Anticorrosion nitrided layers on unalloyed and alloyed steels

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Abstract. In the paper, nitrided layers on unalloyed and alloyed steels and their corrosion properties are presented. Nitrided layers in the controlled gas nitriding process on C10 and 42CrMo4 steels were formed. Two types of nitrided layers are presented: with nitride iron layers above and below 15 µm. Nitrided layer with nitride layer above 15 µm has good corrosion resistance, but after nitriding of machine parts were subsequently oxidised and impregnated. In the second type of nitrided layer, the surface layers of iron nitrides had a thickness of 3.0 to 11.0 µm. Nitrided layers with a surface layer of iron nitrides with the γ' (Fe,N) structure were formed on unalloyed steel and investigated. The so-formed layers were subject to basic metallographic, X-ray diffraction and corrosion resistance studies carried out by electrochemical methods and in a neutral salt spray chamber. It was found that the layers consisting only of γ' phase had a good corrosion resistance. Necessary requirements for achieving an enhanced resistance comprise their complete tightness and thickness not lower than 9.0 µm. Thinner layers had good electrochemical properties but did not exhibit corrosion resistance in the salt spray chamber.

1 Introduction
Corrosion resistance is exhibited by nitrided layers with a surface layer of iron nitrides formed both on structural carbon steels and alloyed steels, and – to a lesser degree – on cast iron, because a continuous surface layer of iron nitrides is difficult to obtain on them. Nitrided machine parts undergo, most of all, pitting corrosion. In the process of destruction, the base corrodes, therefore the corrosion resistance depends on the tightness of the surface layer of iron nitrides [1]. The corrosion of elements with a nitrided layer made of an unalloyed steel, may be divided into three stages [2]:

- I initiation of corrosion in the pores of the iron nitrides’ layer,
- II development of pitting corrosion through the pores in the nitrides’ layer,
- III development of corrosion under the nitrides’ layer.

The development of corrosion in the nitrided layer on carbon steels is caused by micropores and the phase composition of the iron nitrides’ layer, contributing into formation of local galvanic cells [1,3]. In the industry, anticorrosive nitrided layers with a surface layer of iron nitrides with the ε+(ε+γ’prec.) structure are widely used. In order for the layers to achieve a good corrosion resistance, they are subject to additional treatment, such as grinding, polishing [4,5], steam oxidation [6] and impregnation [7].

Grinding and polishing remove the porous layer. Oxidation leads to formation of a tight oxide layer on the surface. The impregnant penetrates the porous layer and efficiently seals the surface layers of iron nitrides, thus decreasing its susceptibility to the pitting corrosion. Additionally, by steam oxidation of the layers before their impregnation, its corrosion resistance is increased [8].
However, these operations significantly increase the cost of the process. Thus, studies aimed at production of compact layers of γ' iron nitrides or γ' iron nitrides with a limited content of the ε phase, which would not require any additional treatment and would have a good corrosion resistance, are purposeful. The paper presents the resistance of corrosion layers of the nitrided 1010 steel with a monophase surface layer of γ' type iron nitrides formed on C10 and 42CrMo4 steels.

2 Methodology and research material

Samples nitriding was performed using the Nitreg regulated gas nitriding method in the Nx609 industrial soaking furnace with the retort dimensions of Φ600x900mm featuring computer process control, as manufactured by Nitrex Metal Inc. The process parameters are shown in Table 1. 1010 normalized steel (AISI standard) and 42CrMo4 toughened steels were used in the tests.

