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Direct Current and Pulsed Direct Current Plasma Nitriding of Ferrous Materials – a Critical Review

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DIRECT CURRENT AND PULSED DIRECT CURRENT PLASMA NITRIDING OF FERROUS MATERIALS
A CRITICAL REVIEW

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Abstract: Nowadays, the improvement of ferrous materials performance is a problem of high interest. One of well-known wear- and corrosion properties improving technique is plasma nitriding, in which elemental nitrogen is introduced to the surface of a metal part for subsequent diffusion into the material. As a result, a compound, "white" layer and a diffusion zone are formed at the detail's surface. Most of the authors positively describe the effects of surface ion nitiding. On the other hand, there are also reports on adverse effects of direct current and pulsed direct current plasma nitriding on ferrous materials performance. Therefore, an attempt to provide comprehensive summary on direct current and pulsed direct current ion nitriding and its influence on ferrous materials' mechanical and corrosion properties has been made. According to the results, some of the technique drawbacks are hard to avoid in mass production.

Key words: Plasma Nitriding, Ion Nitriding, Direct Current Plasma Nitriding, Pulsed Direct Current Plasma Nitriding, Edge Effect

1. INTRODUCTION

Used in industry for more than 30 years (Soltani Asadi and Mahboubi, 2012), plasma nitriding (PN), called also ion nitriding or plasma ion nitriding (Szilágyiné Biró, 2013), has become an acceptable alternative to conventional gas nitriding because it is a non-pollutant, energy-saving and easy time- and temperature control process (Olzon-Dionysio et al., 2010; Brühl et al. 2010; Szilágyiné Biró, 2013). Currently it is used in a great number of industry branches, e.g. in automotive in engine components (Sirin and Kaluc, 2012), in order to maximize performance and service life of various ferrous materials, e.g. ferritic and austenitic steels, bearing steels, martensitic steels, as well as non-ferrous metals, such as titanium (Musil et al., 2000).

Nowadays, the plasma nitriding process is carried out by variety of methods. The most popular one is the DC (direct current) plasma nitriding, referred also to cathodic nitriding or conventional plasma nitriding (Musil et al., 2010; Li et al., 2014), which is extensively used in commercial ion nitriding reactors (Baldwin et al., 1998).

2. GENERAL INFORMATION

According to Li et al. (2010), in the DC nitriding process the components to be treated act as a cathode, whereas the grounded walls of the furnace form the anode. The treated material is directly involved in the discharge process. Typically, the applied voltage between the anode and the cathode is from 400 to 700 V. The positive ions produced by glow discharge are accelerated near the cathode surface and bombard the surface of the treated specimen. Due to ion bombardment the active nitrogen is sputtered, the workpiece is heated and its surface is cleaned (Brühl et al., 2010; Sirin and Kaluc, 2012). As a result, the "white" layer and the diffusion layer with altered mechanical properties are

formed. The "white" layer term originates from the white color on the microscopy of the compound layer after Nital etch application.

In particular, low-temperature plasma nitriding (<420°C) of austenitic stainless steels such as AISI 304 or 316L results in formation of a metastable austenite phase supersaturated with nitrogen atoms (nitrogen concentration is 20-30 at%) (Madjarov and Russeva, 2007; Li et al., 2008; Wang et al., 2009). This phase is usually called expanded austenite, S-phase or γ_N (Toshkov et al., 2007; Li et al., 2008; Wang et al., 2009) and exhibits significant improvement in substrate hardness while the wear resistance is enhanced by several orders of magnitude (Menthe et al., 2000). What is more, some authors attribute γ_N excellent anticorrosive properties (Fossati et al., 2006b). In temperatures exceeding 420°C, due to sufficient diffusivity of chromium in the austenite the precipitation of Cr_xN starts (Tab. 1, 2), resulting in depletion of Cr from austenitic matrix and, usually, decrease in corrosion resistance (Wang et al., 2009). Unfortunately, the rate of plasma nitriding processes and nitrogen diffusion in temperatures below 450°C is low and leads to a very long duration of the nitriding process for getting appropriate layer thickness (Wang et al., 2013). As a result, the process becomes ineffective and too expensive to apply in mass production. According to the literature (Tab. 1), in order to obtain a 5 μm nitride layer at least a 2 h lasting process must be applied (Li et al., 2008).

In martensitic stainless steels, the usually ca. 25 μm thick (Podgornik et al., 1998) outer, compound layer consists mainly of γ'-Fe_4N or ε-$Fe_{2,3}N$ intermetallic phases – iron nitrides (Sirin and Kaluc, 2012; Mashreghi et al., 2013). Study by Weber et al. (Weber et al., 1995) revealed that the corrosion rate of iron in an acidic solution can be reduced by one order of magnitude when the ε-$Fe_{2,6}N$ phases are formed, and reduced by three orders of magnitude by the formation of γ'-Fe_4N. Composition and thickness of the "white" layer highly depends on the used in the nitriding process gas composition, treatment time and temperature

(Tab. 1, 2), as well as the carbon content (Sirin and Kaluc, 2012). In general, the more homogenous and monolithic is the outer phase, the better. When nitriding martensitic steels, the homogenous monolayer can be obtained with elongation of treatment time (>15 h for AISI 4140) (Corengia et al., 2005). Nevertheless, temperature of 500°C must be applied. According to Corengia et al.

