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Plasma Nitriding and Its Effect on the Corrosion Resistance of Stainless Steel 1.4006

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Abstract: The plasma nitriding (PN) technology was applied on the martensitic stainless steel 1.4006. The influence of PN on the corrosion resistance of selected material was investigated. The chemical composition of selected steel was verified using the Q4 TASMAN device. The PN process was performed using two stage nitriding procedure. After plasma cleaning procedure at 515 °C for 45 min in a nitriding atmosphere ratio 20H2:2N2 (l/h) was the first stage nitriding procedure performed at 520°C for 16 hours in a nitriding atmosphere ratio 25H2:5N2 (l/h) and followed by the second stage of nitriding procedure performed at 525°C for 4 hours in a nitriding atmosphere ratio 28H2:4N2 (l/h). The microstructure and mechanical properties of the nitride layers were studied using OES spectrometry, optical microscopy, and hardness testing. The depths of plasma nitride layers were also estimated using a cross-sectional microhardness profiles measurement. The corrosion resistance testing of PN stainless steel 1.4006 samples were carried out in a 5 % neutral sodium chloride solution (NSS) in accordance with ISO 9227 standard in the VLM GmbH SAL 400-FL corrosion chamber and visually evaluated. Microhardness and surface hardness of experimental samples were significantly increased, but the corrosion resistance remarkably decreased.

Keywords: Plasma nitriding, Stainless steel, Nitride layer, Corrosion resistance

1. Introduction

Stainless steel belongs to an extremely versatile family of engineering materials, which are used primarily for their corrosion and heat resistance. All stainless steels contain principally iron and a minimum of 10.5 wt.% Cr. At this content level, chromium reacts with oxygen and humidity presented in the environment to form a protective, adherent and coherent, this very thin oxide film (known as the passive or boundary layer), of about 2-3 nanometres, which covers the entire surface of the material. The passive layer exhibits a truly remarkable property: when is damaged (e.g. abraded), it is able to self-repair as chromium in the steel reacts rapidly with oxygen and humidity presented in the environment to reform the oxide layer [1, 2].

PN of high alloyed steels is carried out primarily to increase the surface hardness, which is very high, typically higher than 65 HRC. The difference in the measurement of hardness and microhardness is determined by the degree of load used. Nitride layers of stainless steels are characterized by small depth and very steep hardness profile from the surface to the core of material. This statement is also confirmed by the authors' publications [3, 4]. Therefore, these steels are not resistant to higher loads, but they are characterized by increased wear resistance. For Cr and Cr-Mo steels with chromium content up to 14 wt% maximal depth of nitride layer can be the achieved up to 0.3 mm and for high alloyed Cr-Ni austenitic steels up to 0.15 mm. The disadvantage of PN steel is generally decreased corrosion resistance, because of redistribution of

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chromium and chromium nitrides formation [5]. The surface is deprived of chromium, thanks to a reduction of chromium content in the vicinity the grains boundaries in a diffusion layer formerly evenly distributed in the grains. This reduces its resistance to intergranular and local types of corrosion (pitting) [6, 7]. PN stainless steel is therefore not appropriate for the usage in aggressive environments or for components stressed by high surface tension [8, 9].

The paper describes problematic of the PN stainless steel 1.4006 in terms of its chemical composition, physical and mechanical properties. Furthermore, the paper tries to find out the ideal process of chemical heat treatment to prolong the life of a selected component manufactured of the a forehand-mentioned PN stainless steel.

2. Experimental

For the experimental purposes, a wheel with blades was designed as depicted in Fig. 1. The diameter of the wheel was 230 mm with 18 blades. The material of the wheel is the martensitic X12Cr13 stainless steel. This stainless steel grade is used for steam valves, pump shafts, bolts and miscellaneous parts production, requiring corrosion resistance and moderate strength up to 500°C.

Figure 1: Experimental 1.4006 stainless steel wheel with blades

Table. 1: Chemical composition of 1.4006 steel: EN 10088-2-2005 (in wt. %)

C	Si	Mn	Ni	Cr	Mo	P	S
Q4 TASMAN – measured							
0,127	0,428	0,594	0,476	13,30	0,069	0,016	0,0026
1,4006: EN 10088-2-2005							
0,08 -0,15	max 1	max 1,5	max 0,75	11,5 -13,5	0,15– 0,25	max 0,035	max 0,035

Table. 2: PN parameters

Nitriding process	Temperature [°C]	Nitriding duration [h]	Gas flow H2/N2 $[l.min^{-1}]$	Voltage [V]	Pressure [Pa]
Plasma cleaning	515	3/4h	20/2	800	80
1. stage of PN	520	16h	25/5	530	270
2. stage of PN	525	4h	28/2	540	250

The experimental wheel was split into the individual blades. The individual blades were marked, while by the 6 of them the PN technology was applied.

The chemical composition of selected steel was verified by Q4 TASMAN device, which is an advanced CCD based optical emission spectrometer designed for chemical analysis of metallic materials. The results of the chemical composition measurements are displayed in Table 1 [11, 12].

