INFLUENCE OF HIGH TEMPERATURE PLASMA NITRIDING ON CORROSION RESISTANCE OF X12Cr13 STEEL

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Abstract

The martensitic stainless steel AISI 410 was subjected to plasma nitriding at an increased temperature of 550 °C, 24 h in $3H_2$:$1N_2$ (l/h) nitriding gas ratio and compared to untreated one. The microstructure and microhardness of the untreated and nitrided stainless steel were evaluated. The corrosion properties of the untreated and plasma nitrided steel samples were evaluated using the anodic potentiodynamic polarization tests in neutral 2.5% NaCl deaerated solution. The phase analysis of nitrided steel sample was compared to untreated one. The results showed that plasma nitriding process on the X12Cr13 Steel (AISI 410) stainless steel produced a nitride layer consisting of compound layer and a nitrogen rich diffusion layer with iron carbides Fe_3C, iron nitrides Fe_4N, chromium nitrides Cr_4N_4 and chromium iron carbide $Cr_{15}Fe_7C_6$. Plasma nitriding process significantly increased the surface hardness of the martensitic stainless steel but also decreased the corrosion resistance. The pitting and type of corrosion were evaluated, and the pitting coefficient was calculated. During electrochemical corrosion tests, the nitrided AISI 410 stainless steel showed lower corrosion potentials (more negative), higher current densities (nearly forty times higher) and nearly forty times increased corrosion rates compared to untreated X12Cr13 stainless steel.

Keywords: Plasma nitriding, stainless steel, corrosion resistance

1. INTRODUCTION

One of the processes of surface treatment based on chemical-heat treatment is the plasma nitriding (PN) process. This PN process is used to improve the mechanical properties such as surface hardness, fatigue strength [1,2] and tribological properties [3,4] of structural steels. On the other hand, some of the mechanical properties, for example notch toughness, are reduced by plasma nitriding process [5]. Plasma nitriding of structural carbon steels is typically carried out in the range of 450 ÷ 550 °C [1,2]. Increase of corrosion resistance may occur under certain conditions after plasma nitriding in the case of structural steels [6].

The improvement of mechanical properties of plasma nitride stainless steels is similar to the improvement of mechanical propertied of plasma nitrided structural carbon steels. For example, surface hardness is increased rapidly of AISI 410 stainless steel after plasma nitriding at 400 °C, 20 hours and with working atmosphere $1H_2$:$3N_2$, up to 1275 HV [3]. The corrosion resistance of stainless steels is directly dependent on plasma nitriding parameters as time duration of process, composition of nitriding (working) atmosphere and especially the temperature of the PN process. The authors state, that the corrosion resistance of stainless steels can be impaired if the process of plasma nitriding is carried out at temperatures 450 °C [7], 460 °C for AISI 304 stainless steel [8], 475 °C [9] and 480 °C [10]. For example, plasma nitrided AISI 410 steel at temperature 420 °C for 6 hours obtained better corrosion resistance than the un-nitrided one [11]. On the other hand, same steel (AISI 410) plasma nitrided at temperature 500 °C had been affected by decreased corrosion resistance [12].

It is stated that above threshold of 450 °C ÷ 480 °C (depends on type of steel) the precipitation of iron and chromium nitrides (CrN) on the grain boundaries in case layer occurs [10]. At PN temperature of 500 °C the nitride layer consists of CrN, Fe_3N and Fe_4N phases for AISI 304 steel and the pitting corrosion was observed [8]. Similar behaviour was observed at 500 °C for plasma nitrided AISI 410 stainless steel as well [12].

2. EXPERIMENTAL

For the study was the X12Cr13 martensitic stainless steel (AISI 410), used for production of turbochargers. Chemical composition has been verified using the spectrometer Tasman Q4 and compared to inspection certificate, summarized in **Table 1**.

Table 1 Chemical composition of X12Cr13 (wt. %)

	C	Si	Mn	Cr	Ni	Mo	V	Cu	W	N2	P	S
Tasman Q4	0.11	0.3	0.54	12.91	0.36	0.07	0.05	0.12	1.14	0.02	0.08	0.01

For phase analysis were the original 70 x 40 mm plasma nitrided and untreated turbochargers blades used, grinded to roughness of Ra = 0,4 μm by the manufacturer and then degreased in ethanol prior plasma nitriding process and before every measurement. The experimental material for specimens was in the form of blades of turbochargers. These were cut into samples for potentiodynamic polarization testing needed. Standard samples for potentiodynamic testing with diameter of 13 mm and thickness of 10 mm were prepared.