(2004a), the single-phase γ'-Fe$_4$N layers exhibit better tribological properties than two-phase compound layers. In supermartensitic stainless steels, beside the γ'-Fe$_4$N and ε-Fe$_{2,3}$N intermetallic phases, α$_N$, the "nitrogen expanded martensite" phase is also distinguished (Kurelo et al., 2015).

Tab. 1. Data on the direct current (DCPN) plasma nitriding collected from the literature; CD – case depth

Material	Parameters	Temp. (°C)	Time (h)	Nitride layer characteristics	Hardness	Ref.
AISI 1020	350 Pa N$_2$:H$_2$ 4:1	400-480	3	γ'-Fe$_4$N + ε-Fe$_{2,3}$N 2.5-5 μm CD: 30.3-58.5 μm	350-500 HV$_{0.05}$	(de Sousa et al., 2014)
AISI 304	2.67 Pa N$_2$:H$_2$ 1:4	500	8	γ$_N$ 4 μm	600 VHN$_{25gf}$	(Balusamy et al., 2013)
AISI 304	100 Pa N$_2$:H$_2$ 1:3	400	8	γ$_N$ CD: 51.7 μm	-	(Wang et al., 2013)
AISI 304	666-1332 Pa N$_2$:H$_2$ 19:1	450-570	4	γ'-Fe$_4$N + ε-Fe$_{2,3}$N + CrN	-	(Borges et al., 2000)
AISI 304	100 Pa NH$_3$	420	2-44	γ$_N$ 3-27 μm	600-1200 HV$_{0.05}$	(Wang et al., 2006)
AISI 304	N$_2$	420	6	γ$_N$ CD: 12 μm	15.4 GPa	(Raman and Jayaprakash, 2007)
AISI 304	500 Pa NH$_3$	400-500	2	γ$_N$ 2-13 μm	440-1300 HV$_{0.1}$	(Liang et al., 2001)
AISI 304L	200-600 Pa N$_2$:H$_2$ 1:4	350-480	4-8	γ$_N$ + CrN + α$_N$	630-1200 HV$_{0.1}$	(Wang et al., 2009)
AISI 316	500 Pa N$_2$:H$_2$ 1:3	450-550	5	γ$_N$ + CrN 15-60 μm	1100-1500 HV$_{0.05}$	(Sun and Bell, 1998)
AISI 316	667 Pa N$_2$:H$_2$ 1:3	450	5	γ$_N$ + γ'-Fe$_4$N 6 μm	-	(Karimzadeh et al., 2013)
AISI 316L	500 Pa NH$_3$	520-560	1/12-2	γ$_N$ + CrN + γ'-Fe$_4$N 1.5-12 μm	400-1200 HV$_{0.05}$	(Li et al., 2014)
AISI 316	500 Pa N$_2$:H$_2$ 1:3	300-450	20	γ$_N$ 2-20 μm	1400-1600 HV$_{0.05}$	(Bell, 2002)
AISI 316L	530 Pa N$_2$:H$_2$ 1:4	400	4	γ$_N$ + ε-Fe$_{2+x}$N + γ'-Fe$_4$N 1.5-2.3 μm	183 HV$_{0.01}$	(Olzon-Dionysio et al., 2010)
AISI 316L	600 Pa N$_2$:H$_2$ 1:4	350-480	2	γ$_N$ + CrN 5 μm	740-1100 HV$_{0.1}$	(Li et al., 2008)
AISI 316L	250 Pa N$_2$:H$_2$ 1:1	440	6	γ$_N$ + CrN 3.5 μm	1200 HV$_{0.05}$	(Skolek-Stefaniszyn et al., 2010)
AISI 316L	N$_2$:H$_2$ 1:1	440	6	γ$_N$ 20 μm	1240 HV$_{0.05}$	(Borowski et al., 2010)
AISI 316L	1000 Pa N$_2$:H$_2$ 4:1	430	1-5	γ$_N$ 3-10 μm	300-1400 HK$_{0.1}$	(Fossati et al., 2006b)
AISI 316L	150-2000 Pa	430	5	γ$_N$ + γ'-Fe$_4$N + CrN 9-15 μm	1380-1430 HK$_{0.01}$	(Borgioli et al., 2006)
AISI 316L	1000 Pa N$_2$:H$_2$ 4:1	400-500	5	γ$_N$ + γ'-Fe$_4$N + CrN 4-47 μm	373-1605 HK$_{0.1}$	(Fossati et al., 2006a)
AISI 316L	1000 Pa N$_2$:H$_2$ 4:1	400-500	5	γ$_N$ + γ'-Fe$_4$N + CrN 4-47 μm	800-1580 HK$_{0.01}$	(Borgioli et al., 2005)
AISI 316L	400 Pa N$_2$:H$_2$ 1:3	425	12	γ$_N$ 10 μm	1240 HV$_{0.01}$	(Dong et al., 2006)
AISI 316L	600 Pa N$_2$:H$_2$ 1:4	400	2-7	γ$_N$ + γ'-Fe$_4$N + ε-Fe$_{2,3}$N + CrN +Cr$_2$N 8 μm	-	(Olzon-Dionysio et al., 2008)
AISI 316L	600 Pa N$_2$:H$_2$ 1:4	400	2-7	γ$_N$ + γ'-Fe$_4$N + CrN 6 μm	-	(de Souza et al., 2010)
AISI 410	500 Pa N$_2$:H$_2$ 1:3	240-500	20	γ'-Fe$_4$N + ε-Fe$_{2,3}$N + CrN + α$_N$ 47-135 μm CD: 77-186 μm	1000-1200 HK$_{0.1}$	(Li and Bell, 2006)
AISI 420	650 Pa N$_2$:H$_2$ 1:3	300	20	γ'-Fe$_4$N + ε-Fe$_{2,3}$N + CrN	-	(Tuckart et al., 2007)
AISI 420	300-400 Pa N$_2$:H$_2$ 1:4	530	20	γ'-Fe$_4$N + ε-Fe$_3$N + CrN CD: 61 μm	1300 HV$_{0.1}$	(Alphonsa et al., 2002)
AISI 4340	NH$_3$	500-540	2-16	γ'-Fe$_4$N + ε-Fe$_3$N 2.6-8.8 μm CD: 280-510 μm	500-640 HV$_{0.2}$	(Sirin et al., 2008; Sirin and Kaluc, 2012)
AISI CA6NM	400 Pa N$_2$:H$_2$ 1:4	500	1-5	γ'-Fe$_4$N + ε-Fe$_{2,3}$N + CrN 2-6 μm	1245-1309 HV$_{0.05}$	(Winck et al., 2013)
AISI H12	600 Pa N$_2$:H$_2$ 1:4	500	1-6	γ'-Fe$_4$N + ε-Fe$_{2,3}$N + α''-Fe$_{16}$N$_2$ CD: 38-85 μm	1240 HV$_{70gf}$	(Miola et al., 1999)
AISI HNV3	N$_2$:H$_2$	450-650	3-6	-	5.39-13.14 GPa	(Sobiecki et al., 2004)
HP13Cr	300 Pa N$_2$:H$_2$ 1:4	350-450	6	γ'-Fe$_4$N + ε-Fe$_{2+x}$N + CrN + α$_N$ CD: 16-61 μm	12-14 GPa	(Kurelo et al., 2015)
UNS S31254	500 Pa N$_2$:H$_2$ 1:4	400-500	5	γ$_N$ + CrN + Cr$_2$N 10 μm	980-1380 HV$_{0.025}$	(Fernandes et al., 2010)

