# Material Characteristics of Low Carbon Steel Sheets Treated by Nitro-Oxidation in Fluid Environment

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**Abstract:** The paper deals with a detailed analysis of deep drawing DC 01/DIN EN 10130-9 steel sheets of 1 mm in thickness treated by nitro-oxidation in fluid environment. The nitridation at 580°C/45 min and oxidation at 350°C/5 min was used. The surface $Fe_3O_4$ and $Fe_2O_3$ oxide layer, as well as the presence of $Fe_{2-3}N$, $\gamma'$-$Fe_4N$ nitrides and ferritic matrix, was proved by X-ray diffraction. The $Fe_{2-3}N$ nitrides formed a continuous $\varepsilon$-phase of 7,1 μm in thickness with the microhardness 6,5 times higher than the base material. Corrosion resistance test revealed the highest level according to STN EN ISO 10286/C standard in comparison to the non-treated material. Analysis of mechanical properties showed a significant increase of tensile strength. Ductility decreased approximately by 7,5 %. Erichsen cupping test showed a 15 % decrease of Erichsen cupping index. Fukui deep-drawing test of nitro-oxidised steel exhibited 1,5 % increase of "m" deep-drawing coefficient.

**Keywords:** corrosion; low carbon steel; mechanical properties; nitro-oxidation

## 1 INTRODUCTION

Development of new materials is frequently focused on increasing their mechanical, tribological and corrosion and wear-resistance characteristics [1, 8]. Recently, surface modification of engineering materials has become a fast developing field of materials science. The most widely used surface modification processes comprise the ones providing a nitrogen layer deposition or nitrogen implantation. These processes however pertain to the most financially demanding. Therefore, besides the development of new methods of surface treatment, the research focuses also on the innovation of already known thermo-chemical treatment processes, including nitro-oxidation in fluid layer, where oxidation follows the surface saturation by nitrogen [2, 7].

The nitro-oxidation process developed by a German company is known as TUFFTRIDE process in nitrogen salts. Used under this name in English-speaking and Asian countries, the process is denoted as TENIFER in Europe and German-speaking countries, and as MELONITE in the USA. TUFFTRIDE, QPQ, TENIFER and MELONITE are registered trademarks of Durferrit GmbH [3].

Despite lower environmental impact and lower cost when compared to the nitrogen salts and cyanides typical for the above mentioned TUFFTRIDE process, the application of nitro-oxidation by utilizing fluid technology is not widely known [4].

The nitro-oxidation process is applicable particularly for the steel components where prolonged lifetime is a prerequisite (mainly for the components operating in humid environments). Weight of the components can also be decreased by increasing the strength and other required mechanical properties of a material [5]. Currently, these factors are being applied in special equipment as well as in automotive and consumer goods industries.

The nitro-oxidation brings the biggest benefit in the field of alloyed steels, e. g. Cr-Mo steels, where nitrides of chromium are formed [9]. Yet the main objective of this paper was to provide a deep analysis of the nitro-oxidation influence on low carbon steel sheets.

## 2 MATERIALS AND METHODS

The material used for the experiments was DC 01/DIN EN 10130-9 (1.0330/EN 10130:2006) thin steel sheet of 1 mm in thickness. The typical chemical composition of the material is given in Tab. 1.

**Table 1** Chemical composition of DC 01/DIN EN 10130-9 steel

| EN Marking | C (%) | Mn (%) | P (%) | S (%) | Si (%) |
|---|---|---|---|---|---|
| DC 01 | 0,12 | 0,60 | 0,045 | 0,045 | 0,1 |

The thermo-chemical treatment by nitro-oxidation in fluidised bed consisted of nitridation immediately followed by oxidation. Fluidized medium was composed of $Al_2O_3$ with the grain size of 120 μm. The waft of the fluidized medium was provided by gaseous ammonia which simultaneously acted as a source of nitrogen. During the oxidation process, the vapour of distilled water was supplied to the furnace chamber. The parameters of nitro-oxidation treatment are shown in Tab. 2.