The parameters of the PN process, performed in a RÜBIG PN 70/120 device, were designed according to the applied component and selected martensitic stainless steel. The process parameters are listed in Table 2.

After the PN process, the obtained plasma nitride layer was documented and evaluated using an optical microscope Olympus GX51 (see Fig. 2 and Fig. 3), whereby the observation was carried out using a magnification of 50x and 500x.

Hardness was measured using the Vickers microhardness method before corrosion tests, consisting of 5 measurements, where the average value was calculated. Since the nitriding layer has a significantly higher hardness than the base material, this method could also be used to measure the thickness of the nitriding layer. In this respect, the surface hardness of the non-plasma nitrided sample was 236 HV 1 and the surface hardness of the PN sample increased to 1170 HV1 [13, 14].

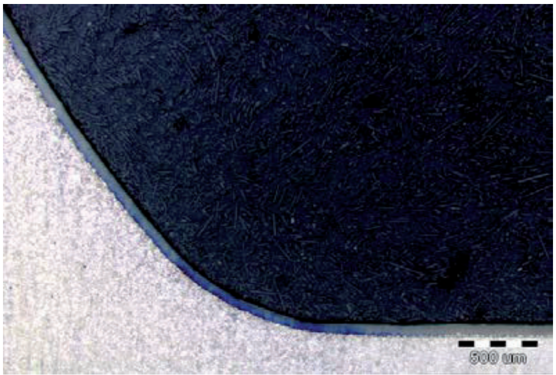

Figure 2: Overall cross section of the nitriding layer on 1.4006 steel

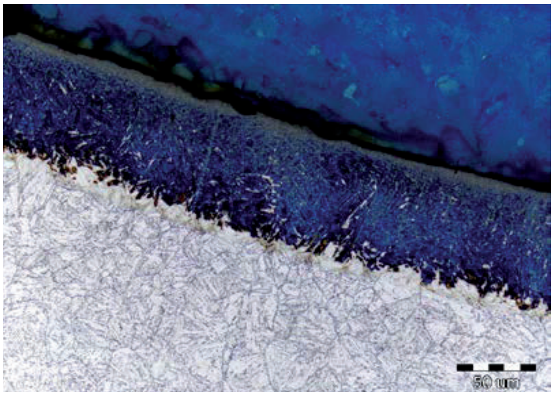

Figure 3: Nitriding layer thickness of 1.4006 steel

The salt spray test, which is a standardized and a popular corrosion test method, was used to evaluate the corrosion resistance of selected experimental samples. The test was carried out according to DIN EN ISO 9227 standard in a SAL 400-FL corrosion cabinet [15].

Figure 4: Samples in the corrosion cabinet

The SAL 400-FL corrosion test cabinet is designed for carrying out Salt Spray tests according to the DIN EN ISO 9227 (NSS, ESS, CASS) and ASTM B 117-73 standards. It is also possible to conduct the condensation test according to ISO 6270-2 (CH) by operating the cabinet manually [16, 17].

The samples were thoroughly cleaned prior to the insertion into the chamber by technical petrol and an ultrasonic cleaning device. After degreasing, the samples were placed into the corrosion chamber, where the effect of corrosion environment was simulated. The test was carried out at 35 ± 2 °C in a 5% sodium chloride solution. Sodium chloride was consistent to the ISO 9227 standard. The amount of vapour condensation was set for 1-2 $ml.h^{-1}$ at the surface of 80 cm^2 and pH 6.5 to 7.2. The samples were placed by an angle of 20 ± 5 ° from the vertical to the plastic supports (Fig 4). The evaluation periods were set according to the ISO 9227 standard recommendations. For a uniform distribution of the observation period, the tested samples were evaluated after 2, 4, 8, 24, 48 and 72 hours. In this experiment the total number of samples was 12. After each tested time, the samples were removed from the corrosion chamber, dried in a vacuum dryer for 20 min at 45 °C and subsequently photographically documented [16, 17].

3. Results and Discussion

The assumption that the PN process decreases the corrosion resistance of selected material, was confirmed experimentally in case of the martensitic 1.4006 stainless steel. The surface hardness after PN increased from 258 to 1180 HV0.05 as it can be seen from the microhardness profile displayed in Fig. 5. Microhardness and nitride layers' depths were measured in accordance with the DIN 50190 standard. The microhardness progress, plotted in Fig. 5, represents microhardness through the diffusion layer. It can be noted that all measurements were performed under the same conditions. Wherein microhardness was measured for all investigated samples. Measurements of microhardness have shown that the PN process had a significant influence on the hardness increase of the selected steel [18,19], i.e. is obvious that the application of PN increases the microhardness and hardness of the selected steel. While analysing the obtained results, it was found that the nitride layer depth was 0.148 mm.

