

INFLUENCE OF NITRIDATION AND NITROOXIDATION PROCESSES ON MICROSTRUCTURE AND CORROSION PROPERTIES OF LOW CARBON DEEP-DRAWING STEELS

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Abstract

The aim of this investigation was to analyse the influence of two methods of nitridation- the conventional in ammonia medium and in fluid bed furnace- on microstructure and corrosion resistance of 11 321 (DC 01) low carbon deep-drawing steel sheets. To investigate the combined effect of nitridation as well as subsequent oxidation on given properties two different nitriding temperatures and three oxidation times were chosen.

By application of fluid bed environment it was possible to reach nitrogen affected surface layer into depth from 250 μm up to 270 μm , depending on treatment temperature. The surface saturation by conventional nitridation method was not sufficient and the depth of microstructure surface changes did not exceed 50 μm . Corrosion tests showed, that by use of both nitridation and nitrooxidation processes in fluid bed it is possible to markedly increase the resistance of low carbon deep-drawing steel to atmospheric corrosion as well as to decrease the corrosion rate of the surface. Different time of subsequent oxidation had no significant effect on the final extent of corrosion attack. In spite of insufficient surface saturation during nitridation in gaseous ammonia, these specimen showed the corrosion resistance comparable to former samples. In all cases was the intensity of corrosion attack primarily depending on the sufficient thickness and the continuity of formed surface ϵ - phase.

Key words

low carbon deep-drawing steel, nitridation, nitrooxidation, microstructure, corrosion tests

Introduction

Steels for deep drawing form a separate group of steel sheets and strips. The steels of this grade are produced as cold or hot sheets suitable for further cold processing. They have a good plastic properties, homogeneous in whole forming volume, conforming to the diameter tolerance, the minimal tendency to aging and low price [1-4]. Mentioned properties give them an excellent presumption for successful technical applications, especially in automotive industry [5-7].

Moreover here, more often attempts for lowering of fuel consumption of vehicles at maintaining of mechanical properties on used construction materials led to some investigations on surface treatment technologies of these steel grades. There were some new modified methods of thermochemical treatment. It was also the case of nitridation or nitrooxidation in fluid bed furnace of deep-drawing sheets, where for example good weldability was shown [8-10].

Experimental material and methodology of experiments

In this investigation, the experimental material was low carbon deep-drawing steel 11 321 (DC 01), which chemical composition is presented in Table 1 and its basic characteristics are shown in Table 2.

CHEMICAL COMPOSITION OF INVESTIGATED STEEL [wt.%] Table 1

Steel	C	Mn	S	P
11 321 (DC 01)	0,1	0,45	< 0,03	< 0,03
Steel	C	Mn	S	P
11 321 (DC 01)	0,1	0,45	< 0,03	< 0,03

BASIC CHARACTERISTICS OF EXPERIMENTAL STEEL [11] Table 2

<i>Re</i> [MPa]	max. 235
<i>Rm</i> [MPa]	max. 280 – 380
<i>A₈₀</i> [%]	min. 29

Steel was delivered in the form of sheet with thickness of 2 mm and dimensions 1 x 2 m, in the state after recrystallisation annealing and light re-rolling. From basic dimension of the sheet, samples of size 250 x 250 mm were prepared. These were then subjected to nitridation in fluid bed furnace at temperatures 620 °C and 580 °C and selected samples also to subsequent oxidation in a vapour of distilled water at operating temperature of 380 °C (see Table 3).