Prepared samples were subjected to plasma nitriding process with following plasma nitriding parameters: Operational nitriding atmosphere with gas ratio $3H_2$:$1N_2$ (l/h), time duration of nitriding process of 36 hours at temperature 520 °C in RUBIG PN 60/60 device.

Samples were studied by optical microscopy (OLYMPUS DSX 100). Existence of martensitic structure was observed in **Figure 1**. Thanks to etching by 5 % Nital the diffusion layer and compound (white) layer were observed. Compound layer of approximately 3.69 μm was measured using Olympus DSX 100.

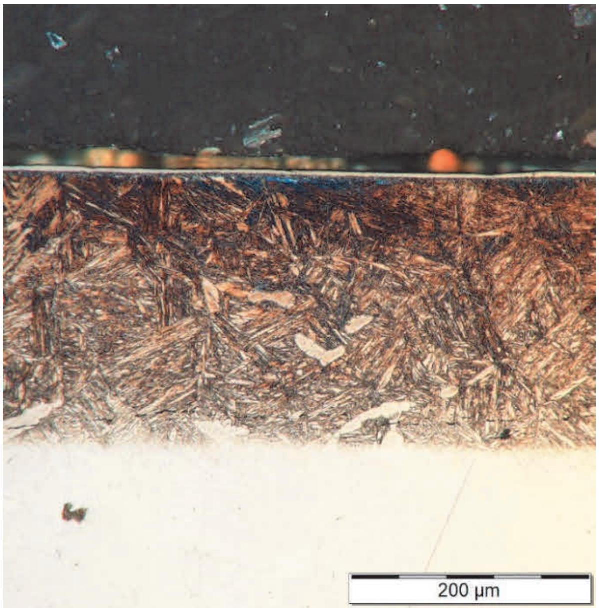

Figure 1 Microstructure of plasma nitrided X12Cr13 with visible compound and diffusion layer after etching by 5% Nital

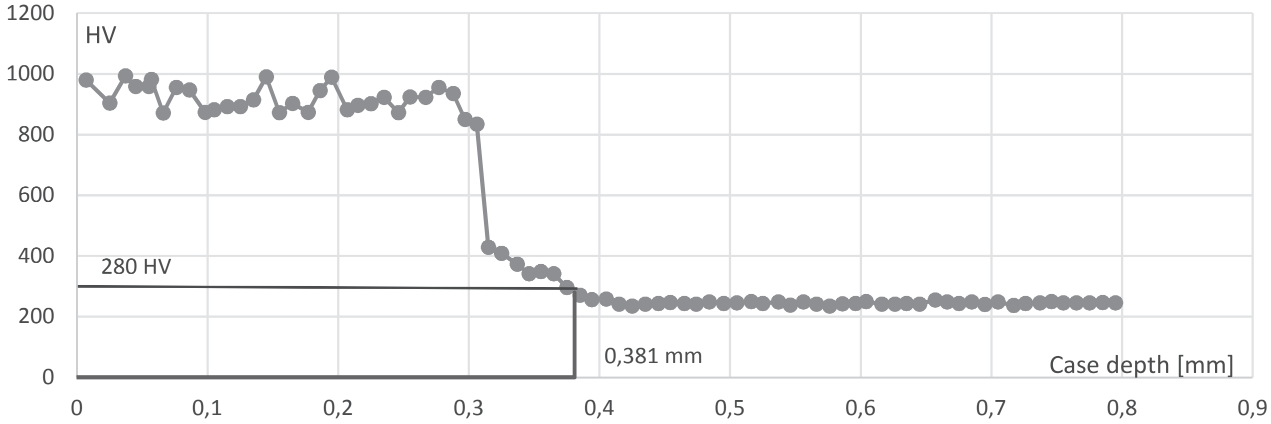

Figure 2 Microhardness measurement and nitride layer case depth evaluation

The case layer depth reached 0.381 mm, evaluated by microhardness measuring using LECO LM247 AT microhardness tester according to standard EN ISO 18203:2016 (see **Figure 2**).

Surface hardness was measured after plasma nitriding. Initial surface hardness of un-treated stainless-steel sample was measured 241 ± 5 HV and after plasma nitriding surface hardness increased to value 982 ± 11 HV.

Surfaces of plasma nitrided and untreated samples were additionally documented by the optical microscopy (OLYMPUS DSX 100) after anodic potentiodynamic polarization tests (see **Figure 3**). The pitting was evaluated using laser confocal microscopy LEXT OLS 3000 and pitting factor (PF) was calculated according to standard ISO 11463 for untreated and plasma nitrided X12Cr13 steel samples. The calculated pitting factor represents a ratio of deepest pit to the average depth of 10 measured pits. Pitting factor of value 1 indicates general corrosion and with increased value of pitting factor the pitting corrosion is more prominent.