Samples of 42CrMo4 steels with thickness of nitrides layer about 20 μm after nitriding were subjected to oxidation and impregnation (process Nx620). Samples of nitrided 1010 steel with nitrides layer 3-12 μm were without impregnation and oxidation.

| Process No. | Temperature [°C] | Heating atmosphere | Process temperature atmosphere | Nitriding potential value at the process temperature | Time [h] |
|-------------|------------------|--------------------|-------------------------------|---------------------------------|---------|
| Nx620       | 570              | NH₃                | NH₃                           | 2,50                            | 4       |
| Nx300       | 490              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 1,98                            | 4       |
| Nx428       | 490              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 2,08                            | 12      |
| Nx301       | 490              | NH₃diss            | NH₃-NH₃diss                   | 1,98                            | 4       |
| Nx369       | 530              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 1,24                            | 4       |
| Nx625       | 530              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 1,48                            | 12      |
| Nx354       | 560              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,82                            | 4       |
| Nx355       | 560              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,82                            | 4       |
| Nx418       | 560              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,92                            | 8       |
| Nx319       | 580              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,50                            | 4       |
| Nx322       | 580              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,80                            | 4       |
| Nx422       | 580              | NH₃-NH₃diss        | NH₃-NH₃diss                   | 0,57                            | 8       |

The metallographic studies of the nitried layers were carried out on microsections perpendicular to the nitrided layer surface. On the microsections, the thickness of the surface layer of iron nitrides was determined and the structures of the layer and the base were observed. The structure of the nitried layers was revealed using Nital (4% HNO₃ solution in C₂H₅OH). The structural observations were carried out using Neophot-2 and Nikon ECLIPSE LV150 optical microscopes. The thickness of the surface layers of iron nitrides was determined as an arithmetic mean of at least 6 measurements. The measurement error was estimated by calculating standard deviation.

Studies of the surface topography were carried out using a DSM 942 scanning microscope from Zeiss, LEO.

Studies of the phase composition were carried out using an XRD 3003T-T X-ray diffractometer from Seifert and a Dron 2.0 diffractometer. During the phase analysis, CoKα radiation with a wavelength of λ = 1.79021 Å and a penetration distance of ~20 μm was used.
Potentiodynamic electrochemical measurements of the corrosion resistance were carried out using an electrochemical microcell with a working surface of 0.066 cm². Electrochemical tests were conducted using a three-electrode cell with the sample as the working electrode, a platinum electrode and saturated calomel electrode (SCE) as reference electrode. Open circuit potential ($E_{ocp}$) and polarisation curve from the potential of approx. 500 mV more cathodic than the $E_{ocp}$, towards the anode, with a potential change rate of 1 mV/s, were recorded. The polarisation curve was recorded up to approx. +2000 mV. A 3% aqueous solution of NaCl, imitating seawater and simulating the conditions of salt spray chambers to a significant degree, was used as the electrolyte. During the investigations, the corrosion current density $i_{kor}$ and the passivation current density $i_{pas}$ were determined, and the degree of corrosion protection $\beta$ was calculated:

$$\beta = \left(1 - \frac{i_{kor}}{i_{kor}^o}\right) \cdot 100 \, [\%]$$

(1)

where:
- $i_{kor}$ - the corrosion current density of a nitrided material,
- $i_{kor}^o$ - the corrosion current density of a non-nitrided material.

For a preliminary evaluation of the improvement of electrochemical properties of the nitrided layers, the following parameters and their corresponding values were selected:
- corrosion currents $i_{kor} < 0.75 \, \mu A/cm^2$,
- degree of protection $\beta > 80\%$,
- passive currents $i_p < 100 \, \mu A/cm^2$,
- open circuit potential $E_{ocp} > -100 \, mV$.

The studies of the corrosion resistance to the neutral salt spray (NSS) effect were carried out in an accredited IMP laboratory according to the PB/2-50B/LB-3 procedure: „Resistance to the neutral salt spray (NSS). Metals, metallic and other inorganic coatings.” According to this procedure, accelerated studies in a neutral salt spray of the corrosion resistance are carried out for: metals and their alloys, metal coatings (anodic and cathodic), non-metallic coatings, inorganic coatings applied to a metal surface (conversion, oxide anodic). Visual inspection of the samples (three pieces from each process) were carried out in equal time intervals every 24 h or to the occurrence of defined corrosive changes. The appearance of the samples was evaluated according to the PN-EN ISO10289:2002 standard “Methods For Corrosion Testing Of Metallic And Other Inorganic Coatings On Metallic Substrates – Rating Of Test Specimens And Manufactured Articles Subjected To Corrosion Tests”.