SELECTED REGIMES OF THERMOCHEMICAL TREATMENT Table 3

<i>Sample labelling</i>	<i>Furnace environment</i>	<i>Treatment</i>	
		<i>nitridation</i>	<i>oxidation</i>
<i>V</i>	fluid bed	without treatment	
<i>F1</i>		620 °C/ 90 min.	5 min
<i>F2</i>			10 min
<i>F3</i>			15 min
<i>F4</i>			-
<i>F5</i>		580 °C /120 min.	5 min
<i>F6</i>			-
<i>G1</i>	gaseous ammonia	580 °C/ 60 min.	-
<i>G2</i>		580 °C/ 120 min.	-
<i>G3</i>		580 °C/ 240 min.	-
<i>G4</i>		580 °C/ 480 min.	-

As a fluid medium the fine coarsed Al₂O₃ was used, the saturating medium was the ammonia. All samples were after treatment air cooled. Another set of samples was subjected to nitridation in gaseous ammonia at 580 °C. They were cooled in shielding atmosphere down up to 250 °C, then subsequently followed by air cooling. Details of performed sample treatments are summarily listed in Table 3.

Microstructures of samples were evaluated metallographically using light microscope NEOPHOT 30 with application program IMPOR 32.

To clarify the phase composition of all samples the RTG diffractometer PHILIPS PW1710 with a cobalt anode with Bragg-Brentan semifocustion geometry was used. The measurements were focused to obtain information on the phase composition of layer to a depth of ~ 35 µm.

To investigate the depth of oxide layers on nitrooxidised samples as well as the extent of nitrogen saturation the scanning electron microscope SMQA was used. For the measurements the point analysis in direction from the surface was utilized. The accelerating voltage was 20 kV and the downstream was 25 nA.

Sample resistance to atmospheric corrosion was evaluated in the corrosion chamber type ZKO 1 in accordance to the relevant STN 03 813 standard at 100 % relative humidity and temperature 35 °C. The samples were visually evaluated during the test after 16, 48, 72, 96, 144 and 240 hours of exposure. Corrosion resistance of samples in salt environment was evaluated by salt spray test in accordance to STN ISO 9227 standard. The test was carried out in the corrosion chamber VSC-450 type with the salt fog, in the environment of 5 % neutral sodium chloride at 35 °C. Samples were evaluated visually during the test after 1, 4 and 16 hours. Evaluation of corrosion resistance was in both cases focused on the formation of corrosion points on the surfaces of samples after a given period of exposure.

To completely clarify the corrosion properties of treated samples also sensitive electrochemical potentiokinetic reactivation (EPR) test was used. This was performed according to the ASTM G 108 standard in 3% solution of NaCl, the change of potential was 10mV/sec. The whole process was controlled and recorded by computer routine Voltalab 21, the results were in the form of polarization curves. The corrosion rate of steel sheets was then calculated as the reverse value of measured polarization resistance, as it was shown in [12].

Results

- **Microstructure and phase composition**

Microstructure of experimental steel in basic state (V) was composed of polyedric ferrite grains, with tertiary cementite precipitated at grain boundaries. There was observed some heterogeneity in grain size of as-received steel state, its mean value was in rolling direction about 20 μm .

Figure 1 shows the microstructure of the experimental sample after nitridation in fluidized bed furnace at 580 $^{\circ}\text{C}$ (F6). At this process the typical microstructure on the sample surface was produced, to the depth $\sim 250 \mu\text{m}$ below the surface. This can be divided into two typical zones: the compound and the diffusion zone. The compound zone was composed of continuous layer of ϵ - phase (Fe_{2-3}N) with thickness of about 10 μm , below which the layer consisting of ferritic matrix with a needle-shaped nitrides was observed. These were identified by X-ray analysis as Fe_4N nitrides. The total depth of compound zone was about 50 μm . Below first zone the diffusion layer of thickness of about 200 μm was observed, with precipitated fine nitrides Fe_{16}N_2 . Observed microstructure characteristics were also well confirmed by other investigations [13-15].

Figure 2 shows the example of the microstructure of the sample F4 nitrided in fluidized bed furnace at 620 $^{\circ}\text{C}$. In this case the microstructure composition and its total thickness was approximately identical to former sample and it was about 270 μm .