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Tab. 2. Data on pulsed direct current plasma nitriding collected from the literature; CD – case depth

Material	Parameters	Temp. (°C)	Time (h)	Nitride layer characteristics	Hardness	Ref.
AISI 2205	300 Pa $N_2:H_2:Ar$ 4-8:1-3:1-3	250-500	8-60	γ_N + γ'-Fe_4N + CrN 1.7 µm	-	(Larisch et al., 1999)
AISI 2205	250 Pa $N_2:H_2$ 2:1	400	20	γ'-Fe_4N + ε-Fe_3N + CrN 12 µm	1420-1960 $HV_{0.01}$	(Kliauga and Pohl, 1998)
AISI 304	300 Pa NH_3	350-540	4	γ_N + γ'-Fe_4N + CrN 2-12 µm	3-14.7 GPa	(Liang, 2003)
AISI 304	400 Pa $N_2:H_2$ 1:4	560	24	γ'-Fe_4N + ε-Fe_3N + CrN CD: 40-90 µm	900-1100 $HV_{0.1}$	(Singh et al., 2006)
AISI 304	400 Pa $N_2:H_2$ 4:1	560	24	γ'-Fe_4N + ε-Fe_3N + CrN CD: 50-110 µm	1000-1300 $HV_{0.1}$	(Singh et al., 2006)
AISI 304	250 Pa $N_2:H_2$ 1:2	-	-	γ_N + CrN CD: 22 µm		(Michler, 2008)
AISI 304L	600 Pa $N_2:H_2$ 1:4	450	1/2-16	γ_N + CrN	1500-1600 $HK_{0.01}$	(Menthe and Rie, 1999)
AISI 316L	250 Pa $N_2:H_2$ 1:3	400-550	12	γ_N + γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN + Cr_2N	1450-1500 $HV_{0.025}$	(Mingolo et al., 2006)
AISI 316L	250 Pa $N_2:H_2$ 3:1	400-550	12	γ_N + γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN + Cr_2N	1400-1500 $HV_{0.025}$	(Mingolo et al., 2006)
AISI 316L	173 Pa $N_2:H_2$ 1:1	400	-	γ_N 3.4-4.8 µm	1245 $HV_{0.025}$	(Díaz-Guillén et al., 2015)
AISI 316L	533 Pa $N_2:H_2$ 4:1	400-500	5	γ_N + γ'-Fe_4N + CrN 5-70 µm	1115-1315 $HV_{0.1}$	(Jeong and Kim, 2001)
AISI 321	300 Pa $N_2:H_2:Ar$ 4-8:1-3:1-3	250-500	8-60	γ_N + γ'-Fe_4N + CrN 2.5 µm	3305-8292 $HV_{0.0001}$	(Larisch et al., 1999)
AISI 410	600 Pa $N_2:H_2$ 1:3	350-500	20-28	γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN + α_N CD: 30 µm	1150-1400 $HV_{0.025}$	(Corengia et al., 2004b)
AISI 420	600 Pa $N_2:H_2$ 1:3	350-550	15	ε-Fe_3N + γ'-Fe_4N + α_N CD: 90-130 µm	1000-1200 $HK_{0.025}$	(Xi et al., 2008a; Xi et al., 2008b)
AISI 420	250 Pa $N_2:H_2$ 3:1	480-560	4	γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN CD: 80 µm	1525 $HV_{0.025}$	(Pinedo and Monteiro, 2004)
AISI 430	300 Pa $N_2:H_2:Ar$ 4-8:1-3:1-3	250-500	8-60	γ_N + γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN 14.6 µm	-	(Larisch et al., 1999)
AISI 4140	500 Pa $N_2:H_2$ 17:3	570-620	5	γ'-Fe_4N + ε-$Fe_{2,3}N$ CD: 42 µm	-	(Fattah and Mahboubi, 2010)
AISI 4140	600 Pa $N_2:H_2$ 1:3	500	2-28	γ'-Fe_4N + ε-$Fe_{2,3}N$ 3-7.5 µm CD: 220-600 µm	650-850 $HV_{0.1}$	(Corengia et al., 2005)
AISI 4340	173 Pa $N_2:H_2$ 1:1	540	4	γ'-Fe_4N 7.5-14.5 µm CD: <350 µm	700-825 $HV_{0.05}$	(Díaz-Guillén et al., 2009)
AISI 52100	500 Pa $N_2:H_2$ 7:13	450-560	1-5	ε-$Fe_{2,3}N$ + γ'-Fe_4N	-	(Basu et al., 2008)
AISI CA6NM	532 Pa $N_2:H_2$ 1:4	500	2	γ'-Fe_4N + ε-$Fe_{2,3}N$ + CrN CD: 25 µm	1240 $HV_{0.5}$	(Allenstein et al., 2013)
AISI H12	600 Pa $N_2:H_2$ 1:4	500	1-6	γ'-Fe_4N + ε-$Fe_{2,3}N$ + α''-$Fe_{16}N_2$	-	(Miola et al., 1999)
AISI L2	666 Pa $N_2:H_2$ 3:7	450-550	6-9	γ'-Fe_4N + ε-Fe_3N CD: 110-330 µm	480-510 $HV_{0.02}$	(Soleimani et al., 2012)
AISI M2	400 Pa $N_2:H_2$ 4:1	50-570	5	4-6 µm	-	(Jeong and Kim, 2001)
AISI P21	600 Pa $N_2:H_2$ 1:3	475-525	10	γ'-Fe_4N + ε-$Fe_{2,3}N$ 2.8-5 µm CD: 100-200 µm	640-710 $HV_{0.05}$	(Wen, 2009)
Corrax	$N_2:H_2$ 1:4	360	10	γ_N 10-12 µm	1290 $HV_{0.05}$	(Brühl et al., 2010)
