35th EPS Conference on Plasma Phys. Hersonissos, 9 - 13 June 2008 ECA Vol.**32D**, P-1.166 (2008)

PLASMA PROCESSING FOR IMPROVEMENTS OF STRUCTURAL MATERIALS PROPERTIES

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1. INTRODUCTION

Plasma Electrolysis (PE) is a generic term which is used to describe a variety of high voltage electrochemical processes, which feature plasma-discharge phenomena occurring at an electrode-electrolyte interface /1/. Extensive trials were carried out in order to develop nitrating and nitro-carburizing plasma electrolytic diffusion treatments for a group of materials, including stainless steels. However, major uncertainties remained concerning the process optimization, control and repeatability, which were mainly caused by the fact that the scientific understanding of key process fundamentals and discharge phenomena lagged well behind empirically based treatment trials then in progress.

Duplex treatments which include plasma electrolytic techniques are extremely useful where, in practical tribological situations, the application of a liquid lubricant is impossible and a thin top layer of a material with lubricious properties should be applied as part of a surface composite coating/1/.

Presently, there is great interest in deposition on various substrates of amorphous carbon (a-C) films, which contain significant fractions of sp^3 bonding/2/. Diamond-like carbon (DLC) is a well-known anti-friction and wear-resistant material. Thin DLC films deposited by various methods, usually suffer from a lack of load support when deposited on soft and ductile substrates, such as austenitic stainless steels.

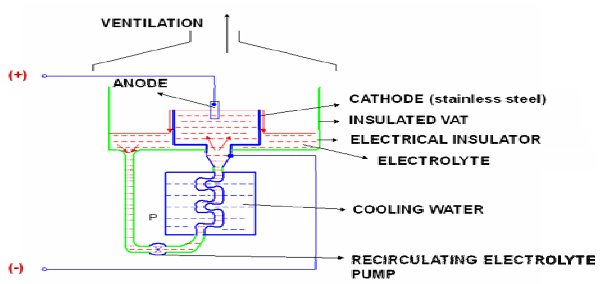
In this paper we try to eliminate this drawback, when combining plasma electrolytic pre-treatments of these substrates/1,3/ with subsequent deposition of thin carbonic films using Thermionic Vacuum Arc Plasma (TVA) processes/4/.

2. EXPERIMENTAL

Thermo-electrochemical treatments of carburizing and nitrating bath were applied using the equipment TEC100 (SCINTI-Moldova) on austenitic steel 304. The experimental setup was identically for carburizing (using glycerine solution as electrolyte) and nitrating (using NH_4OH solution as electrolyte) treatments.

Thermionic Vacuum Arc (TVA) is an externally heated cathode arc, which can be established, in high vacuum conditions, in vapours of the anode material /4/.

Thermionic Vacuum Arc is ignited between a heated cathode surrounded by an electron-focusing Wehnelt cylinder and an anode (tungsten crucible) containing the material to be deposited. Because of the electron bombardment of the anode by the accelerated thermo-electrons from the grounded cathode towards the anode (which is at high voltage), the anode material first melts and afterwards starts to evaporate, ensuring a steady state concentration of the evaporated atoms in the cathode-anode space.



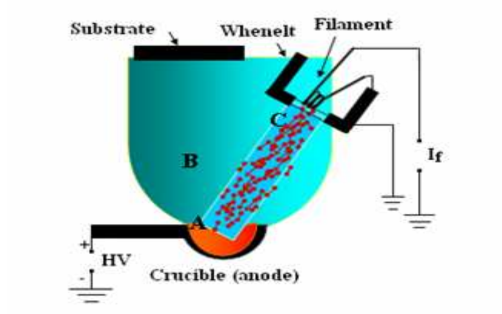


Fig.1. a) Experimental setup for thermo-electrochemical treatments b) TVA principle scheme

The surfaces films developed by thermo-electrochemical treatments on the austenitic stainless steel were investigated by optical microscopy, ESCA, XRD and Electrochemical Impedance Spectroscopy/3/. Corrosion behaviour was evaluated by electrochemical techniques.

The carbonic thin films were deposited on the carburized austenitic substrate, and the interface carbonic layer/ steel substrate was analysed by XPS and depth profiling/2/.

Optical measurements were performed with NEOPHOT 2 optical microscope, XPS analysis of the deposited films have been performed with an ESCALAB 250 (Thermo Fisher Scientific) spectrometer, the XRD data were collected with a DRON UM1 diffractometer, Electrochemical impedance spectroscopy (EIS) measurements were performed using an PAR 273 System (Potentiostat/ Galvanostat), with Model 5210 Lock-in Amplifier. EIS measurements were performed at the open circuit potential, which correspond of the very small current into oxide layer, and the thickness of this oxide is not modified. The solution used in tests was the boric acid/ borax because that is a chemical inert environment for the superficial films developed on the samples.

3. RESULTS

The results about the microstructures of treated samples and about corrosion rates (determined by Polarization Resistance Method) are presented in the Table 1.