**Table 2** Nitro-oxidation treatment parameters

| Group | Nitridation | Oxidation |
|---|---|---|
| 1 | – | – |
| 2 | 540 °C / 45 min | 380 °C / 5 min |
| 3 | 580 °C / 45 min | 350 °C / 10 min |
| 4 | 580 °C / 45 min | 350 °C / 15 min |

In order to investigate microstructure of the treated material, the optical, scanning and transmission electron microscopy was used. The identification of surface oxides and the phases present in material was evaluated by X-ray diffraction and electron diffraction respectively. The chemical composition of the surface layer was examined by GDOES analysis. The mechanical properties were evaluated by tensile strength test (ISO 4136, ISO 6892-1) and microhardness measurement. Erichsen cupping test (ISO 20482:2013) and Fukui test were carried out in order to examine the influence of nitro-oxidation process on formability. The Fukui conical cup test involves both stretching and drawing over a ball. The diameter of the ball was 17,6 mm. The diameter of the base of the conical cup formed is determined and divided by the diameter of

the original specimen to provide the Fukui conical cup value.

The evaluation of corrosion resistance was performed in a condensed water test chamber.

## 3 RESULTS

The attained results were organised into several parts, focusing on material analysis, corrosion resistance, as well as mechanical and technological properties.

### 3.1 Structural Analysis

Nitro-oxidation treatment in our research influenced the base metal into the depth of about 260 µm in thickness, while the depth consisted of two zones (Fig. 1). The first zone, also called a compound layer, consisted of a continuous thin $Fe_3O_4$ a $Fe_2O_3$ layer of 0,3 to 0,7 µm in thickness, $\varepsilon$-phase ($Fe_{2-3}N$) with approximate thickness of 7 µm and a layer of ferritic matrix with needle-shaped $\gamma'$-$Fe_4N$ nitrides (Fig. 2) connected to $\varepsilon$-phase. Total thickness of the compound layer was approximately 50 µm.
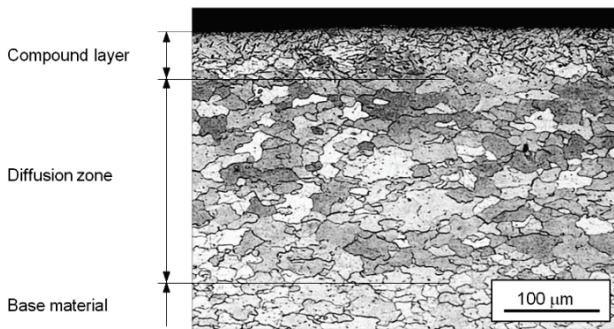


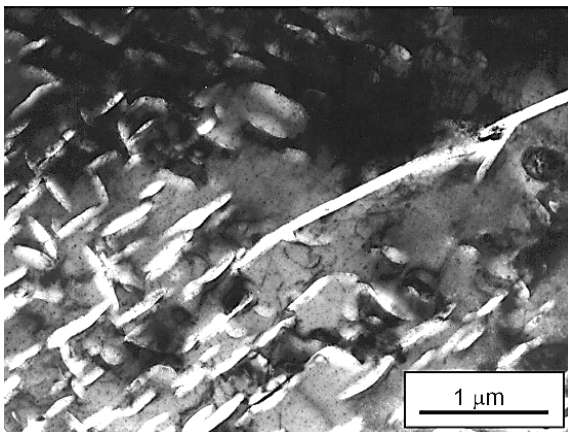**Figure 1** Microstructure of nitro-oxidised low-carbon steel DC 01



**Figure 2** Detail of ferritic matrix with needle-shaped $\gamma'$- $Fe_4N$ nitride

The second zone, a diffusion layer, was connected to the compound layer and formed the transition to the base material. The diffusion layer consisted of the ferritic matrix with dispersed fine $\alpha''$- $Fe_{16}N_2$ precipitates (Fig. 3) with the thickness of approximately 210 µm.

Figs. 4 and 5 present the surface layer after nitro-oxidation process. The diffraction spectrum of the surface layer, confirming the presence of $Fe_2O_3$ and $Fe_3O_4$ oxides as well as $Fe_{2-3}N$ and $Fe_4N$ nitrides and ferritic matrix, is shown in Fig. 6.
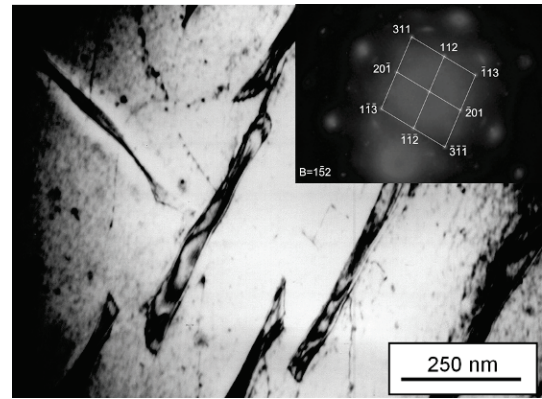