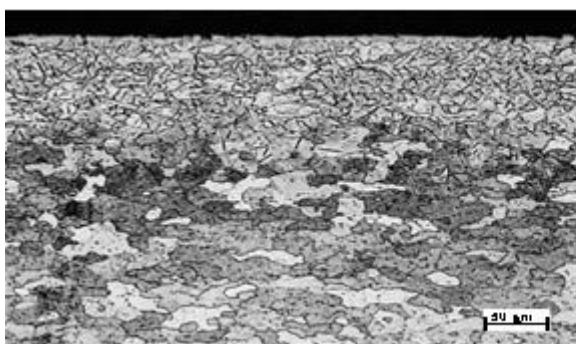


Fig. 1 Microstructure of sample F6 nitrided in fluidized bed furnace at 580 $^{\circ}\text{C}$

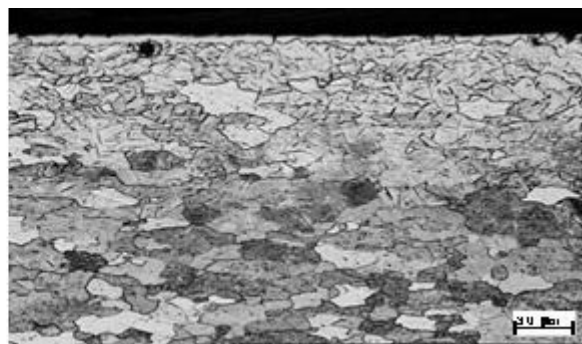


Fig. 2 Microstructure of sample F4 nitrided in fluidized bed furnace at 620 $^{\circ}\text{C}$

Oxide layers on the surface of nitrooxidised samples (F1, F2, F3 and F5) were not observable in light microscope. The presence of oxide layers and their actual phase composition was primarily identified by X-ray diffraction analysis. It was shown that the oxide layers were composed of two oxide types: Fe_2O_3 (hematite) and Fe_3O_4 (magnetite). At the same time from point analysis the approximate thickness of formed oxide layers was

stated (Fig. 3). It was also found out that depending on the time of oxidation there were no significant differences in the thickness of formed oxide layers and these were ranging from 2 to 3 μm .

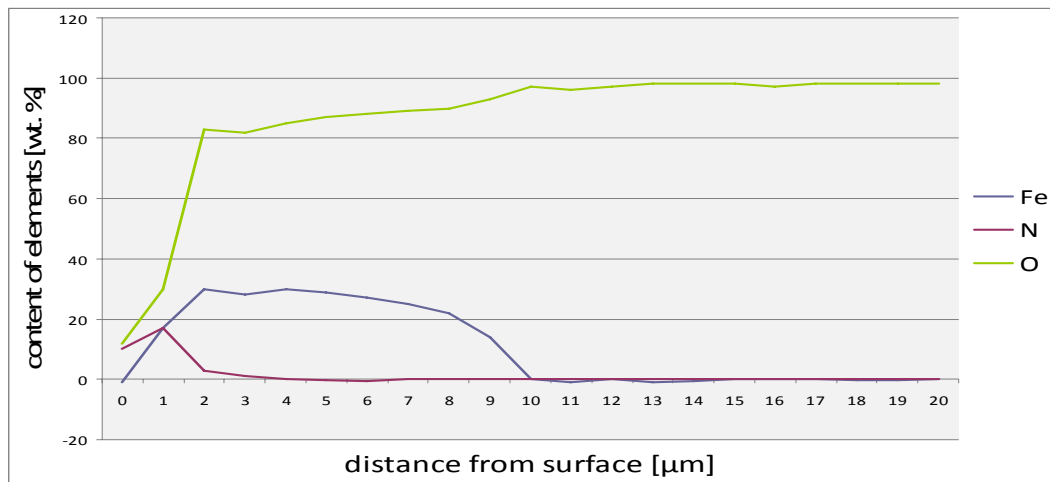


Fig. 3 Example of oxygen, nitrogen and iron concentration profiles of F5 sample surface

Figures 4 and 5 show the examples of microstructures of samples G1 and G4 treated by conventional nitridation process at temperature of 580 $^{\circ}\text{C}$ in furnace with ammonia medium.