3 Results of experiments

3.1 Metallographic and X-ray diffraction studies

Samples of 42CrMo4 steel nitrided in the Nx620 process had thick subsurface layer of iron nitrides. Their thickness was about 20 μm (Figure 1). X-ray analysis confirmed that at the sample surface there is sub-surface nitrided layer consisting of the ε and γ' phases (Figure 2).
In case of 1010 steel, after the process of the controlled gas nitriding, a thickness of the surface layers of iron nitrides from 3.5 to 11.8 µm was obtained. The thicknesses of the surface layers of iron nitrides are shown in figure 3.
All nitrided layers had a surface layer of iron nitrides of $\gamma'$ type, confirmed by the X-ray diffraction studies. In figure 4, exemplary structures of the nitrided layers from representative Nx301, Nx625 and Nx418 processes are shown.

![Figure 4](image)

**Figure 4.** Structures and diffractograms of phase composition of the surface layers of iron nitrides on the 1010 steel after the processes: (a) Nx625, (b) Nx418, and (c) Nx301.

The layers formed below 560°C did not have a porous zone. On the other hand, those formed at a higher temperature had a porous zone from 0.5 to 2.0 $\mu$m.

### 3.2 Corrosion resistance studies

In figure 5, the electrochemical parameters and corrosion current (Figure 5a), passivation current (Figure 5b), open circuit potential (Figure 5c) and the degree of corrosion protection (Figure 5d) obtained in a 3% NaCl solution, characterising the corrosion resistance of the nitrided steel with iron nitrides' layers with a thickness of 3.5$\div$5.7 $\mu$m, are shown.
Figure 5. Basic electrochemical parameters and corrosion current (a), passivation current (b), open circuit potential (c), degree of corrosion protection (d), obtained in a 3% NaCl solution for the nitrided 1010 steel with iron nitrides’ layers with a thickness of 3.5÷5.7 μm.

All four criteria of electrochemical resistance were met by the iron nitrides’ layers with a thickness of 3.5÷3.8 μm obtained on the 1010 steel, nitrided in the Nx300 and Nx301 processes. The iron nitrides’ layer with a thickness of 5.7 μm obtained in the Nx354 process exceeded the limit value of the open circuit potential $E_{ocp}$. On the other hand, it was characterised by the lowest corrosion current $i_{kor}$ and passivation current $i_p$, and the highest degree of protection $\beta$.

In figure 6, the electrochemical parameters and corrosion current (Figure 6a), passivation current (Figure 6b), open circuit potential (Figure 6c) and the degree of corrosion protection (Figure 6d) obtained in a 3% NaCl solution, characterising the corrosion resistance of the nitrided 10 steel with iron nitrides’ layers with a thickness of 7.0÷11.8 μm, are shown.

All four criteria of electrochemical resistance were met by the iron nitrides’ layers with a thickness of 8.5 μm obtained on the 1010 steel, nitrided in the Nx322 process. The iron nitrides’ layer with a thickness of 9.0 μm obtained in the Nx418 process exceeded the limit value of the open circuit potential $E_{ocp}$. On the other hand, it was characterised by the lowest corrosion current $i_{kor}$ and passivation current $i_p$, as well as the highest degree of protection $\beta$, while the iron nitrides’ layer with a thickness of 7.0 μm, obtained in the Nx355 process, also exceeded the limit value of the corrosion current $i_{kor}$. Moreover, it was characterised by the highest open circuit potential $E_{ocp}$, a relatively low passivation current $i_p$, as well as the highest degree of protection $\beta$. 
As it results from the investigations, in the group of layers with thicknesses of 3.5÷5.7 μm, the assumed criteria of the corrosion resistance were met by the layers with a thickness of 3.5 and 5.8 μm formed at a temperature of 490°C. In the group of layers with thicknesses of 7.0÷11.8 μm, the assumed criteria of the corrosion resistance were met by only one layer with a thickness of 8.5 μm formed at a temperature of 580°C. Thus, there is no distinct dependence between the thickness of an iron nitrides’ layer and the process temperature, and the layer’s electrochemical parameters.

