

EFFECTIVENESS OF THE ION NITRIDING OF STEELS X5CrNi18-10, X2CrNiMo17-12-2

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Abstract: Based on testing the short-term and low-temperature glow-discharge nitriding of X5CrNi18-10 and X2CrNiMo17-12-2 austenitic steels, the calculation of the effectiveness of this process was made. The partial effectiveness was related to the nitrogen diffusion depth. The nitriding process was conducted with the following parameters: the temperature in the range of $T = 325\div 400$ °C; the duration in the range of $t = 2 \div 4$ h, the working atmosphere, $H_2 75\% + N_2 25\%$; and the pressure, $p = 150$ Pa. Two variants of locating the samples in the glow discharge chamber were adopted in carrying out the nitriding process: directly on the cathode, and on the cathode under the active screen.

Keywords: effectiveness, glow discharge nitriding, active screens, austenitic steels

1. Introduction

The world's production of crude steel in 2011 amounted to 1527 million Mg, having increased since the preceding year by 6.8% (in Poland, 8.8 million Mg with an increase by 9.8% since 2010) [1, 2, 3]. So, regardless of the progress in science and technology, steel has remained one of the key constructional and engineering materials in the contemporary world. The desirable mechanical and engineering properties of this material are obtained, for example, by using appropriate alloy additions and employing plastic working, heat treatment or thermochemical treatment.

Introducing new constructional solutions that require improved mechanical and service properties of materials to reduce energy consumption and operational costs, while complying with the environmental proportion rules, has driven an intensive development of, e.g., surface engineering methods in recent decades [4, 5]. The practical application of new, innovative solutions is conditioned, however, by the capability to achieve the desired material properties at costs lower than in the currently functioning industrial methods. One of the measures of the economic aspect of a given technological process is the effectiveness, being the ratio of the obtained effect to the incurred outlay [6].

Nitriding is one of the thermochemical treatment types which belongs now to the group of the fastest developing surface engineering methods. This process enhances the service properties of machine and structure parts, especially their tribological properties and corrosion resistance. Such a potential for shaping the top layer characteristics seems to be particularly attractive for austenitic steels, amongst others, whose too low hardness and abrasion resistance significantly limit their application [7].

The process of nitriding high-chromium is, however, difficult to carry out due to the occurrence of a thick film of chromium oxides on the steel surface, which prevents the nitrogen from penetrating into the material. A method that enables the austenitic steel nitriding process to be effected is by ion nitriding. It allows the film of oxides to be removed by cathode spraying [8]. The conditions of glow-discharge nitriding are defined by parameters, such as time, temperature, glow discharge voltage and current intensity, and

chemical composition of the gas mixture along with its pressure in the working chamber [9].

The development glow-discharge heating techniques and associated glow discharge-radiator and resistance-glow discharge heating, make it possible to shorten the heating duration. A reduction in energy intensity might be provided by developing technologies carried out at low temperature and with a short process duration, as well as energy efficient technologies able to be conducted in vacuum and glow-discharge conditions, and the modification of the CVD and PVD methods [10].

Glow-discharge active-screen nitriding enables the formation of nitrides layers of a greater depth and of expected service properties. The development of this technology should proceed towards reducing the temperature and duration of the nitriding process [10].

2. Effectiveness

The definition of the word "effective" given in a dictionary says: "efficient, producing the intended or expected result", derived from the Latin *effectivus* – efficient, *effectus* – result" [11].

Effectiveness arouses the interest of many areas of learning (economics, organization and management, cybernetics), which makes this notion to assume multiple meanings expressed by terms, such as efficiency, productivity, rationality, performance, profitability, economy, cost-effectiveness, etc. [12].

Looking at the various definitions of effectiveness, the following features of this notion can be noticed: an activity is considered effective, whose results enable the goals to be achieved with the minimization of the costs [12].