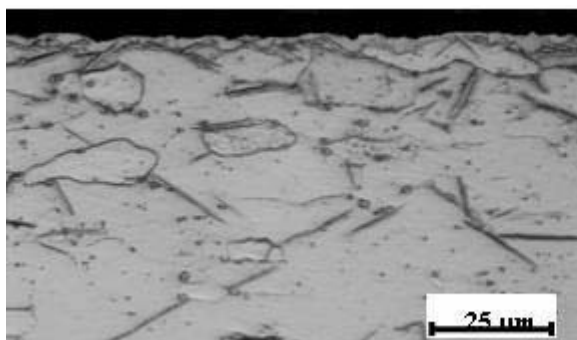


Fig. 4 Example of microstructure of nitrated sample G1

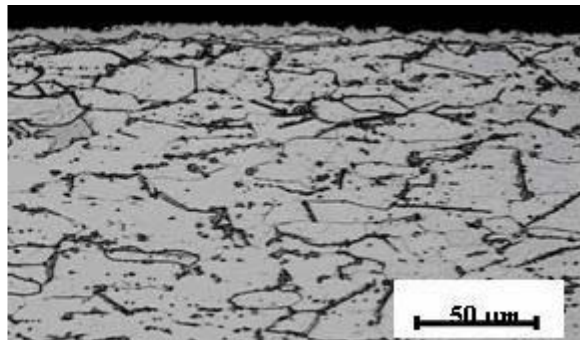


Fig. 5 Example of microstructure of nitrated sample G4

There was formed a typical microstructure on the steel samples treated by conventional nitriding process in ammonia (samples G1 to G4). The surface layer of all samples was composed only of compound zone. The thin ϵ -phase (nitride Fe_{2-3}N) layer of thickness increasing with the time of nitriding from 4 μm up to 10 μm was observed on sample surfaces and well confirmed by point measurement of nitrogen content profile (Fig. 6). Below this continuous layer it was located the ferritic matrix with massive needle-shaped precipitates. These were identified by X-ray analysis as Fe_4N nitrides. The thickness of this zone was on all investigated samples G1 to G4 not exceeding 50 μm .

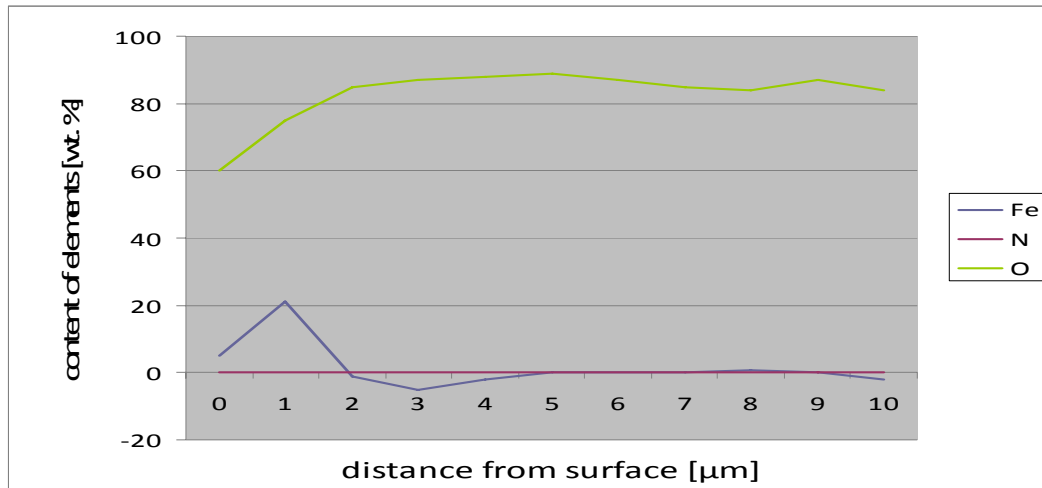


Fig. 6 Nitrogen, oxygen and iron concentration profiles of G1 sample surface

Considering all these results showing absence of diffusion zone and Fe_{16}N_2 nitrides in the microstructure and comparing to observation on samples treated in fluid bed furnace it was stated that the saturation of the surface by nitrogen was by the conventional treatment not sufficient.