**Figure 3** Precipitated needle-shaped tetragonal nitrides $\alpha''$- $Fe_{16}N_2$ in diffusion zone
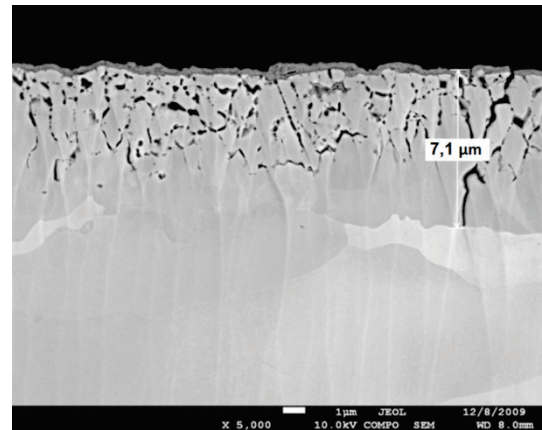


**Figure 4** Structure of ε-phase layer with a thickness of 7,1 µm
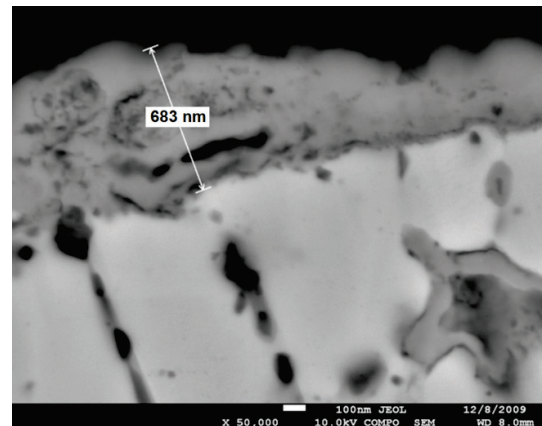


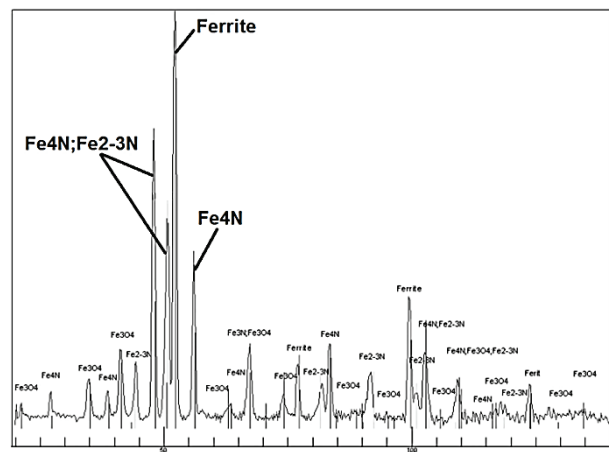**Figure 5** Detailed view of surface oxide layer after 5-minute oxidation



**Figure 6** Diffraction X-ray spectrum of the nitro-oxidised DC01/DIN EN 10130-9 steel surface

## 3.2 GDOES Analysis

The analysis confirmed a high content of oxygen near the surface, thus indicating the presence of oxide layer across the depth of approximately 0,5 µm. A higher content of nitrogen observed from 0,5 to 7 µm beneath the surface, represented the ε-phase layer (Fig. 7).
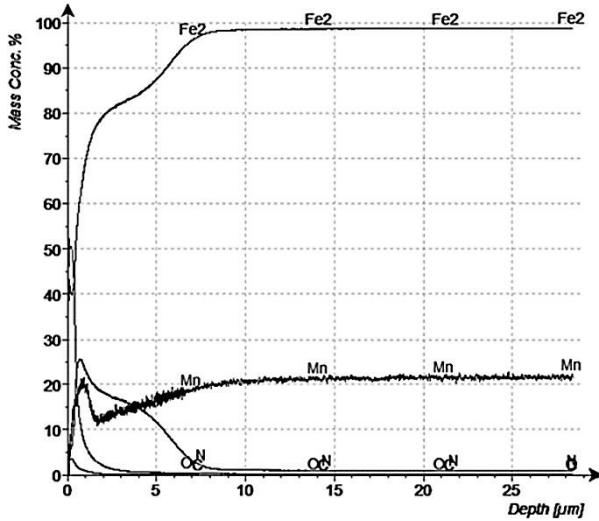


**Figure 7** Results of GDOES analysis of the surface layer

## 3.3 Corrosion Resistance Properties

The material treated by nitro-oxidation was tested for the corrosion resistance in KB 300 condensation chamber at the temperature of $35 \pm 0.1$ °C in a distilled water environment. The corrosion attack was analysed after 16, 48, 72, 144 and 240 hours respectively and evaluated by gravimetric analysis. Results of the gravimetric analysis are presented in Tab. 3.