The concept of effectiveness has many years' tradition. First, effectiveness was associated with efficiency only in the technical and economic sense as understood by H. Emerson. Nowadays, other effectiveness criteria are considered, such as efficiency in the praxeological sense of T. Kotarbiński, competency in M. Weber's sense, functionality in the humanistic sense of R. Beckhard, communicativeness in the personality sense of D. J. Lawless and morality in the behavioural sense of K. Obuchowski and B. K. Saanlan. According to M. Holstain-Beck, an aspect that links all categories of effectiveness is ecology [12].

In the literature of management sciences, effectiveness is regarded as [13]:

- a key factor enabling the optimization of processes,
- a factor enabling decision-making,
- the determinant of the essence of activity, and
- a condition for achieving the goals.

Effectiveness is characterized by the broadest scope of encompassed contents and refers to relationships between effects, goals, expenditures and costs in a structural and dynamic aspect. Effectiveness is a positive result of efficiency, competence and skills [14].

The ISO 9000:2000 standard provides the following definition of effectiveness: "effectiveness is the relationship between the achieved outcomes and the resources used". So, effectiveness is the result of undertaken actions, as described by the relationship of achieved effects versus incurred expenditures. It means the best effects of manufacturing, distribution, sales and promotion [15].

Effectiveness is measured by using partial synthetic indicators of resource utilization productivity. Effectiveness can be defined using either an ex post or an ex ante approach. When calculating the ex ante effectiveness, the results expected by employing specific

resources and time are estimated. The ex post effectiveness refers to determining the results of specific activities [16].

We distinguish various indicators and formulas of effectiveness, of which all rely on the transformation of the functions (formula 1):

$$E = f(Ef, N, t) \quad (1)$$

where:

- E – effectiveness indicator,
- Ef – magnitude of achieved effects,
- N – amount of incurred expenditures,
- t – testing period.

The most commonly used indicator is the quotient indicator (formula 2) [16]:

$$E(t) = \frac{Ef(t)}{N(t)} \quad (2)$$

where:

- E(t) – indicator of effectiveness in time t,
- Ef(t) – magnitude of effects achieved in time t,
- N(t) – amount of expenditures incurred in time t,

The effectiveness assessment can be made according to the following rule:

- $E \geq 1$ the process is effective,
- $E < 1$ the process is ineffective.

3. Nitriding

Many variations of nitriding have been developed in recent years. These include nitriding in gaseous atmospheres under normal or reduced pressure, in an atmosphere of glow-discharge ionized gas, as well as in salt baths, powders and fluidized beds. Nowadays, the highest development potential is shown by the methods of vacuum nitriding, ring ion nitriding, pulse ion nitriding and laser nitriding.

The history of glow discharge techniques commences in the 30s of the 20th century with Berghaus patenting the idea of the process in 1932 [17] and then the glow-discharge heated vacuum furnace in 1939 [18]. The first practical application of the glow discharge techniques took place at the end of World Word II, when gun tubes were subjected to nitriding to increase their durability. In spite of this, ion nitriding technologies are regarded as new-generation technologies, as it was not until the 70s that research started on the stabilization of glow discharge when using high current intensities. Thanks to the application of state-of-the-art surface treatment technologies in various branches of industry, a new glow-discharge nitriding installation was put on the market. That was the installation by KlöcknerIonon GmbH [19].

Ion nitriding, called also glow-discharge or plasma nitriding, relies on active nitrogen species obtained through the ionization of a reactive atmosphere by glow discharge, which are introduced to the metal.

The ion nitriding process can be divided into two parts. The first part includes heating the furnace's working chamber to the expected temperature. During heating, the cathode sputtering phenomenon, activation of the surfaces treated, and oxide film removal take place. When the appropriate temperature has been attained, the nitriding process proper starts.

Temperature and time are the main parameters of the nitriding process; other important parameters include pressure, gas mixture composition, as well as glow discharge current intensity and power [20].