- **Corrosion resistance**

All thermochemically treated samples were tested for corrosion resistance in salt environment as well as for atmospheric corrosion resistance.

When tested in salt fog, the corrosion resistance of samples nitrated and nitrooxidised in fluid bed furnace was evaluated in comparison to the basic steel state. Basic state sample showed the corrosion attack at 100% of steel surface after 1 hour of exposure. Therefore the further testing of this sample state was stopped and its corrosion properties were evaluated as insufficient. Figure 7 shows the example of the fluid bed furnace samples appearance after 16 hours of exposure in salt fog. Despite of rapid corrosion attack on samples tested in salt fog environment it was shown, that the samples nitrooxidised in fluid bed have a better corrosion resistance than sample nitrated in this environment.

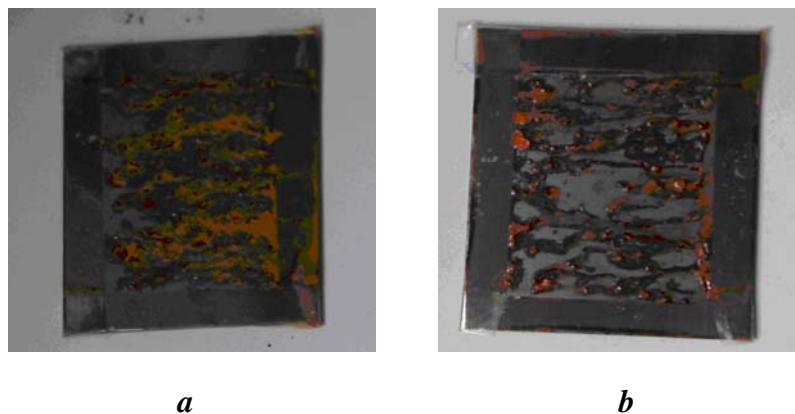


Fig. 7 Samples after 16 hours of exposure in salt fog:
a) sample F6: 90% of attacked area; b) sample F5: 70% of attacked area

Figure 8 shows an example of the appearance of samples treated in fluid bed after corrosion test in the condensation chamber. It was evaluated the corrosion resistance of nitrooxidised sheets itself as well as compared to basic steel state and nitrided samples.

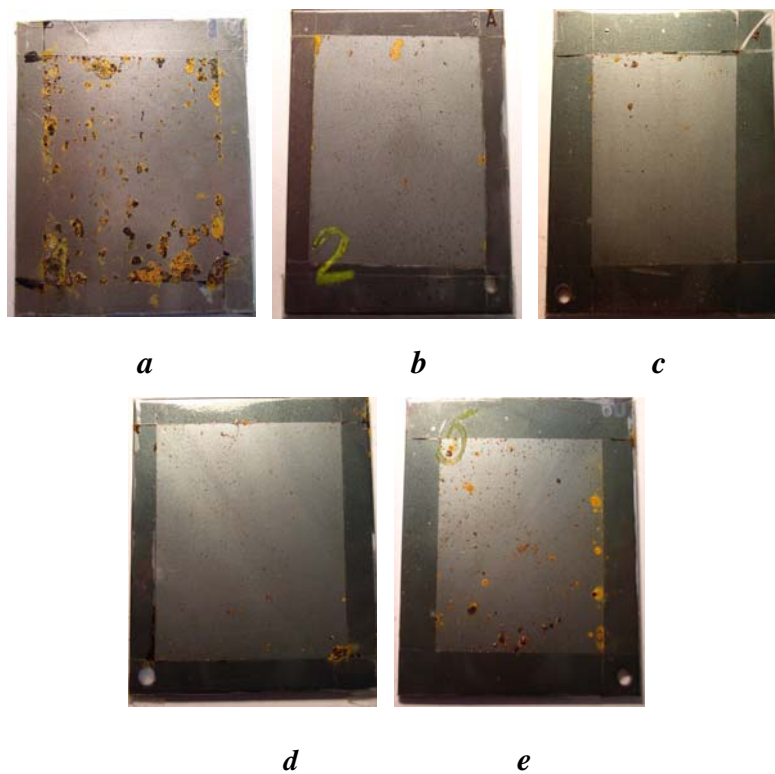


Fig. 8 Samples after 240 hours of exposure in the condensation chamber: a) sample V; b) sample F1; c) sample F2; d) sample F3; e) sample F4