Nitrided layers formed on the 1010 steels at temperatures of 490, 530, and 560°C (selection after a preliminary electrochemical assessment) were subject to studies in the salt spray chamber. The Nx625 process is a process at a temperature of 530°C elongated to 12 h. The results of these studies are reported in table 2.

A better corrosion resistance on 1010 steel was obtained for the layer formed in the Nx625 process than for that of Nx418 process, in spite of the same thickness of iron nitrides (9.0 μm). The difference in the behaviours of the layers resulted from the presence of a porous zone (1.0 μm) on the surface of the nitrides’ layer formed in the Nx418 process. As one can see in figure 7, the layer obtained in this process at a temperature of 560°C had more local discontinuities and porosities (Figure 7a) than the layer from the Nx625 process carried out at a temperature of 530°C (Figure 7b).
Table 2: Results of the salt spray chamber studies of the nitried layers on 1010 and 42CrMo4 steel.

| Process No./Temp./Time | Appearance of the samples after exposure for: | 24 h | 48 h | 72 h | 96 h |
|------------------------|---------------------------------------------|------|------|------|------|
|                        | 3.5÷6.0 μm layers of iron nitrides 1010 steel |      |      |      |      |
| Nx301/490°C/4h         | 1 corrosion spot                             |      |      |      |      |
|                        | Corrosion on approx. 45% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 45% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 60% of the surface       |      |      |      |      |
| Nx428/490°C/4h         | No change                                    |      |      |      |      |
|                        | Corrosion on approx. 50% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 60% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 70% of the surface       |      |      |      |      |
|                        | 7.0÷9.0 μm layers of iron nitrides 1010 steel |      |      |      |      |
| Nx418/560°C/8h         | No change                                    |      |      |      |      |
|                        | Corrosion on approx. 20% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 40% of the surface       |      |      |      |      |
|                        | Corrosion on approx. 70% of the surface       |      |      |      |      |
| Nx625/530°C/12h        | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | Corrosion on approx. 50% of the surface       |      |      |      |      |
|                        | 20 μm layers of iron nitrides 42CrMo4 steel   |      |      |      |      |
| Nx620/570°C/4h         | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | No change                                    |      |      |      |      |
|                        | Corrosion on approx. 10% of the surface       |      |      |      |      |
|                        | after 240h                                    |      |      |      |      |

In case of 42CrMo steel with a thick surface layer of the iron nitrides (20 μm), after the oxidation and impregnation the high corrosion resistance (above 240 h in salt spray chamber) was achieved.

![a) b)](image)

Figure 7. Appearance of the surfaces of the nitried layers formed in Nx418 (a) and Nx625 (b) processes.

4 Conclusions

- Forming of thick subsurface layers of iron nitrides by nitriding with subsequent processes of oxidation and impregnation allows to achieve a very high corrosion resistance (over 240 h in salt spray chamber).
- The stage of heating in the nitriding process has a great influence on the formation of iron nitrides layer, especially on their final phase composition and morphology. Conducting of heating to a fixed process temperature with the adjusting of the nitriding potential guarantees formation from the beginning of tight subsurface layer of iron nitrides with a defined phase composition.
- Monophase surface iron nitrides' layers with the \( \gamma' \) structure, formed on unalloyed steels have a good corrosion resistance (to 72 h in salt spray test).
- A necessary requirement for a good resistance of nitried unalloyed steel consists in a formation of the tight surface layers of iron nitrides.
- Unalloyed steels with a tight layer of iron nitrides with a thickness of 9.0 \( \mu m \) have a higher corrosion resistance (confirmed by the studies in the salt spray chamber) than that of the thinner layers.
- It is more favourable to generate nitried layers with a good corrosion resistance at temperatures below 530\(^\circ\)C than at higher temperatures. It results from a higher propensity to form porous zones at higher temperatures of the nitriding process.

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