The process is conducted in the pressure range of 100 – 1300 Pa in dynamic vacuum conditions, that is at the constant flow of the gas mixture through furnace chamber. This allows a fixed nitriding mixture to be maintained. The nitriding atmosphere is a mixture of nitrogen and hydrogen in varying proportions. Argon is added during heating of the charge, and due to its large atomic mass, the addition of argon facilitates the breaking away of the passive film [21]. The voltage is dependent on the desired process temperature, pressure and nitriding atmosphere. Normally, the voltage range of 400 - 1800 V is used [19, 22]. The preset temperature and duration of the glow discharge nitriding process are lower compared to gas nitriding because of the activation of atoms occurring in the glow-discharge environment. The joint nitriding temperature is in the range of 400 - 500°C, and the selection of duration and temperature is dependent on what nitrated layer properties are desired to be obtained [23].

The basic ion nitriding device consists of a working chamber, an electric power supply, a system supplying appropriate gases and a vacuum pump. Parts to be nitrated are connected to the negative pole of the power supply to form the cathode, while the anode being the furnace chamber walls. With a specific voltage between the electrodes, a current flow takes place and a strongly ionized purple cathodic glow forms around the parts being nitrated. The formed high-energy molecules and ions bombard the surface of the part and heat it up to the appropriate temperature, which allows the nitrogen to penetrate into the metal [19].

4. Material and testing methodology

The aim of the undertaken tests was to compare the effectiveness of the active-screen nitriding process with the cathodic nitriding process. The tests were carried out on a JON-600 glow-discharge treatment stand with a cooled anode supplied by a Dora Power System MSS-10 pulse power supply (for the detailed description of the test stand see references [26, 27]). Two variants of locating the samples in the glow discharge chamber were adopted in carrying out the nitriding process: directly on the cathode and on the cathode under the active screen (the samples were in the working chamber at the same time).

The test material was an austenitic steel from the group of nickel-chromium steels X5CrNi18-10 acc. to standard PN-EN 10088-1:1998 (AISI 304) and a steel from the chromium-nickel-molybdenum steels X2CrNiMo17-12-2 acc. to standard PN-EN 10088-1:1998 (AISI 316L).

The ion nitriding process was carried out following a mathematical model for experiment planning developed according to the so called Latin square. A schematic of mathematical experiment planning is shown in Figure 1.

The range of the employed nitriding duration and temperature was adopted based on preliminary tests of short-duration and low-temperature glow-discharge nitriding of austenitic steels [24, 25]. The most important objective determining the selection of the nitriding parameters was to achieve nitrided layers of satisfactory tribological properties, while retaining the good corrosion resistance of the nitrided austenitic steel (no occurring chromium nitride precipitation processes that would lead to the dechroming of the austenitic matrix).

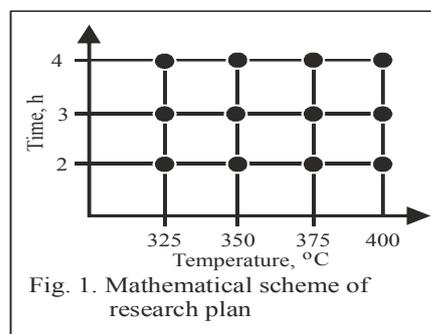


Fig. 1. Mathematical scheme of research plan

5. Testing results

During testing, the value of power supplied to the glow discharge-generating power supply was measured. On this basis, the average power used for nitriding was calculated. The power measurements were calculated from the arithmetic mean from 12 processes. The results of these measurements are summarized in Table 1 - 2.