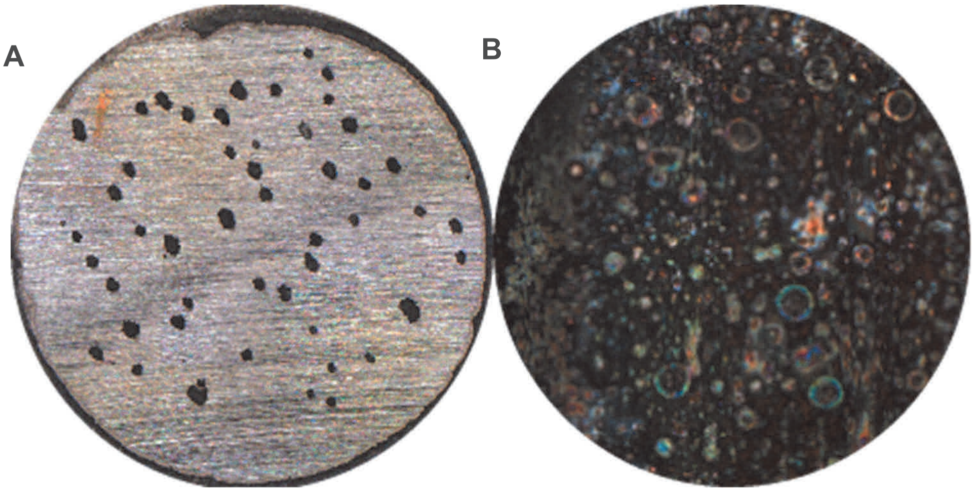

Figure 3 Pitting on the X12Cr13 stainless steel after anodic potentiodynamic tests (A) untreated, (B) plasma nitrided

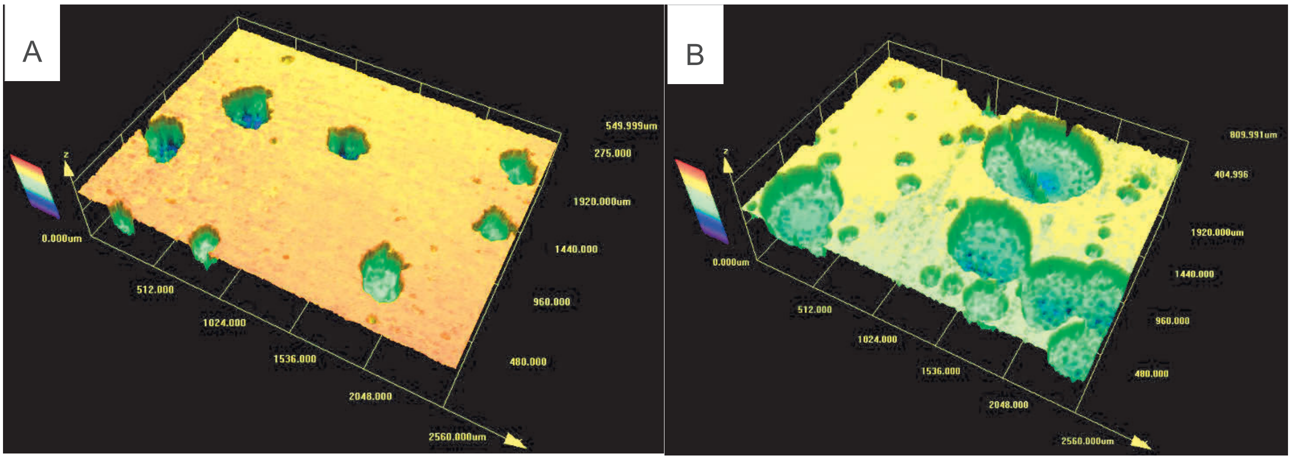

Figure 4 Pitting of X12Cr13 after potentiodynamic corrosion tests A - untreated steel, B - plasma nitrided steel (Laser confocal microscopy LEXT OLS 3000)

Pitting factor calculated for untreated stainless steel sample reached value of PF 1.21 and for plasma nitrided sample value of PF 1.87. The deepest hole of untreated and plasma nitrided samples values of 310 μm and 341 μm respectively were measured. Additionally, average width of holes for untreated samples reached value of 145 μm and 207 μm for plasma nitrided samples. The holes were observed by laser confocal microscopy LEXT OLS 3000 (see **Figure 4**).