M340	$N_2:H_2$ 1:4	360	10	γ_N + CrN + $M_{23}C_6$ 9-10 µm	1100 $HV_{0.05}$	(Brühl et al., 2010)
N695	$N_2:H_2$ 1:4	360	10	γ_N + CrN + $M_{23}C_6$ 14-15 µm	1130 $HV_{0.05}$	(Brühl et al., 2010)

Because of the different unit cell parameters of the cited γ' and ε phases, the mixture of crystalline structures can generate stress at the boundaries of the grains, increasing the fragility of the layer (Sirin and Kaluc, 2012). Delayed cracking of the nitride layers on AISI 420 martensitic stainless steel has been reported by Tuckart et al. (2007). After 24 months incubation time, without any external disturbance, the cracks were formed in the nitrided specimens. According to O'Brien and Goodman (1991), the weak bonding at the interphases or different thermal expansion coefficients of the phases can be the cause of this phenomena.

In the plasma nitrided workpieces, beneath the compound layer, the diffusion layer is formed. The diffusion layer consists mainly of interstitial atoms in solid solution and fine and coherent nitride precipitates (Sirin and Kaluc, 2012; Mashreghi, 2013). The hardness and wear resistance of the diffusion layer depends on the time and temperature of the treatment, the gaseous mixture composition, the concentration of the alloying elements on the steel, the amount of precipitated nitrides and the initial microstructure of the material (Sirin and Kaluc, 2012). In order to determine the nitrogen influence depth, the effective depth case

is measured (Tab. 1, CD). It is the thickness of the hardened layer of a specimen, understood as the depth up to a further point for which a specified level of hardness is maintained. As can be seen in Tab. 1, in the case of ion nitrided materials, the layer thickness is not identical as the effective depth case.

The mechanisms of conventional DC plasma nitriding have been extensively studied and discussed by many authors, but the consensus has not been reached up to date. The dominant mechanisms for nitrogen mass transfer are claimed to be: nitrogen implantation (Xu and Zhang, 1986), low energetic $N_mH_n^+$ bombardment (Hudis, 1973), nitrogen adsorption (Tibbetts, 1974), neutral and ion adsorption (Szabo and Wilhelmi, 1984).

According to Zlatanović and Popović (2010), a significant advance in plasma surface engineering, as well as in control and stability of the processing, was provided with introduction of pulsed DC power supply in plasma deposition techniques. In pulsed DC supply, the number of parameters which determine the quality of obtained surface, process characteristics and operating procedure is greater than in conventional DC process. Properties of the surface are directly affected by the power supply pulse frequency, duty cycle and output voltage, while the process stability and control are significantly improved (Zlatanović and Popović, 2010). Pye (2003) claims that in plasma nitriding systems, the DC supply power is adjusted as required to the component geometry and chamber configuration. In conventional DC plasma nitriding technique, it is difficult to provide proper process temperature when the user has a mixed load of different part geometries and sizes. The pulsed technique enables operator adaption of the minimum power input necessary for the abnormal glow discharge (Pye, 2003).