Tab. 1. The average power used during heating X5CrNi18-10 steel and X2CrNiMo17-12-2 steel

HEATING			
Temperature [°C]	Average total heating power [kW]	Average circulated heating power [kW]	Average efficient heating power [kW]
325	4,70/3,70	1,10/0,81	3,60/2,89
350	4,90/4,21	1,15/0,88	3,75/3,33
375	5,12/4,41	1,31/0,91	3,81/3,50
400	5,26/4,75	1,39/0,95	3,87/3,80

p=150 Pa, H₂ 80% + Ar 20%

where: total power – the power supplied from the mains to the power supply system, being the sum of effective power and circulating power;

effective power – the power used for making the phenomena occur in the glow discharge chamber;

circulating power – the power recycled to the power supply; its occurrence is associated with the inability to use the whole supplied energy due to the insufficient quantity of electric energy carriers which are ionized gas molecules.

Nitrogen diffusion depth testing results are given in Table 3. On the basis of the obtained results it was found that the cathodic nitriding of the X5CrNi18-10 austenitic steel tested, within the adopted experiment plan, resulted in the formation of nitrided layers of a depth contained in the range from 0.3 to 2.5 μm, while with the use of the active screen, in the range from 0.5 to 7.3 μm.

In the case of the X2CrNiMo17-12-2 steel, similarly, the nitrated layers lay in the range from 0.56 to 2.51 μm , and with the use of the active screen, in the range from 1.07 to 6.34 μm .

Tab. 2. The average power used during nitriding process X5CrNi18-10 steel and X2CrNiMo17-12-2 steel

NITRIDING PROCESS			
Temperature [°C]	Average total nitriding process power [kW]	Average circulated nitriding process power [kW]	Average efficient nitriding process power [kW]
325	3,61/3,58	0,43/0,60	3,18/2,98
350	4,08/3,83	0,44/0,63	3,64/3,20
375	4,50/4,24	0,45/0,64	4,05/3,60
400	5,06/4,58	0,46/0,69	4,60/3,89/
p=150 Pa, H ₂ 75% + N ₂ 25%			

Tab. 3. Nitrogen diffusion depth X5CrNi18-10 steel and X2CrNiMo17-12-2 steel

NITROGEN DIFFUSION DEPTH [μm]						
Temperature [°C]	Cathode			Active screen		
	Time [h]			Time [h]		
	2	3	4	2	3	4
325	0,3/0,56	0,4/0,98	0,5/1,01	0,5/1,07	0,9/1,78	1,6/2,61
350	0,4/0,88	0,6/1,38	0,8/1,80	1,3/2,45	2,2/3,28	2,8/3,68
375	0,5/1,44	0,7/1,96	1,9/2,15	2,8/3,69	4,2/3,81	4,6/4,01
400	1,1/1,61	1,6/2,26	2,5/2,51	5,3/4,62	6,1/5,02	7,3/6,34

Note: The depth of nitrogen diffusion into the top layer was measured with a GDS GD PROFILER HR spectrometer.

At this stage of investigation it was only possible to calculate the partial effectiveness related to the depth of the nitrated layer for the steel under investigation. Comparing directly these quantities came down in practice to juxtaposing the nitrogen diffusion depths for both samples (the cathode and the cathode with the screen), since for the experiment carried out at the same temperature and for the same nitriding duration the energy expenditures were identical - Figure 2.

The analysis of the presented data indicates that, in the identical conditions, the use of the active screen for the X5CrNi18-10 steel and the adopted testing range results in a 2 ÷ 6 time increase in the depth of obtained nitrated layers compared to the cathodic process. This corresponds to a percentage nitrogen diffusion depth increase from 67% to 500% (Figure 2A). For the X2CrNiMo17-12-2 steel, the active screen has caused a 2 – 3 time increase in nitrated layer depth (from 82% to 186% - Figure 2B).

Also the dynamic of diffusion nitrogen layer increase in the active screen process is distinctly greater, in terms of both nitriding duration and temperature – Figures 3 through 6.