Anodic potentiodynamic polarization tests were carried out on untreated and plasma nitrided samples of X12Cr13 martensitic stainless steel. The Biologic SP 150 potentiostat as main measuring device with software EC-Lab V11.10. used for calculating values of corrosion characteristics. The Cyclic Potentiodynamic Polarization method (ASTM-61) was chosen as method for measuring chosen corrosion characteristics. Parameters of this method were following: sweep speed dE/dt = 0.166 mV/s, Ei = -0.25 V, EL = 2 V, Ip = 25 mA, E range (-2 V;2 V) at ambient temperature. Measured surface of steel samples was 0.865 cm^2. Samples were exposed to neutral deaerated 2.5% NaCl solution. Anodic potentiodynamic measurement involves polarizing the working electrode (sample) from its equilibrium potential Eoc (OCP - open circuit potential), by steadily shifting DC potential difference between the working electrode and the counter electrode (Supersaturated Calomel Electrode) by the potentiostat, while recording the current response (see **Figure 5**.). The Tafels constants β_a and β_c and calculations represent average values of three measurements are summarized in **Table 2**.

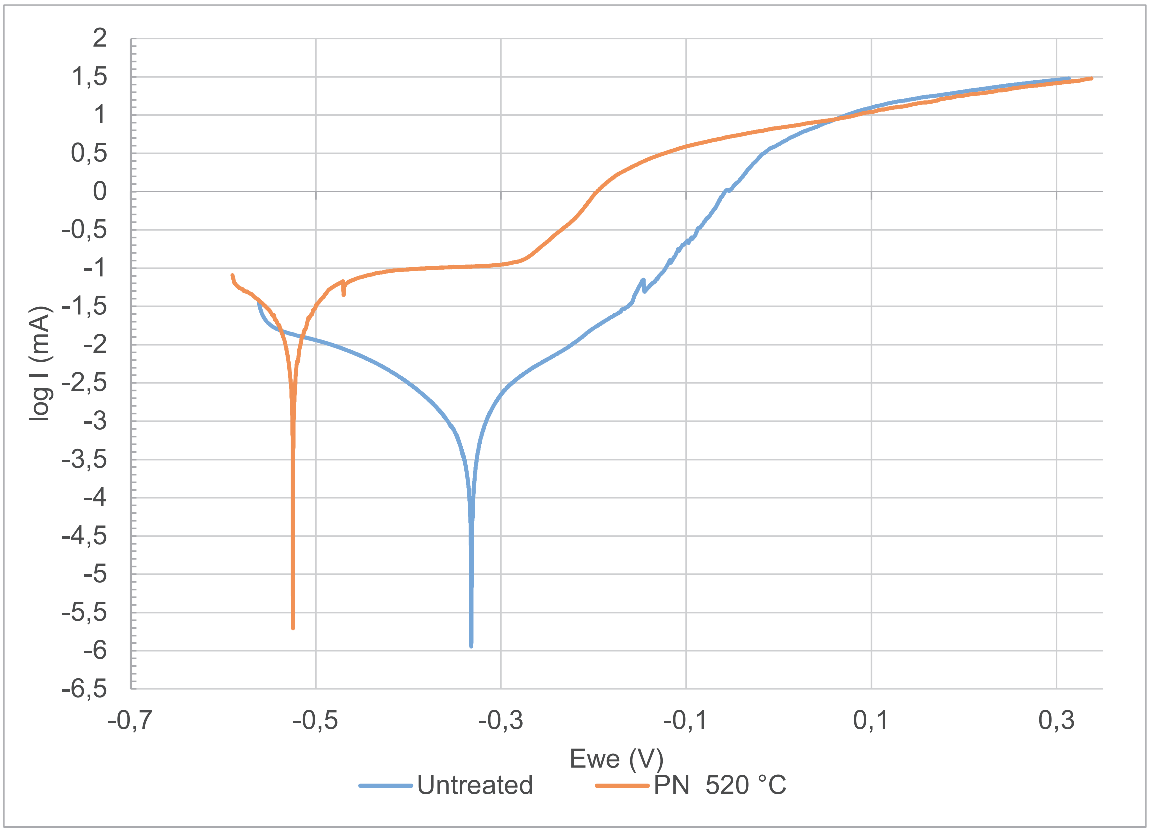

Figure 5 Potentiodynamic curves of X12Cr13 stainless steel in deaerated 2.5% NaCl solution. (orange line) Plasma nitrided at 520°C, (blue line) untreated steel

