Electrochemical determination of corrosion protection and phase composition of nitride layers on steels

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Electrochemical method providing the possibility to check the penetrating porosity, corrosion resistance and phase composition of nitrided surface has been developed and applied for high-speed SW18 steel nitrided from plasma excited H₂ + N₂ gas mixture and for structural 10A and 45A steels nitrided from NH₃ gas dissociated at different parameters. By selection the appropriate electrolytes, the phase composition of nitrided layer in SW18 steel, and the corrosion resistance of ε or γ' compact nitride layer on 10A and 45A steels have been evaluated and confirmed by material science and corrosion tests. Electrochemical methods may be applied to control the quality of obtained nitrided layer, and to correct or modify the program of technological process. Electrochemical method provided the possibility to check the penetrating porosity, corrosion resistance and phase composition of nitride layers formed on SW18, 10A and 45A steels were established in accordance with the material investigation and corrosion tests data.

Key words: high speed SW18 steel, 10A steel, 45A steel, plasma nitriding, γ' phase, ε phase, H₃PO₄, borate, NaCl.

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1 Introduction

Nitriding has been commonly used to increase the hardness, wear resistance, and the corrosion resistance of steels. Depending on steel composition and the kind and parameters of nitriding process, the surface layers consisting of diffusion zone, zones of compact γ, γ', ε nitrides or their mixture, as well as the carbo-nitrides may be formed. Transformation of carbides to carbo-nitrides, presence of porous ε nitride or non-porous γ' nitride layer affect the corrosion resistance. Using the modern facilities and the computer control of process (especially the nitriding potential and the heating rate) the layers of various phase composition and structure may be obtained [1-4]. In order to control the quality of obtained layer, and to correct or modify the program of technological process, the express method for determining the properties and composition of nitrided layer should be elaborated and applied. This possibility provides the electrochemical methods. Application of potentiostatic or potentiodynamic electrochemical tests allows to establish the phase (or chemical) composition of nitrided surface [5-9], to measure the penetrating porosity of the surface layer [10-16] and to evaluate the comparative corrosion resistance of nitrided steel in various environments.

In present work, the results of potentiodynamic tests done in selected electrolytes enabling to check the corrosion resistance and the phase composition of nitrided layers formed under conditions providing the various nitride phase composition are shown. Chemical composition of used high speed SW18 and structural 10A and 45A steels is shown in Table 1. Structural steels were nitrided from NH₃ gas phase, in a stepwise process. Specimens were heated at 450°C in pure, non dissociated NH₃ and then for short time in the 100% dissociated NH₃. In a next step, nitriding proceeded at 490°C in the gas
containing mixture of 45%: 55% of dissociated to non dissociated NH₃ (process N40) and the mixture of 38%: 62% dissociated to non dissociated NH₃ (process N60). The final step of nitriding was done at parameters shown in Table 1. As a result, the compact nitride layers consisting on ε (process N40) and of γ'+ε (process N60) of thickness shown in Table 1, have been obtained. At nitriding of high-speed SW18 steel in a plasma excited gas mixture at parameters shown in Table 1, the nitride layer exhibiting only diffusion zone of different thickness was obtained.

Table 1 – Studied steel composition and the parameters of nitriding processes

| Steel  | Specimen code | Parameters of nitriding process                  | Nitriding layer structure | Nitriding layer thickness, pm |
|--------|---------------|-------------------------------------------------|---------------------------|-------------------------------|
| 10A    | N40           | 530°C, NH₃:NH₃dys=40:60, 4h                      | compact ε                 | 6                             |
| as above | N60           | 530°C, NH₃:NH₃dys=57:43, 4h                      | compact (γ'+ε)            | 7                             |
| 45A    | N40           | 530°C, NH₃:NH₃dys=40:60, 4h                      | compact ε                 | 4                             |
| as above | N60           | 530°C, NH₃:NH₃dys=57:43, 4h                      | compact (γ'+s)            | 5                             |
| SW18   | N1            | plasma assisted, 490°C, H₂:N₂=3:1. 1h.           | diffusion layer.          | 15                            |
| as above | N10           | plasma assisted, 490°C, H₂:N₂=3:1. 10h           | diffusion layer.          | 45                            |

Polarization curves were recorded with a potential scan rate 1 mV/s, using microcell of working area 0.05 cm², placed on the nitrided surface. The 20% H₃PO₄ and borate (0.024M Na₂B₄O₇ + 0.12M H₃BO₃) electrolytes [17-25] were selected in order to evaluate the phase composition of nitrided layer. The 3% NaCl was used to check the relative susceptibility of nitrided layers formed on low alloy structural steels to corrosion in Cl containing environments.

2 Results and discussion

Electrochemical results have been compared with the results of microscopic and SEM observations, microhardness measurements, X-ray and GDS analysis and with results of corrosion tests.