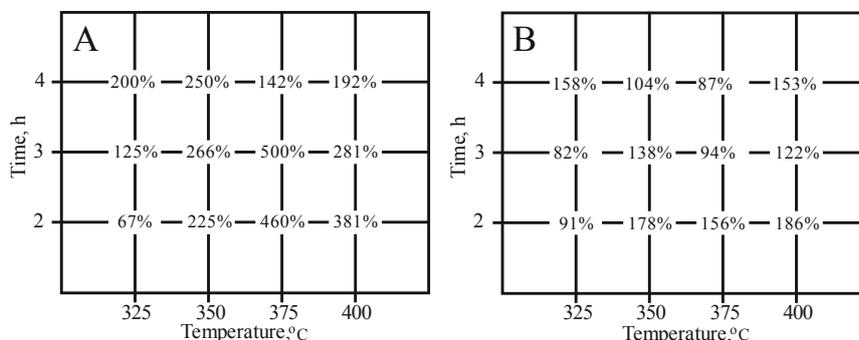


Fig. 2. Percentage increase of nitrogen diffusion depth in samples placed on cathode with active screen to nitrogen diffusion depth in samples placed on cathode a) X5CrNi18-10 steel, b) X2CrNiMo17-12-2 steel

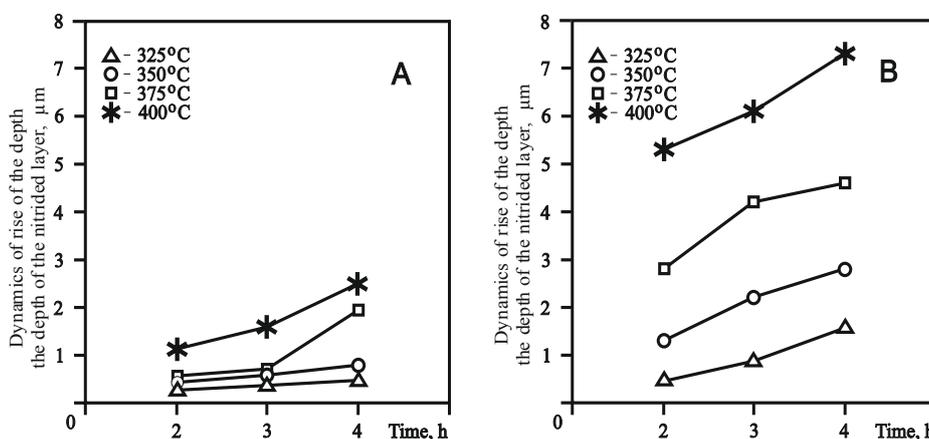


Fig. 3. Dynamics of rise of the depth of the nitrated layer in X5CrNi18-10 steel in function on nitriding time a) cathode, b) cathode with active screen

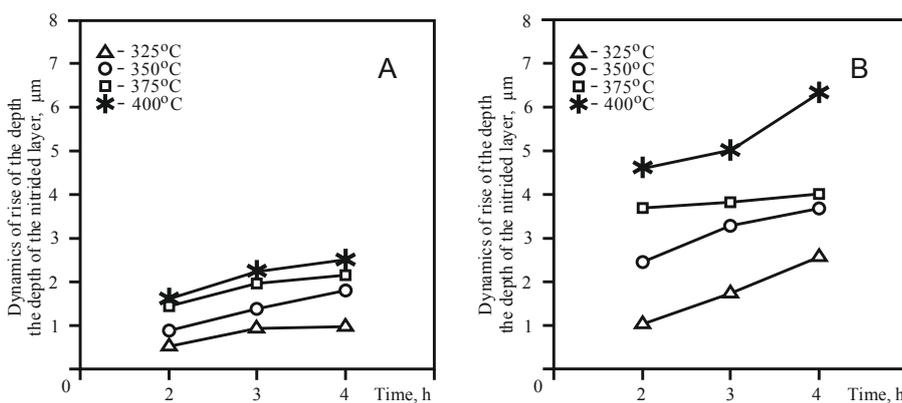


Fig. 4. Dynamics of rise of the depth of the nitrated layer in X2CrNiMo17-12-2 steel in function on nitriding time a) cathode, b) cathode with active screen