**Table 3** Nitro-oxidation treatment parameters

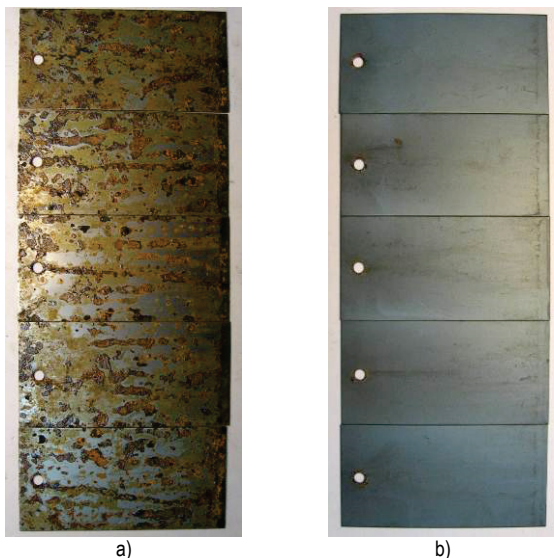| State | Exposure time (h) | | | | |
|---|---|---|---|---|---|
| | 16 | 48 | 72 | 144 | 240 |
| | Mass increase (g/m²) | | | | |
| Without nitro-oxidation | 0,05 | 0,18 | 0,64 | 6,99 | 8,49 |
| After nitro-oxidation | 0,08 | 0,08 | 0,11 | 0,12 | 0,13 |



a)            b)

**Figure 8** Sample appearance after 240 h of corrosion resistance test: a) base material without treatment, b) material treated by nitro-oxidation

The appearance of the samples after 240 hours of corrosion test is presented in Fig. 8. The nitro-oxidised steel exhibited the highest possible level of atmospheric corrosion resistance (level 10 according to STN EN ISO 10286/C standard) in comparison to the non-treated steel [5].

The corrosion resistance depends significantly on continuity of ε-phase layer. If cracks are present in the surface layer, material is more sensitive to corrosion. It is therefore very important to strictly control the nitro-oxidation process.

## 3.4 Analysis of Mechanical Properties

Measurements of mechanical properties comprised a tensile strength test and microhardness measurements.

The transverse tensile test was carried out according to ISO 4136 and ISO 6892-1 standards. The data obtained and calculated from the tensile test are shown in Tab. 4.

**Table 4** Nitro-oxidation treatment parameters

| Group | $R_e$ (MPa) | $R_m$ (MPa) | $A_{10}$ (%) |
|---|---|---|---|
| 1 | 200 | 282,3 | 31,2 |
| 2 | 308 | 377,3 | 23,7 |
| 3 | 304 | 400,7 | 23,7 |
| 4 | 307 | 383 | 23,3 |

The typical tensile test graph of steels with and without nitro-oxidation treatment is shown in Fig. 9 (the graph showing the test results after surface treatment applies also to the other two groups, as the results were similar).
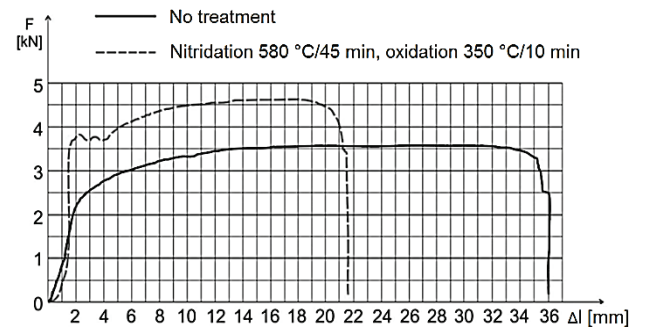

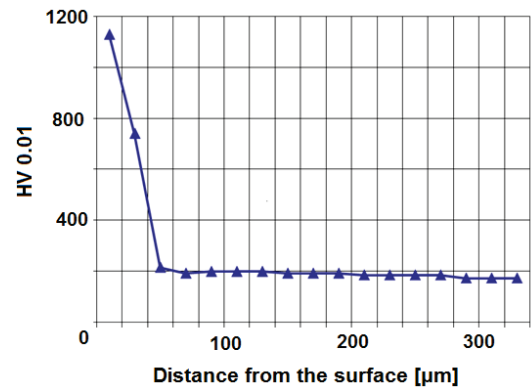
**Figure 9** Tensile test graph of selected samples



**Figure 10** Microhardness measurement of surface layer

Tensile test exhibited the maximum strength enhancement of 34÷42 % for nitro-oxidised materials, and also yield strength enhancement of 52÷54 %, in

comparison to the base material without treatment. Ductility decreased approximately by 7,5 %. The differences among the treated groups were insignificant, representing about 6 %.

