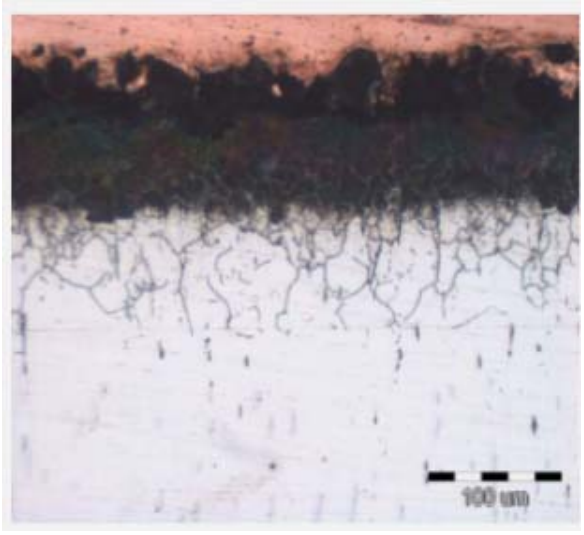


Fig. 3. Metallographic image of the coating section for the EPP treated SS 316L

SEM microscopy

Fig. 4 shows a SEM microscopy image of the EPP treated SS 316L sample. As one can see the coating is characterized by the presence of micro-craters and spheroids.

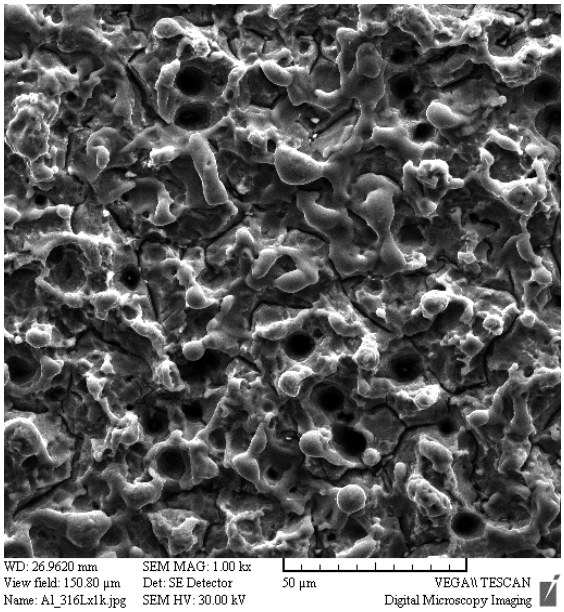


Fig. 4. SEM micrograph of EPP treated stainless steel 316L

Energy-Dispersive X-ray Spectroscopy – EDS

Fig. 5 shows maps obtained by EDS analysis with distribution of chemical elements in the coating (see Table 1).

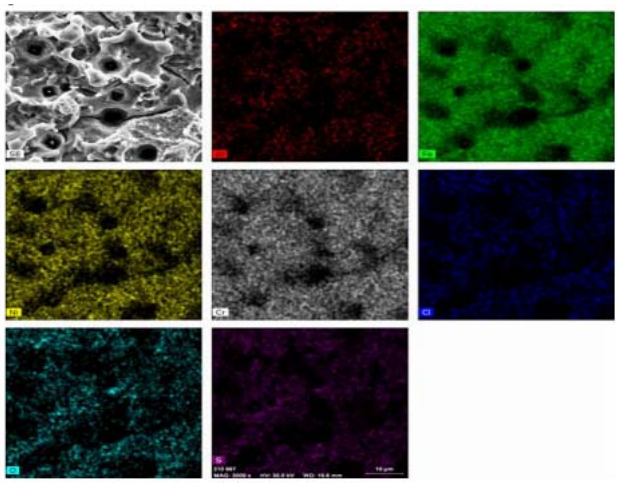


Fig. 5 Distribution of elements on the surface of EPP treated stainless steel 316L; maps obtained by EDS

Table 1. Results of EDS elemental analysis for EPP treated stainless steel 316L

Elements	Al	Fe	Cr	Ni	Mn	S	C	O
Concentration [% at]	17.5	49.5	15.6	8.2	1.1	1.9	3.2	3.0

X-ray diffraction - XRD

Figs. 6 and 7 show the diffraction spectra on the 316L stainless steel substrate and on the *EPP* treated 316L stainless steel. The diffractogram of the *EPP* treated 316L, obtained with small incidence angles (3° and 5°, respectively), highlights the presence of Fe_2Al intermetallic compound on the surface layer. The network parameters determined for this compound are a'=3.639 Å and a=3.750 Å.