TABLE 1- MICROSTRUCTURE OF THE FILMS AND CORROSION RATE

Sample	Surface film structure	Corrosion rate (mm/y)
Carburized 304	Surface film -50μ	0.07 x10^{-6}
Nitro-carburized 304	Surface film -10 μ	1.14 x10^{-6}
304 as received		2 x10^{-6}

EIS method provides qualitative information about surface thin films from Bode and Nyquist plots analysis/3/. In the case of carburized and nitrating 304 samples the highest impedance values are closed to 10^5 Ω. The angle phases are smaller than 90˚ that signifies that films are not fully capacitive. For carburized 304 sample the angle phase has a greater value than nitrating 304 sample so, the films obtained by carburization are less porous. Smaller values of the capacitances correspond to a slow growth of the layers indicating a stability of this passive layer. The very high values of electrical resistances demonstrate a good corrosion resistance.

XRD analysis of carburized austenitic steel proves the presence of Fe_3O_4, $(Cr,Fe)_7C_3$, $Fe_{15}Cr_4Ni_2$, CrN, CrFe.

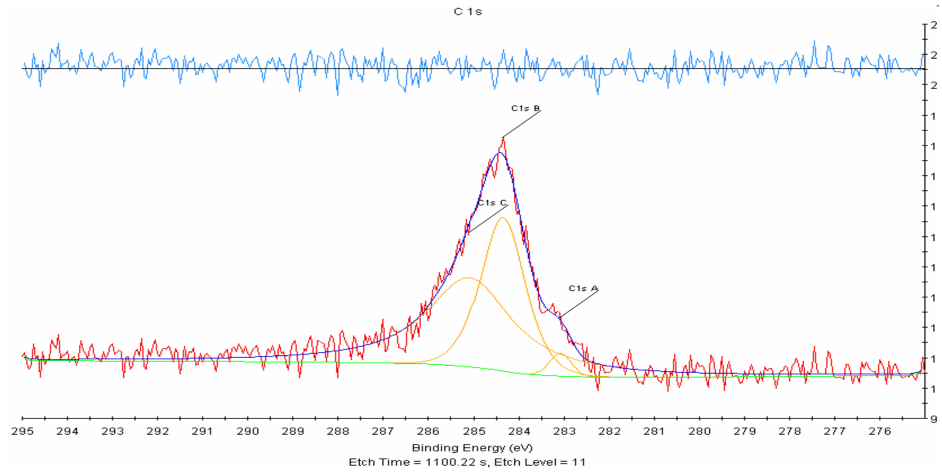


Fig.1. XPS analysis of interface carbonic film/ substrate (region I)

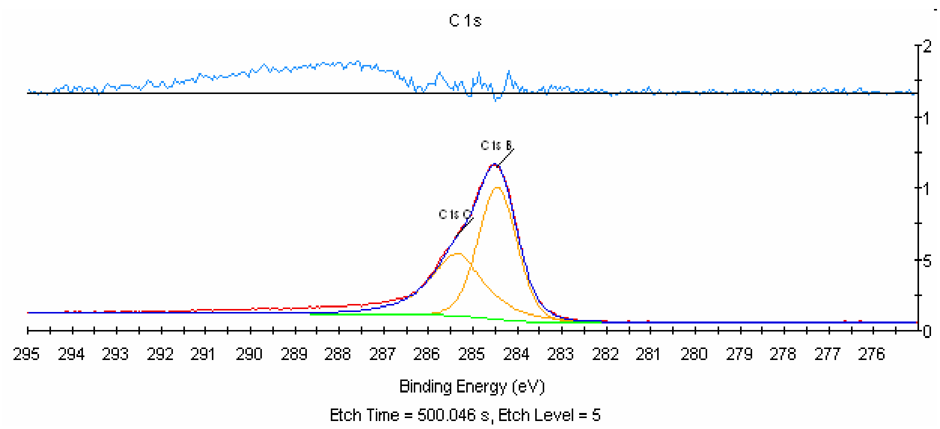


Fig.2. XPS analysis of carbonic film (region II)

Region	Chemical state of C	Concentration At%
Interface carbonic film/ substrate (I)	Cr_7C_3 (283 eV)	3
	sp^2(284.4 eV)	40
	sp^3 (285.4 eV)	57
Carbonic film (II)	sp^2(284.4 eV)	56
	sp^3 (285.4 eV)	44

4. CONCLUSIONS

In this paper, we have presented the preliminary results on duplex treatments which include plasma electrolytic carburization of the austenitic steels and subsequent deposition of thin carbonic films using Thermionic Vacuum Arc Plasma (TVA) processes.

The XPS analysis of the interface carbon layer/ substrate proves the 43% sp^3 carbon bonds in the carbonic deposited layer.

Further developments related to the improvement of the duplex treatments are required to increase the sp^3 bonds concentration in the carbonic layer.

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