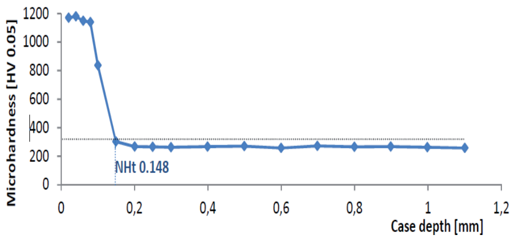

Figure 5: Microhardness depth profile

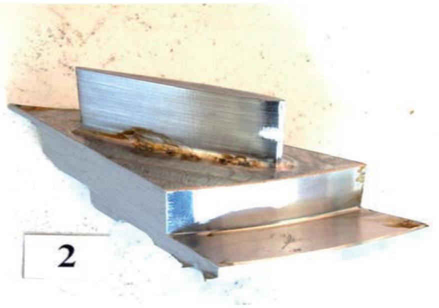

Figure 6: Sample without PN after 2h in NSS

Figure 7: PN sample after 2h in NSS

The reduced corrosion resistance after PN process of the selected material compared to the initial situation (Fig. 6) was evident after just 2h in the corrosion cabinet, (Fig. 7).

The non-nitrided and PN samples after 8 hours of corrosion test can be seen in Fig. 8 and 9 and samples of final period of corrosion tests, i.e. after 72 hours, are presented in Fig. 10 and 11, respectively.

After corrosion tests, the surface topography was documented and evaluated using the opto-digital microscope Olympus DSX500 and laser confocal microscopy Olympus OLS 3000, see Fig. 12, 13 and 14. In the given figures it is possible to observe pitting corrosion with a significantly broken nitriding layer. It is also clearly visible that the depth of corrosion during PN of the sample after 72 hours reached approximately a depth of 104 µm.

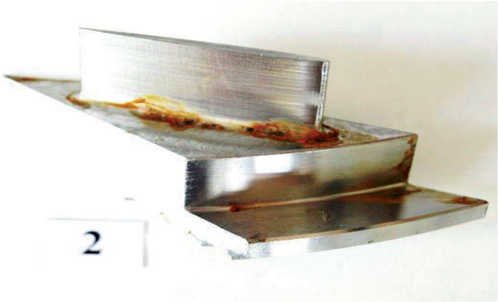

Figure 8: Sample without PN after 8h in NSS

Figure 9: Sample after 8h in NSS

Figure 10: Sample without PN after 72h in NSS

Figure 11: PN sample after 72h in NSS

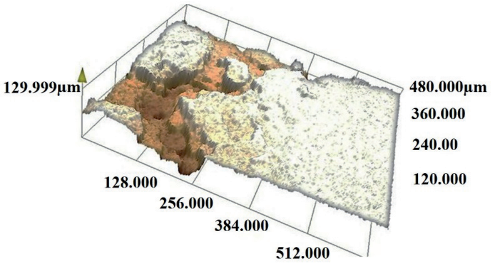

Figure 12: Corroded surface topography after corrosion tests (Olympus OLS 3000)

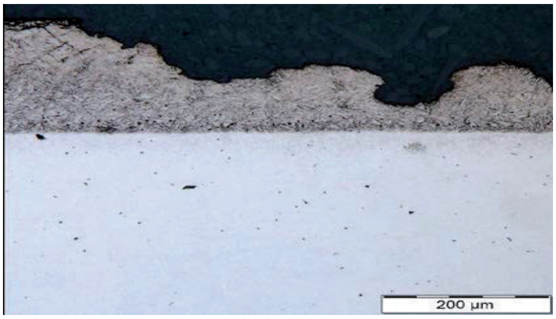

Figure 13: Corroded nitride layer

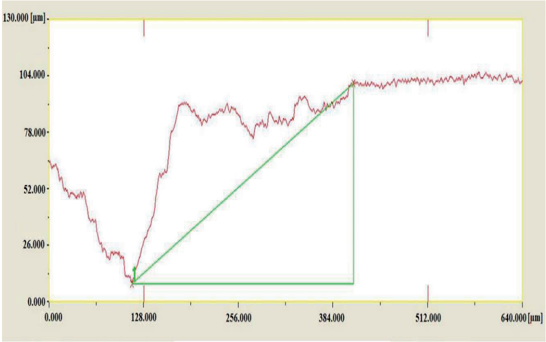

Figure 14: Corrosion depth profile

4. Conclusions

The experiment showed that the PN of martensitic X12Cr13 stainless steel formed a layer which comprises of a white (compound) layer and the diffusion layer. After PN, the surface hardness and microhardness of steels was improved. The experimental results showed that PN of the martensitic 1.4006 stainless steel increases the microhardness and surface hardness but significantly decreases the corrosion resistance in neutral sodium chloride solution (NSS). Pitting corrosion was observed at the nitrided surface, which penetrates surface layers (compound layer and diffusion layer). The depth of corroded surface reached up to 104 μm. Reasons for corrosion attack are a possible formation of chromium nitride, depletion of chromium from solid solution and defects in the compound layer.

Acknowledgments

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