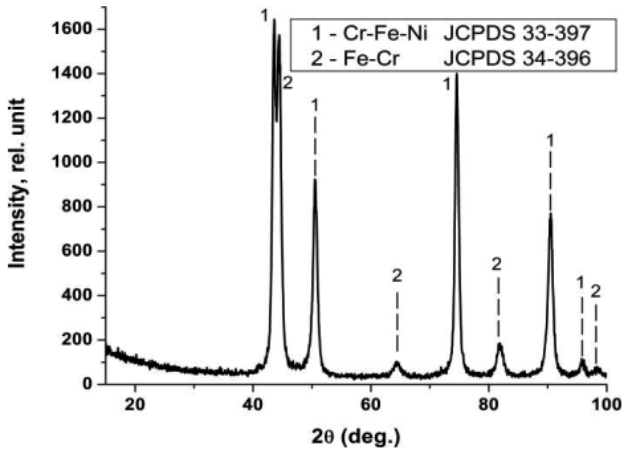


Fig. 6. XRD diffraction spectrum of the 316L substrate

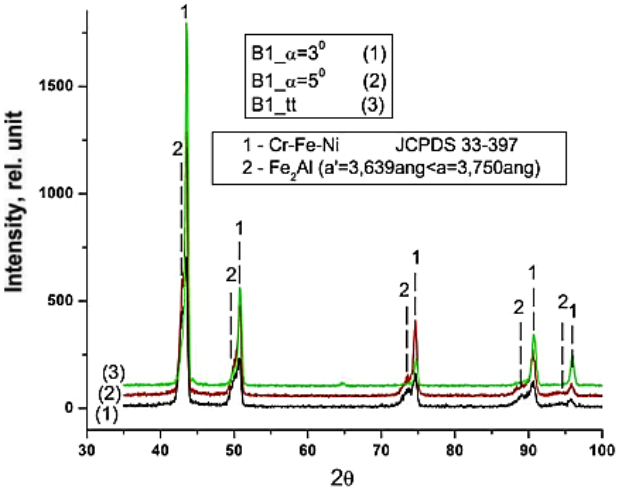


Fig. 7. XRD diffraction spectrum of the EPP treated 316L

Electrochemical measurements

The potentiodynamic polarization curves (Fig. 8) illustrate the corrosion behaviour in the 0.5 M NaCl aqueous solution of the 316L substrate and the EPP treated 316L.

The corrosion potential (see Table 2) of the substrate (-324 V) moves towards more positive values in the case of the EPP treated 316L (-283 V), indicating that the treatment of the sample by EPP leads to the formation of a passive, protective layer against corrosion.

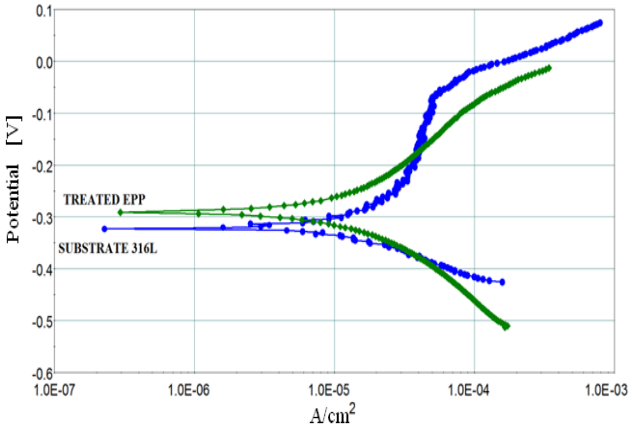


Fig. 8. Potentiodynamic polarization curves for 316L steel samples (substrate and EPP treated) in 0.5M NaCl aqueous solution

Table 2 Corrosion potential and corrosion rate values calculated from polarization curves for SS 316L samples (substrate and EPP treated) in 0.5M NaCl aqueous solution

Sample code	Corrosion parameters	
	Corrosion potential, E_{corr} [mV vs. SCE]	Corrosion rate [mm/an]
Substrate SS 316L	-324	0.236
EPP treated SS 316L	-283	0.18

Conclusions

The study presents the results obtained using the electrolytic plasma processing (EPP) technique which has been successfully developed for coating deposition of Al as Fe_2Al on stainless steel 316. The novelty of this method consists in the use of an electrolyte based on a choline chloride-urea eutectic solution containing $AlCl_3$.

The characterization methods show the following results:

- The metallography illustrated a layered structure, the thickness of the superficial layer being ≈ 100 µm.
- The SEM image shows that the obtained layers are uneven and porous.
- The EDS analysis proves that the developed layers contain the elements Al, O.
- DRX diffractogram highlighted the coating crystalline structure, determined by Fe_2Al intermetallic compound.

The polarization diagrams confirm that the corrosion resistance of the Fe_2Al coated 316L stainless steel is higher than that of the substrate.

The Deep Eutectic Solvents used in this work have proved to be an excellent alternative to aqueous-based electroplating solutions for Al intermetallic compound electrodeposition on stainless steel 316L; which has not been reported previously reported.

The Al-containing coatings demonstrated that the EPP technique is an effective method to solve the corrosion issues of advanced next-generation reactors.

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