3. INFLUENCE ON PERFORMANCE OF FERROUS MATERIALS

The influence of DC and pulsed DC plasma nitriding on ferrous materials performance has been extensively described in numerous studies. In this paper, the effect of ion nitriding on corrosion resistance, as well as on wear and fatigue, will be described.

3.1. Corrosion resistance

In recent years, many studies have been performed in order to improve corrosion resistance of austenitic stainless steels by ion nitriding and extend its industrial applications. In contrast, relatively few studies have been conducted so far on low temperature plasma nitriding of martensitic and supermartensitic stainless steels.

In general, many authors have been very positive about the influence of ion nitriding on corrosion resistance of austenitic and superaustenitic steels. In the research by Fossati et al. (2006a; b) it has been stated that the anodic current density in potentiodynamic scans becomes smaller with increase of nitriding treatment time. The authors pointed that in comparison with the untreated samples, the modified AISI 316L is less prone to pitting corrosion. According to the researchers, the repassivation capability of stainless steels is enhanced with γ_N formation due to its high nitrogen concentration. Moreover, in the study by Borgioli et al. (2006) it has been proven that the treatment pressure has a significant influence on performance of AISI 316L steel in 5% NaCl aerated

solution. If the pressure exceeds 1.5 hPa, the chromium nitride precipitates or, if the pressure is extremely high (2.5 hPa), treated samples are unable to form homogenous protective passive layer. In addition, Olzon-Dionysio et al. (2008) demonstrated that treatment time pays an important role for the corrosion resistance. According to the authors, the higher the ε/γ' ratio, the better. Similar findings were obtained by de Souza et al. (2010). Fernandes et al. (2010) reported that plasma nitriding is beneficial also for UNS S31254 superaustenitic stainless steel, regardless of the process temperature ranging from 400 to 500°C.

As mentioned before, plasma nitriding process of austenitic stainless steels is conducted in temperatures below 420°C in order to prevent the chromium nitrides precipitation. It is believed that formation of γ_N phase with enough thickness depends on the temperature (<480°C) and duration of the process (Li et al., 2014a). In study by Li et al. (Li et al., 2014a) nitriding of austenitic AISI 316L steel was carried out at high temperatures (520-560°C) for times ranging from 5 to 120 min. Although the layers obtained in the research consisted of γ_N and a small amount of CrN and iron nitrides, the pitting corrosion resistance of substrate material has been improved even after 5 minutes of treatment.

Nevertheless, there are also some critical voices on performance of ion nitrided austenitic stainless steels. In the electrochemical impedance spectroscopy study by Borowski et al. (2010) it was exhibited that impedance of DC nitrided specimen was reduced by two orders of magnitude with respect to the untreated material. What is more, the polarization curves exhibited that DC nitriding of AISI 316L resulted in increase of corrosion current and shift of corrosion potential towards less noble materials. Liang (2003) reported that nitriding of AISI 304 steel only in temperatures below 450°C resulted in improvement in corrosion resistance, especially pitting corrosion. Samples nitrided at 465°C exhibited poor corrosion resistance, having lower corrosion potential and higher corrosion current density compared to the untreated specimens. In research by Liang et al. (2001) the DC plasma nitrided AISI 304 steel was characterized by low corrosion potential and very high corrosion current density (7.15 $\mu A \times cm^{-2}$), indicating high dissolution rates. As authors suggested, low pressure plasma arc source nitriding provided better substrate material performance than DC nitriding. Reduced corrosion resistance of PN AISI 316L stainless steel has also been reported by Karimzadeh et al. (2013). Inferior corrosion resistance has been attributed to the existence of sliding bands, created as a consequence of γ_N formation. According to the authors, the mentioned sliding bands can provide active sites for corrosion processes development. Menthe et al. (1995) stated that the passive layer obtained in the nitriding process is similar to the one naturally existing on AISI 304L steel by the means of corrosion resistance. Thus, the corrosion performance is not severely affected by surface modification. The corrosion performance of AISI 316L DC nitrided steel did not significantly improve in comparison with the untreated material in the study by Skolek-Stefaniszyn et al. (2010).

In terms of enhancing corrosion resistance, DC and pulsed DC plasma nitriding seems much more efficient when applied on martensitic, supermartensitic and bearing steels. Li and Bell (2006) demonstrated that the corrosion resistance of AISI 410 steel significantly improved after direct current plasma nitriding; in potentiodynamic tests in 3,5% NaCl$_{aq}$, the passivation region occurred only for nitrided samples. What is more, the pitting potential of surface modified specimens shifted towards positive potentials. The nitrided samples exhibited also lower weight loss in immersion tests in 1% HCl solution than untreated material. The