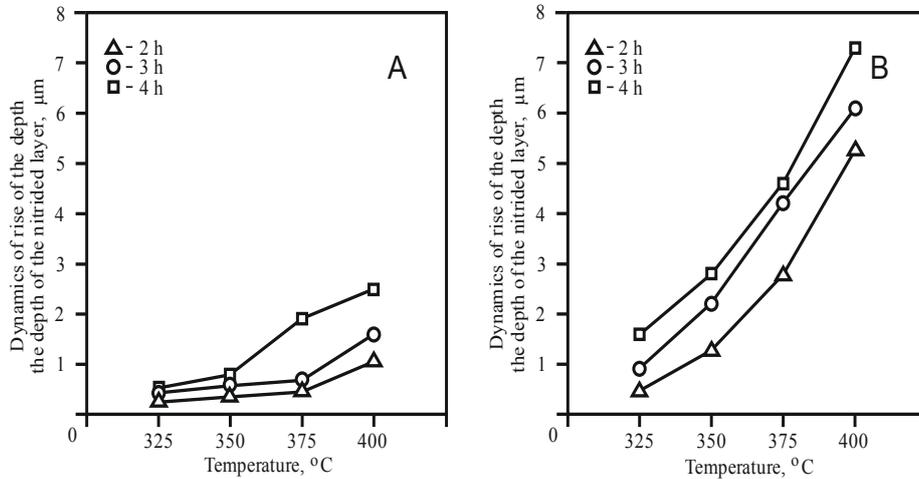


Fig. 5. Dynamics of rise of the depth of the nitrated layer in X5CrNi18-10 steel in function on nitriding temperature a) cathode, b) cathode with active screen

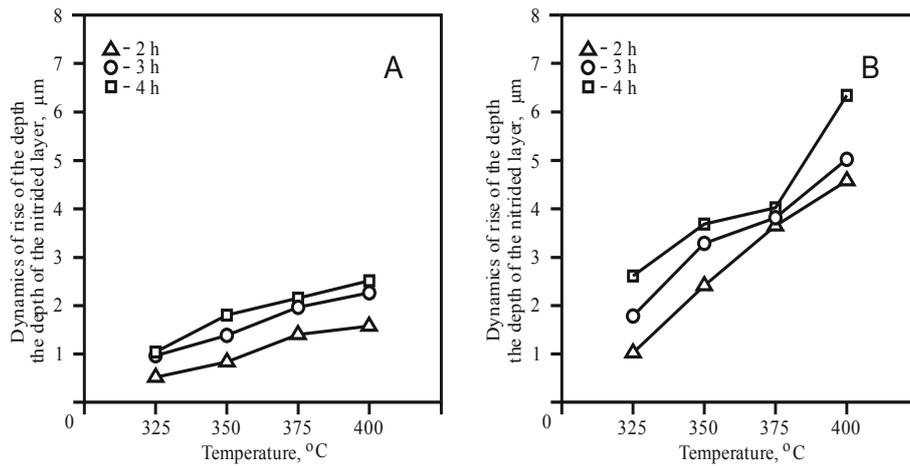


Fig. 6. Dynamics of rise of the depth of the nitrated layer in X2CrNiMo17-12-2 steel in unction on nitriding temperature a) cathode, b) cathode with active screen

In view of the uniform increase of energy (for specific equipment and scope of preset process conditions) required for increasing the duration or temperature of nitriding (Figure 7), future investigations would need to precisely determine the effect of both of these parameters on the depth of nitrated layers.