The difference between the nitrooxidised samples was recorded only in terms of the onset of corrosion points (Table 4). The results showed that nitrooxidised samples had a better corrosion resistance in conditions of high humidity and condensation of water than the sample nitrated as well as the specimen in basic state. Basic sample state had the worst atmospheric corrosion resistance and therefore it was classified as insufficient. The corrosion resistance of nitrooxidised samples compared to basic state, was depending on regime 8-times increased. Based on atmospheric corrosion results as the most suitable regime of experimental steel treatment in fluid bed furnace was suggested the nitridation at 620 °C and subsequent oxidation. It was shown that surface oxidation time had not distinctive influence on the final extent of corrosion attack on these samples. In terms of development of atmospheric corrosion attack was suggested as the best to oxidize sheets for 10 minutes.

SUMMARY OF RESULTS OF CONDENSATION CHAMBER TEST
FOR EXPERIMENTAL SAMPLES

Table 4

<i>Sample labelling</i>	<i>Exposure of</i>				
	<i>16 hours</i>	<i>48 hours</i>	<i>72 hours</i>	<i>144 hours</i>	<i>240 hours</i>
<i>V</i>	attacked 1% of area	attacked 5% of area	attacked 10% of area	attacked 15% of area	attacked 25% of area
<i>F1</i>	2 corrosion pits	attacked 1% of area	attacked 2% of area	attacked 2% of area	attacked 3% of area
<i>F2</i>	without cor. attack	2 corrosion pits	5 corrosion pits	attacked 1% of area	attacked 3% of area
<i>F3</i>	6 corrosion pits	8 corrosion pits	attacked 1% of area	attacked 1% of area	attacked 3% of area
<i>F4</i>	attacked 1% of area	attacked 2% of area	attacked 3% of area	attacked 3% of area	attacked 5% of area
<i>F5</i>	2 corrosion pits	6 corrosion pits	attacked 0,5% of area	attacked 2% of area	attacked 5% of area
<i>F6</i>	attacked 1% of area	attacked 1,5% of area	attacked 4% of area	attacked 15% of area	attacked 20% of area
<i>G1</i>	attacked 1,5% of area	attacked 2% of area	attacked 3% of area	attacked 5% of area	attacked 8% of area
<i>G2</i>	without cor. attack	2 corrosion pits	5 corrosion pits	attacked 1% of area	attacked 3% of area
<i>G3</i>	2 corrosion pits	8 corrosion pits	attacked 1,5% of area	attacked 2% of area	attacked 4% of area
<i>G4</i>	attacked 1,5% of area	attacked 4% of area	attacked 5% of area	attacked 10% of area	attacked 12% of area

The corrosion test results for samples treated by nitridation in furnace with ammonia environment showed that their resistance to atmospheric corrosion is comparable to that observed for samples nitrooxidised in fluid bed furnace. The comparative results of corrosion behavior can be achieved by conventional steel nitridation for 4 to 6 hours (Table 4). Based on a comparison of all corrosion test results obtained from condensation chamber it was shown that the decisive influence on the atmospheric corrosion resistance had the thickness of nitride $Fe_{2-3}N$ (ϵ - phase), which was reflected primarily in samples treated in ammonia medium. Example of appearance these samples after the corrosion test in the condensation chamber are shown in Fig. 9.