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authors claim that superior corrosion resistance of ion nitrided AISI 410 steel was due to ε and γ' iron nitrides precipitation on the material surface. In the research by Corengia et al. (2004b) the positive influence of plasma nitriding on martensitic stainless steels has been proven. However, the authors pointed that samples nitrided for 20 h in 400 and 500°C exhibited decrease in corrosion resistance. Similar findings were obtained by Xi et al. (2008a) for DC-pulsed nitrided AISI 420 steel. The improvement in corrosion resistance was observed for samples treated in 350°C. According to the authors, the beneficial effect could be related to the solid solution of Cr and the ε and α_N phases present in the outer layer. However, corrosion resistance of specimens nitrided in 450 and 550°C has been reduced due to CrN formation and Cr depletion in the solid solution. In other study by these authors (Xi et al., 2008b), resistance to erosion and erosion-corrosion of AISI 420 steel has been examined. According to the results, in both neutral and acidic environment, the erosion-corrosion resistance of investigated steel was improved by means of 350°C nitriding, but decreased through 550°C nitriding for reasons provided earlier in the text. Basu et al. (2008) observed significant improve in corrosion properties of plasma nitrided AISI 52100 bearing steel. The authors attribute good corrosion resistance in aqueous medium to presence of ε and γ' nitrides in the modified layer. The higher temperature and longer time of nitriding process, the greater volume of nitride fraction at the surface.
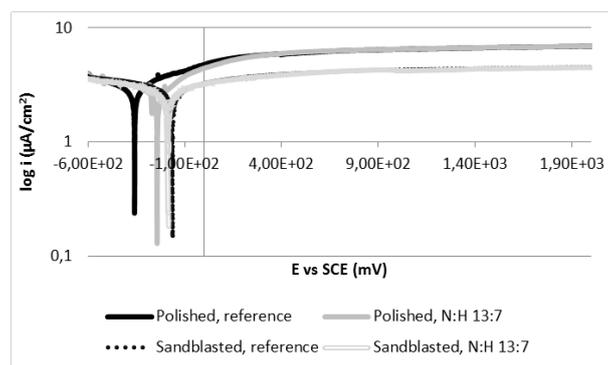

Fig. 1. Potentiodynamic curves of DC plasma nitrided (N₂:H₂ 13:7, 400°C, 200 Pa, 2 h) and reference specimens
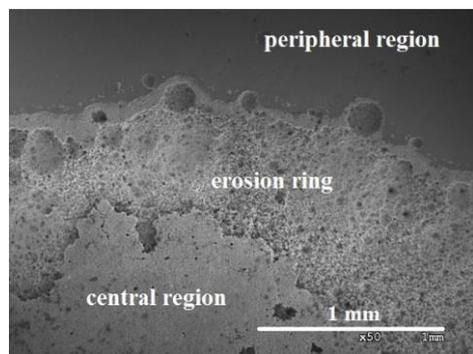

Fig. 2. Corroded surface morphology of DC plasma nitrided specimen, 35% H₂:65% N₂, SEM photograph, magnification 50×

Negative effect of ion nitriding on corrosion performance of martensitic stainless steels was observed by some authors. In research by Wierzchoń et al. (2006), AISI 420F steel nitrided in 530°C in the glow discharge assisted process exhibited slight decrease in corrosion resistance. Potentiodynamic curves of DC

nitrided AISI 410 steel presented by Sobiecki et al. (2004) unequivocally indicate reduction in corrosion resistance of material treated in temperatures exceeding 450°C.

The effect of nitriding on martensitic stainless steel corrosion resistace has also been investigated by the authors of this review. Fig. 1 presents potentiodynamic curves of sandblasted and polished DC plasma nitrided (N₂:H₂ 13:7, 400°C, 200 Pa, 2 h) AISI 440B steel. Taking into account provided results, it may seem that plasma nitriding does not significantly affect corrosion resistance of sandblasted material and slightly improves corrosion properties of polished specimens. Unfortunately, some specimens DC nitrided in slightly different conditions, e.g. nitrogen to hydrogen ratio 7:13, 400°C process temperature, 200 Pa pressure and 2 h lasting process exhibited severe damages after potentiodynamic tests (Fig. 2).

According to Baldwin et al. (1998), the conventional method of plasma nitriding is effective when nitriding low-alloy or tool steels, but is considered less successful with austenitic stainless or high alloy steels. The process is characterized by some inconvenience especially when workpieces of complex geometry are treated (Olzon-Dionysio et al., 2010). Numerous problems have been encountered arising from the direct plasma applied to the specimens. The reports show that the edge effect, arcing, hollow cathode effect, inhomogeneity of the workpiece temperature are observed (Szilágyiné Biró, 2013), as well as problems with treating parts of different dimensions within one batch (Saeed et al., 2013).
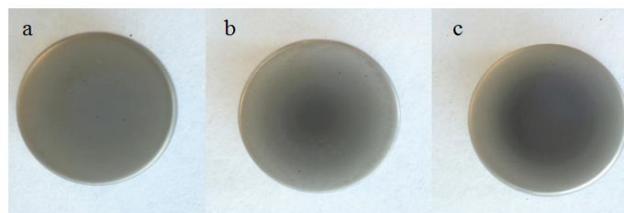