Figure 1 shows the examples of polarization curves obtained for SW18 steel, bare and after N1 nitriding. The broad active peak on polarization curve recorded in H₃PO₄ has been associated with the dissolution of solid solution (matrix) phase, while peaks E₃ and E₄ could be accounted by the presence of MC and MC₆ carbides [2], respectively. Indeed, in a bare SW18 steel, the X-ray examination revealed the presence of those carbides. Nitriding of SW18 steel caused the shift of peaks E₃ and E₄ to more anodic potential and the formation of two new peaks (E₁ and E₂) on polarization curve. Figure 2 shows the position of peaks seen on polarization curves recorded in H₃PO₄ for SW18 steel, nitrided in N10 process, after consequent removing of the surface material. The data show the phase distribution along the depth of nitrided layer. Potentials E₃ and E₄ returned to the values, characteristic for bare steel, at a distance from surface, similar to thickness of nitrided layer, established by microscopic observation and microhardness measurements. The above results of electrochemical tests showed that in a course of nitriding of SW18 steel, the transformation of carbide to the carbo-nitrides occurred and the nitrides were formed.

Figures 3 to 5 show the polarization curves recorded in different solutions for structural steels, bare and nitrided at different parameters. For bare low carbon steel 10A, no E₃ and E₄ peaks were observed on polarization curves recorded in H₃PO₄ solution (Figure 3). This may support the assumption of attributing of those peaks, observed for SW18 steel (Figure 1) to the dissolution of MC and MC₆ carbides, since low carbon 10A steel did not contain such carbides. Nitriding of 10A and 45A steels did not eliminate the active dissolution peak, but decreased its height and reduced the potential range. The new peak could be distinguished on polarization curve for nitrided steel, at potential close to potential of E₁ and E₂ peaks seen in the case of nitrided SW18 steel (cf. Figures 1 and 2).
This indicated the association of new peak with nitrides, formed at nitriding process.

Polarization curve recorded in borate solution for bare structural steel (Figure 4) exhibited two active peaks (E1 and E3). After nitriding in both processes, the new peak (EN) appeared within the passive region. At subsequent removing of nitrided layer, this peak disappeared, revealing that its nature has been associated with the dissolution of nitrides. Unfortunately, at recording polarization curves either in H₃P0₄ or in borate solution, the kind of nitrides (ε or γ'ones) could not be distinguished, and the further studies should be carried out.

As follows from the X-ray examination (Table 1), after N40 and N60 nitriding processes, steels were covered with layers consisting of γ' nitride and of mixture of ε and γ' nitrides, respectively. According to [1], in the first case the nonporous and in a latter case the porous layers can be formed. As seen in Figure 3, steel nitrided in N60 process exhibited in whole potential range, the higher current densities than that nitrided in N40 process, revealing the higher porosity of nitrided layer formed in process N60 and consisting of ε and γ' nitrides, in accordance with [1]. The higher porosity of layer formed in process N60 may be supported by data shown in Figure 4. Polarization curve for N60 specimen exhibited higher current than N40 specimen and the presence of peaks E1 and E2 resembling the peaks seen on polarization curve for bare steel. Therefore, by recording the polarization curve, the relative penetrating porosity of nitrided layer can be evaluated.

![Figure 1](image1.png)

**Figure 1** – Polarization curves recorded for SW18 steel, bare and after plasma assisted nitriding N1. Characteristic potentials associated with different carbides (carbo- nitrides) and nitride phase are marked

![Figure 2](image2.png)

**Figure 2** – Change of the position of characteristic potentials, associated with different phases of N10 nitrided SW18 steel along the distance from the specimen surface
Bare structural steel exhibited the active dissolution at anodic polarization in NaCl solution, while nitriding caused the formation of a wide passive region, (Figure 5). The above results showed that the nitriding of structural steel with formation of compact nitride layer should drastically decrease the susceptibility to the corrosion in Cl containing solution. Those data were confirmed by the established in a special test susceptibility to pitting corrosion. At exposition in FeCl₃ solution, the higher number of pits of larger diameter was formed on bare, than on nitrided steel. The more extended passive region of lower passive current density in the case of N60 than N40 specimens (Figure 5) revealed the lower protection ability of layer formed in N40 process.

Those results seem to be in contrast to the results shown in Figures 3 and 4. However, in a pitting corrosion test, the steels subjected to N60 nitriding exhibited deeper pits than steels nitrided in N40 process. This indicated that the different parameters of nitride layer should be accounted for the penetrating porosity and for the passivation and resistivity to pitting corrosion in the Cl containing solutions.
3 Conclusions

Electrochemical method provided the possibility to check the penetrating porosity, corrosion resistance and phase composition of nitrided surface. By selection the appropriate electrolytes, the phase composition and the corrosion resistance of nitride layers formed on SW18, 10A and 45A steels were established in accordance with the material investigation and corrosion tests data.

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