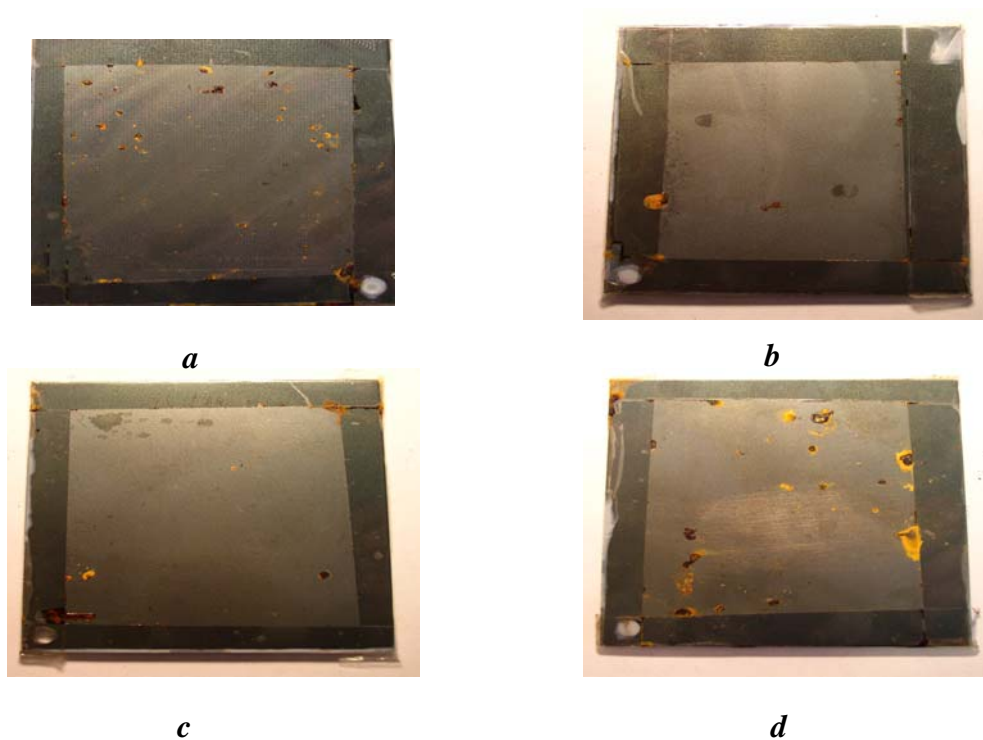


Fig. 9 Appearance of samples treated in the gas after corrosion test in the condensation chamber: a) G1; b) G2; c) G3; d) G4

To clarify the corrosion behaviour of investigated samples the electrochemical potentiokinetic reactivation (EPR) test was carried out. Results of this test are summarized in Table 5.

RESULTS OF EPR TEST FOR EXPERIMENTAL SAMPLES

Table 5

<i>Sample labelling</i>	<i>Maximum current density measured</i> $J_k [\mu A.cm^{-2}]$	<i>Polarisation resistance</i> $R_p [kohm.cm]$	<i>The current rate of corrosion test</i> $[mm/year]$
<i>V</i>	8,9975	2,67	3,75
<i>F1</i>	4,6968	9,7	1,03
<i>F2</i>	3,1363	9,16	1,09
<i>F3</i>	4,0564	13,32	0,75
<i>F4</i>	3,7984	6,73	1,49
<i>F5</i>	1,2191	14,14	0,71
<i>F6</i>	2,2164	7,27	1,38
<i>G1</i>	4,4000	6,34	1,58
<i>G2</i>	2,5700	25,15	0,40
<i>G3</i>	20,270	13,60	0,74
<i>G4</i>	5,3100	7,48	1,34

From Table 5 it is clear that the greatest current density in loop and consequently the maximum corrosion rate of 3,75 mm/year was recorded for basic state steel (V).

Similar corrosion behavior as in the condensation chamber test was also recorded for samples treated in fluid bed furnace. The lowest rate of corrosion among these samples showed the specimen nitrided at 620 °C and then oxidized (samples F1- F3), but the lowest rate of corrosion was recorded for sample oxidized for 15 minutes (F3). For sample nitrided in fluid bed furnace (F4) was compared to nitrooxidised samples the corrosion rate about 1,49 mm/year. Moreover, it can be concluded that the values of corrosion rate of samples nitrided in fluid bed furnace were quite similar, so the effect of temperature in the nitriding environment for this test was shown to be insignificant.