Fig. 3. Plasma nitrided specimens; a – 50% H₂:50% N₂, b – 35% H₂:65% N₂, c – 20% H₂:80% N₂; macro photographs (Łępicka i Grądzka-Dahlke, 2013)
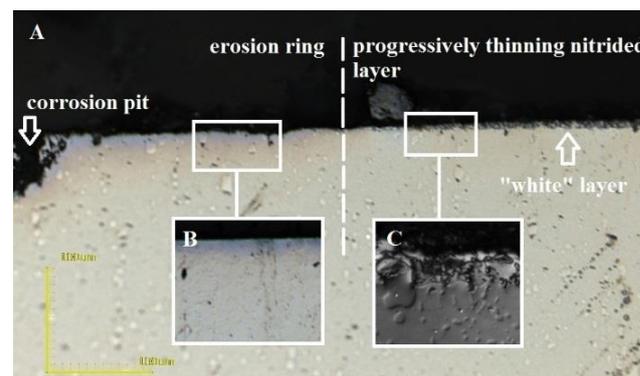

Fig. 4. Cross section of plasma nitrided (N₂:H₂ 1:1) AISI 440B sample after potentiodynamic test. Confocal microscope photograph in: A - 216×, B, C - 2160× magnification

In the edge effect, the nitrogen supersaturated solution is formed on the edges of cylindrical specimens, leading to production of a non-uniform surface with different colors in the central and peripheral regions (Olzon-Dionysio et al., 2010; Szilágyiné Biró, 2013). As mentioned before, in DC plasma nitriding samples

are submitted to a high cathodic potential and the plasma is produced on their surface. In such case, the distortions in the electric field occur around the corners and the edges of the workload and the shape of the plasma sheath, which determines ion flux distribution, create erosion rings characterized by different colors and discontinuous hardness (Alves Jr. et al., 2001; 2006). The edge effect and its influence on corrosion resistance of stainless steels has also been observed by the authors of this review. Fig. 3 presents DC plasma nitrided AISI 440B specimens in three different gaseous mixture compositions. As it can be seen, the less nitrogen, the smaller the erosion ring. According to Figs. 2 and 4, the edge effect deteriorates the corrosion resistance of AISI 440B martensitic stainless steel. The affected by the edge effect area becomes the progressively dissolved anode, whereas tightly covered with inhomogenous nitride layer peripheral and central regions act as cathodes (Fig. 4). Detailed results from our studies on influence of DC plasma nitriding on corrosion resistance of AISI 440B martensitic stainless steel can be found in our previous work (Łępicka and Grądzka-Dahlke, 2013; 2014).

The influence of the edge effect on corrosion resistance of stainless steel has also been investigated by Olzon-Dionysio et al. (2010). The AISI 316L samples affected by the edge effect showed poorer corrosion resistance than those without erosion rings. Nevertheless, all investigated specimens exhibited improvement in corrosion resistance with reference to untreated material. According to de Sousa et al. (2014), the edge effect can be eliminated by using cathodic cage ion nitriding.

3.2. Wear and fatigue

Phases obtained in the DC and pulsed DC ion nitriding processes – γ_N, γ'-Fe$_4$N and ε-Fe$_{2,3}$N – are known for their superior hardness and anti-wear properties. In research by Li et al. (2008) the effect of DC plasma nitriding on dry-sliding wear properties of AISI 316L stainless steel has been evaluated. The ring-on-block dry wear test exhibited significant reduction of wear rate in comparison with unnitrided material. It should be noted, however, that the wear rate of nitrided specimens enhanced with increase of treatment temperature, and, as a consequence, Cr nitrides volume in the modified layer. Wear of the DCPN treated AISI 316L steel was dominated by plastic deformation, slight abrasion and frictional polishing. Nevertheless, microcracking of layers with high CrN content has been observed. Similar findings were obtained by Sun and Bell in ball-on-disc tribosystem (Sun and Bell, 1998) – with increasing nitriding temperature, the wear volume of nitrided surface increased. What is more, the higher was nitriding temperature, the greater was friction coefficient. The positive influence of DC ion nitriding on wear resistance of AISI 316L steel has also been noted by Borowski et al. (2010) and Skolek-Stefaniszyn et al. (2010). Foerster et al. (2007) noticed that in dry sliding tests with WC-Co ball as a counter sample glow discharge ion nitriding reduced the friction coefficient with respect to untreated sample. According to Wang et al. (2009), the DC plasma nitriding significantly improves dry-sliding wear resistance also of AISI 304L steel. In the block-on-ring configuration friction test, the minimum value of wear rate was observed for γ_N-rich specimens. As the other authors, Wang et al. (2009) stressed that increasing concentration of Cr$_x$N in the reaction layer results in decrease in dry-sliding wear resistance. Reduction of AISI 304L wear rate after nitriding was also emphasized by Menthe et al. (2000).

A significant advance in wear rate was also observed in mar-

tensitic, duplex, tool and precipitation hardenable steels.

Xi et al. (2008a) conducted dry ball-on-disc tests on AISI 420 steel nitrided in 350 and 550°C. According to the authors, the anti-wear properties of material nitrided in lower temperature overachieve the 550°C ones. After nitriding the abrasive wear behavior occurred. In other work by the same authors (Xi et al., 2008b) the same data dependency was acknowledged regarding erosion resistance. Sobiecki et al. (2004) stated that glow-discharge assisted nitriding conducted in temperatures ranging from 450 to 650°C remarkably improved frictional wear resistance of AISI HNV3 steel. The harder the surface, the better the anti-wear properties. Similar conclusions were obtained by Kliauga and Pohl (1998) for ion nitrided AISI F51 duplex steel. In research by Wen (2009) friction- and wear tests of AISI P21 DC nitrided steel were conducted under dry conditions on a block-on-ring tribotester. A significant reduction in the wear and friction coefficient was observed. As the author noticed, greater compressive stress and higher hardness of the nitrided specimen translates into its better wear resistance. The anti-wear properties of investigated steel were related to the increase in the thickness of diffusion layer.