Table 2 Results of potentiodynamic polarization tests on X12Cr13 steel

	Ecorr (mV)	**Icorr (μA)**	**βc**	**βa**	**vcorr (mm·a^{-1})**
Untreated	-312.969	1.61	220.6	111.5	0.0204
Plasma nitrided	-589.111	64.71	119.3	11166.3	0.8232

The phase analysis was performed by XRD Rigaku Miniflex 600 device (Rigaku D/teX Ultra 250, Cu Kα radiation), using PDXL software with PDF-2 and Crystallographic Open Database for the quantitative analysis. Results of phase analysis can be observed at **Figure 6**. There can be seen visible peaks of iron nitrideds ε-Fe_{2-3}(N,C) and γ-Fe_4N and chromium nitrides CrN in the case of plasma nitrided sample. Only peak of base material α'-Fe can be seen in untreated sample.

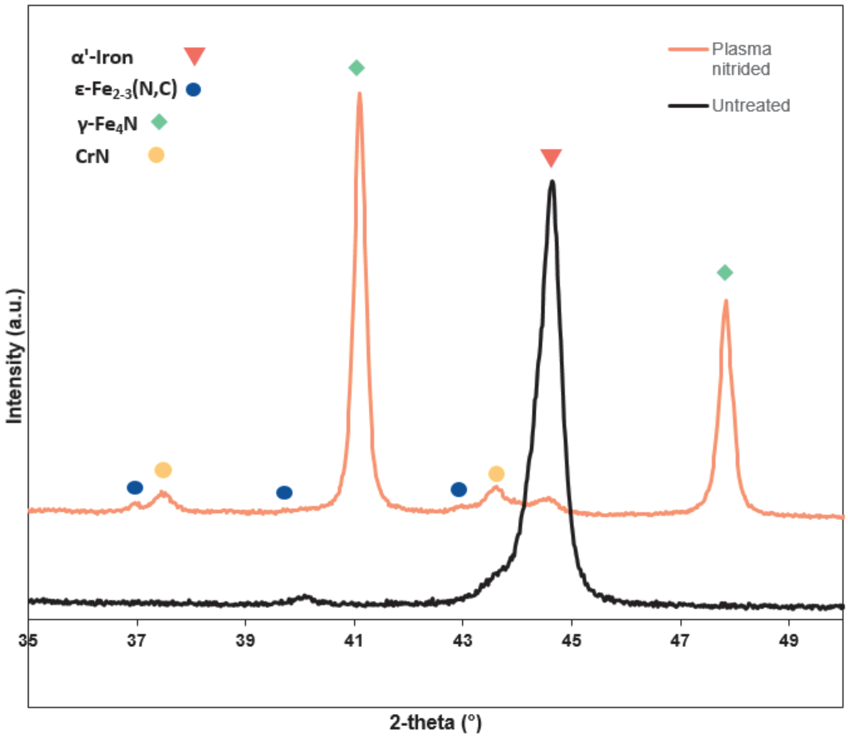

Figure 6 Phase Analysis of untreated and plasma nitrided X12Cr13 stainless steel

3. CONCLUSION

This paper describes corrosion resistance of plasma nitrided X12Cr13 (AISI 410) martensitic stainless steel evaluated using the anodic potentiodynamic tests in deaerated 2.5 % NaCl solution compared to untreated steel sample.

The high-temperature plasma nitriding increased surface hardness from 241 ± 5 HV to 982 ± 11 HV and created case layer of 0.381 mm.

The corrosion resistance of untreated X12Cr13 steel with value of corrosion rate 0.0204 $mm \cdot a^{-1}$ was approximately 40 times lower than corrosion resistance of plasma nitrided X12Cr13 steel with value of corrosion rate 0.8232 $mm \cdot a^{-1}$.

According to calculated pitting factor (PF) can be concluded, the pitting for plasma nitrided steel was increased (PF = 1.87) compared to untreated steel (PF = 1.21), and even average width of pits for plasma nitrided steel (207 μm) has increased compared to untreated one (145 μm).

The presence of chromium nitrides CrN in plasma nitrided X12Cr13 stainless steel indicate reduced chromium content in the solid solution because of precipitation of CrN. That can be reason for lower corrosion resistance after plasma nitridation AISI 410 steel.

Summary, plasma nitridation of martensitic stainless steel at temperature of 520 °C rapidly deteriorated the corrosion resistance in every aspect compared to untreated one. But, the surface hardness of plasma nitrided X12Cr13 stainless steel was greatly increased.

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