Satisfactory corrosion behavior during the EPR test was recorded for samples treated in furnace with ammonia medium. As can be seen from Table 5, the lowest rate of corrosion was recorded for sample G2. EPR test showed, that the samples G1 and G2 have similar corrosion properties as they were observed in the previous methods for evaluation of corrosion resistance. The highest value of corrosion rate was determined for sample G1, nitrided for shortest time in the gas environment.

Based on summary of EPR test results was the corrosion resistance of basic state steel classified as poor. According to calculated rates of corrosion it can be further stated that nitrooxidised samples have better corrosion resistance than the sample nitrided in a fluid bed environment, irrespective of the treatment temperature. Oxidation was not significantly influencing the values of corrosion rate of samples.

The test results also showed, that to achieve adequate corrosion resistance it is sufficient to nitride the samples in ammonia for 4 to 6 hours, and then the results are comparable to the corrosion properties of samples using of fluid layer. In determination of the effect of increasing the corrosion resistance of nitrided specimens had sufficient influence the depth and continuity of Fe_{2-3}N (ϵ - phase) surface layer.

Conclusions

The aim of this investigation was to compare the influence of two methods of nitridation and subsequent nitrooxidation process, respectively, on microstructure and corrosion properties of low carbon deep-drawing steel sheets. The obtained results can be summarized as follows:

- the nitridation in fluid bed furnace affected the microstructure of the surface to a depth of $\sim 250 \mu\text{m}$ to $270 \mu\text{m}$, depending on the nitriding temperature. Surface layer of steel was then divided into two typical zones: so-called compound layer, consisting of a continuous thin layer of ϵ - phase (Fe_{2-3}N) followed by ferritic matrix with precipitated large needle-shaped Fe_4N nitrides. The second- diffusion zone was consisting of ferritic matrix with very fine precipitated Fe_{16}N_2 nitrides.
- on the surface of samples after nitrooxidation in fluidised layer the presence of two-phase oxide layer consisting of Fe_2O_3 and Fe_3O_4 was shown.
- on the surface of the samples treated by conventional nitridation at 580 °C in gaseous ammonia a complex microstructure was formed, consisting only of a zone with a thin continuous layer of ϵ - phase. Its thickness has risen with nitriding time to about $10 \mu\text{m}$. Below this the ferritic matrix with massive needle-shaped precipitates Fe_4N was located.

The thickness of this area did not exceed on all samples the value of 50 μm . The typical diffusion zone was not observed in these samples.

- the depth of elements saturation and its influence on subsequent phase composition of surface were verified by oxygen and nitrogen concentration profiles measurements.
- using the process of nitridation and nitrooxidation in fluidized bed the increased corrosion resistance in salt environment as well as increased atmospheric corrosion resistance were recorded. It was shown that the time of oxidation had no significant effect on the final extent of corrosion attack after testing in condensation chamber. In terms of atmospheric corrosion resistance as the most suitable the regime consisting of nitridation at 620 °C and subsequent oxidation for 10 minutes was suggested.
- corrosion resistance of samples treated by conventional nitridation in ammonia medium was comparable to the resistance of samples nitrooxidised in fluid bed furnace. The comparative results of corrosion behavior can be achieved by nitridation for 4 to 6 hours. The intensity of corrosion attack was primarily depending on the sufficient thickness and the continuity of ϵ - phase.
- based on results of EPR test can be concluded that irrespective to temperature of treatment nitrooxidised samples achieved lower corrosion rates than the sample nitrided in fluid bed. Oxidation was not significantly affecting the values of the actual corrosion rate. EPR test for samples nitrided in conventional ammonia medium showed a comparable corrosion rates to samples treated in a fluid bed. It was sufficient to nitride samples here from 4 to 6 hours, with the decisive influence of thickness of surface ϵ - phase layer.

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