Fatigue strength study of AISI 4340 steel conducted by Sirin et al. (2008) demonstrated that in comparison with untreated steel the fatigue strength of nitrided material increased up to 91%. A linear relationship between the case depth and the fatigue strength was obtained. The fatigue behavior after ion nitriding was also observed for AISI L2 cold work tool steel by Soleimani et al. (2012). The fatigue strength of nitrided in 550°C for 6 h samples improved by about 67%. As in research by Sirin et al. (2008) the dominant fatigue crack initiation mechanism was subsurface "fish eye" type crack formation which originated from nonmetallic inclusions.

The beneficial influence of plasma nitriding on fatigue limit of ferrous materials was also reported by Winck et al. (2013). According to the authors, after just 1 h of nitriding in 500°C the fatigue life of CA6NM type steel increased by 23.67% at 2 million cycles. Fractographic analysis of fracture surfaces showed that the fractured surfaces resembled the structure referred to as "fish eye".

Additionally, the researchers stated that in low stress level (250 MPa) fatigue tests, the fatigue life of nitrided AISI 304L steel is raised by a factor of 10.

However, there are also studies concerning negative effect of plasma nitriding on fatigue life of austenitic steels. In research by Raman and Jayaprakash (2007) the plasma nitrided AISI 304 exhibited inferior plain fatigue and fretting fatigue lives compared with the unmodified material. As the authors claim, this was caused by chromium segregation at the grains boundaries of ion nitrided specimens. The chromium nitrides precipitation might have weakened the grain boundaries, resulting in early crack initiation and its accelerated propagation.

3.3. Direct Current Plasma Nitriding: other shortcomings

As mentioned in the previous paragraphs, beside the edge effect, DC plasma nitriding is characterized also by inconvenience as arcing and hollow cathode effect.

Arcing, caused mainly by degassing in localized area of the specimen surface, leads to local heat up of the part to extreme temperatures and, as an effect, melting or sputtering material from its surface (Szilágyiné Biró, 2013). Severe arcing of the component results in necessity of scraping the metallic part. In order to

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prevent arcing, the batch must be thoroughly cleaned from oil, grease and rust in relatively expensive cleaning routine (Gallo and Dong, 2009). According to Sharma et al. (2006) arcing can also be avoided by optimizing duty factor of the pulse in plasma deposition method.

The hollow cathode effect occurs when nitrided parts are of complex shape or contain deep holes, especially the blind ones (Szilágyiné Biró, 2013). During the ionization process, the gas is trapped in the hollow cavities and immobilized. This causes local heating of the product and can result in structure or property changes that affect the part's performance in service (Szilágyiné Biró, 2013). Soltani Asadi and Mahboubi (Soltani et al., 2012) have conducted research in which the effect of the sample geometry on the DC plasma nitrided steel was investigated. According to the authors, the hollow cathode effect was observed at the sample with 2 mm width groove. The microhardness tests results revealed that the sample was overheated during the plasma nitriding process, whereas samples with grooves of 4, 6, 8 and 10 mm width were not overheated. What is more, the hollow cathode effect led to large in size and prone to coursing nitrides formation.

Surprisingly, the hollow cathode effect found its application in variety of plasma processing techniques, e.g. thin film depositions and surface treatment. For example, in the research by Li et al. (2014c) the hollow cathode discharge effect was used to easily heat batch and working space.

In order to avoid described above common problems attributed with DC nitriding, many efforts have been made over past few years to develop high productive plasma nitriding methods. The same type of complex nitrided layer can be produced by numerous nitriding methods, e.g. RF nitriding (Baldwin et al., 1998), plasma immersion ion implantation (Blawert et al., 1998; Saklakoglu et al., 2007), plasma source ion nitriding (Liang et al., 2001), anodic nitriding (Psyllaki et al., 2008), laser nitriding (Psyllaki et al., 2008), cyclic plasma nitriding catalyzed by rare earth metals (We et al., 2010), cathodic cage plasma nitriding (de Sousa et al., 2007; Ribeiro et al., 2008) or nitrogen ion-beam implantation combined with pulsed plasma nitriding (Ochoa et al., 2005). Due to promising results from numerous studies by many researchers, the influence of mentioned nitriding techniques on ferrous materials performance will be described in the next paper.

4. CONCLUSIONS

The aim of the review was to provide comprehensive summary on direct current and pulsed direct current plasma nitriding of ferrous materials. Used in a great number of industry branches, ion nitriding is an attractive method that maximizes performance and service life of metallic materials.

According to the results, DC and pulsed DC plasma nitriding is an effective surface hardening, anti-wear and anti-corrosion method applied on austenitic, superaustenitic, martensitic, supermartensitic, duplex, tool, valve, precipitation hardened steels. Nevertheless, there are also well documented cases of deteriorating effect of this surface modification method on tribological and corrosion properties of ferrous materials.

The discussed technique has also its drawbacks, e.g. the edge effect, arcing and hollow cathode effect, which result in inhomogeneity of obtained layer. The occurrence of mentioned disadvantages is virtually impossible to prevent in DC method,

especially on small details.

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