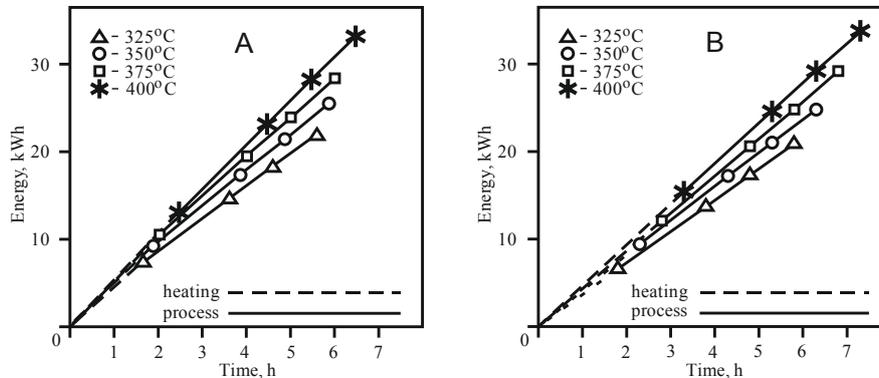


Fig. 7. Energy consumption during heating and nitriding process
a) X5CrNi18-10 steel, b) X2CrNiMo17-12-2 steel

5. Conclusions

The results of the tests of short-duration low-temperature glow discharge nitriding of austenitic steel X2CrNiMo17-12-2 have clearly shown that, under identical conditions, the process of nitriding using the active screen is 2÷3 times more effective than the cathodic process. Admittedly, the effectiveness related exclusively to the nitrided layer depth, though literature data[26, 27] does indicate that other properties, such as hardness or abrasive wear resistance, are also improved. Further research should determine the optimal parameters (pressure, temperature, time) required for achieving the prescribed (mechanical and service) properties of nitrided steel.

The use of the active screen in glow discharge nitriding of the X5CrNi18-10w steel in the adopted testing range resulted in a 2÷6 time increase in the depth of obtained nitride layers compared to the cathodic process.

The greater increase in nitrogen diffusion depth in the case of the Cr-Ni steel compared to the Cr-Ni-Mo steel is probably caused by $M_{23}C_6$ -type secondary chromium carbides and δ and ν intermetallic phases that are likely to occur in Cr-Ni-Mo austenitic steels. A local depletion of the austenitic matrix in Mo might additionally occur in these steels due to the precipitation of the ν intermetallic phase along the grain boundaries [7]. The carbides and intermetallic phases precipitated along the grain boundaries inhibit the nitrogen diffusion into the material through the easy diffusion path along the grain boundaries.

The most commonly used groups of austenitic steels, namely 18-10 and steels with a molybdenum addition, have similar mechanical properties, whereas the corrosion resistance of the molybdenum steels is higher due to a higher nickel content and the 2% molybdenum addition. It should be noted that steels of the molybdenum-addition steel group are over 2 times more expensive than Cr - Ni steels. An alternative solution can be provided by modifying the surface layers of relatively inexpensive austenitic steels, such as those from the 18-10 steel group, thereby enhancing the service life of these steels.

This research was financed from the budget resources allocated for science in the years 2010 – 2013 under Research Project No. N N507 296239.

Literatura:

1. www.worldsteel.org – data wejścia 2012.11.15
2. www.hiph.org - data wejścia 2012.11.15
3. hutnictwo.wnp.pl - data wejścia 2012.11.15
4. Burakowski T.: Rola i znaczenie pojęcia systemu areologicznego. Inżynieria Materiałowa, nr 5, 2005, s.567.
5. Jasiński J.: Oddziaływanie złoza fluidalnego na procesy nasycania dyfuzyjnego warstwy wierzchniej stali. Wyd. WIPMiFS PCz., Częstochowa 2003.
6. Kotliński A.: Przegląd metod i technik oceny efektywności procesu produkcyjnego. Logistyka nr 5, 2011, s.1083.
7. Blicharski M.: Inżynieria materiałowa – stal. WNT, Warszawa 2010.
8. Frączek T., Olejnik M.: Znaczenie rozpylania katodowego w procesie azotowania jarzeniowego stali austenitycznych. Nowe technologie i osiągnięcia w metalurgii i inżynierii materiałowej. Wyd. PCz, Częstochowa 2008, s. 85
9. Groszkowski J.: Technika wysokiej próżni. WNT, Warszawa 1978.
10. Frączek T.: Niekonwencjonalne niskotemperaturowe azotowanie jarzeniowe materiałów metalicznych. Wyd. WIPMiFSPCz, Częstochowa 2011.
11. Kopaliński W.: Słownik wyrazów obcych i zwrotów obcojęzycznych z almanachem. Wyd. Świat Książki, Warszawa 2000.
12. Tyrańska M.: Jakość kapitału ludzkiego a efektywność przedsiębiorstwa. Problemy Jakości, nr 5, 2009, s.
13. Jaki A.: Paradygmat efektywności w zarządzaniu. Przegląd Organizacji, nr 4, 2011, s.
14. Lipka A.: Efektywność strategicznego zarządzania zasobami ludzkimi. Zarządzanie zasobami ludzkimi, nr 3-4, 2008, s.
15. Zapłata S.: Skuteczność i efektywność systemu zarządzania jakością. Problemy Jakości, nr 2, 2003, s.
16. Siwek M., Onyszczyk J., Bagiński J.: Skuteczność, efektywność, a produktywność. Problemy Jakości, nr 9, 2006, s.
17. Berghaus B.: Proces do powierzchniowej obróbki metalowych elementów. Patent niemiecki DRP 668 639, 1932.
18. Berghaus B.: Próżniowy piec ogrzewany wyładowaniem jarzeniowym. Patent niemiecki DRP 851 540, 1939.
19. Burakowski T., Wierzchoń T.: Inżynieria powierzchni metali. WNT, Warszawa 1995.
20. Zdanowski J.: Wyładowania elektryczne w gazach. Wyd. Pol. Wrocławskiej, Wrocław 1975.
21. Frączek T., Olejnik M.: Znaczenie rozpylania katodowego w procesie azotowania jarzeniowego stali austenitycznych. Nowe Technologie i Osiągnięcia w Metalurgii i Inżynierii Materiałowej, IX Międzynarodowa Konferencja Naukowa, Częstochowa 2008, s. 85
22. Burakowski T., Roliński E., Wierzchoń T.: Inżynieria powierzchni metali. Wyd. Pol. Warszawskiej, Warszawa 1992
23. Kowalski S., Łataś Z., Rogalski Z., Sobusiak T., Trojanowski J.: Obróbka cieplna metali. Technika atmosferyczna, fluidalna, próżniowa, jarzeniowa. IMP, Warszawa 1987.

24. Frączek T., Olejnik M., Jasiński J.: Wpływ czasu niskotemperaturowego azotowania jarzeniowego na zużycie tribologiczne stali austenitycznej X2CrNiMo17-12-2. Produkcja i Zarządzanie w Hutnictwie, pr. zbior. pod red. nauk. Ryszarda Budzika, Częstochowa 2010.
25. Frączek T., Olejnik M., Jeziorski L. : Krótkookresowe i niskotemperaturowe azotowanie jonowe stali austenitycznej X2CrNiMo17-12-2. Nowe technologie i osiągnięcia w metalurgii i inżynierii materiałowej, XI Międzynarodowa Konferencja Naukowa, Częstochowa 2010.
26. Olejnik M.: Niskotemperaturowe i krótkookresowe azotowanie jarzeniowe stali austenitycznej X2CrNiMo17-12-2. Praca doktorska, Politechnika Częstochowska, 2001.
27. Olejnik M., Frączek T.: Ocena odporności na zużycie ściernie stali 316L po procesach azotowania jarzeniowego. Inżynieria Materiałowa, nr 6,2008, s. 997.

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