Maximum hardness of 1 130 HV 0.01 was observed in the nitro-oxidation layer, where the surface micro-hardness increased by 653 %, when compared to the steel without nitro-oxidation treatment (Fig. 10).

## 3.5 Technological Properties

Erichsen cupping test performed according to ISO 20482:2013 showed a 15 % decrease of Erichsen cupping index, while the Fukui deep-drawing test of nitro-oxidised steel exhibited a 1.5 % increase of "m" deep-drawing coefficient.

The increase of deformation caused the increase of damage of $\varepsilon$-phase layer. The enhanced fragility was dominant only in the surface $\varepsilon$-phase layer characterised by extensive porosity (Fig. 11).
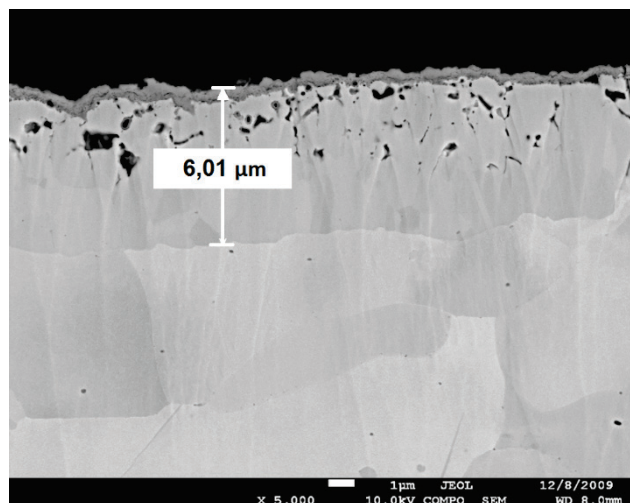


**Figure 11** Presence of porosity in surface layer

On the other hand, the presence of porosity or micro cracks was not observed in the zone composed of ferrite matrix and precipitated $\gamma'$-$Fe_4N$ and $\alpha''$-$Fe_{16}N_2$ nitrides. This indicates that the precipitated nitrides did not have a significant influence on the microstructure change during the forming process, and did not initiate the damage in the surface area of material after nitro-oxidation. The nitride layer is in the state of high internal pressure strain which is opposite to the tensile strain generated during the forming process, thus postponing the cracks initiation.

## 4 DISCUSSION

The parameters of nitro-oxidation can significantly influence the final properties of material. In case of thin sheets, it is important to preserve the original properties of material in the centre. If the excessive thickness of surface layer is formed, substantial structural changes can be observed within the whole cross-section of material. Temperature and time can be therefore considered as the key parameters of the nitro-oxidation process. Regarding the above mentioned, it was necessary to find the appropriate parameters providing a suitable structural influence of the base material, while keeping the

properties important for the subsequent processing of material (forming and welding). Another objective was to produce a continuous surface layer creating a barrier from the surrounding environment and providing the enhanced corrosion resistance.

Having chosen the parameters of the process properly, the nitro-oxidation brings about a positive change in the base metal microstructure. The experiment proved the corrosion resistance of the highest level according to the STN EN ISO 10286/C standard in comparison to the non-treated steel.

Increase of mechanical properties, particularly the yield point (approximately by 53 %) and tensile strength (approx. by 38 %), was observed. The material after nitro-oxidation exhibits a noticeable yield point. As the material is not alloyed, we can assume that the distinct yield point is related to the formation of Cottrell's atmosphere of nitrogen at the dislocation neighbourhood. On the other hand, the increase of tensile strength is related to the precipitation hardening. Therefore, the drop of ductility from 31,2 % to 23,7 % was observed. The oxidation stage in nitro-oxidation process has the minimum or no influence on mechanical properties of the treated materials. In order to prove this assumption, further investigation using DOE should be carried out.

The depth of the indentation, also referred to as Erichsen cupping index, dropped only by 15 %. Regarding the relatively positive results of deep drawability by Erichsen cupping test, the ductility drop can be considered as less significant.

Microhardness values correspond with the character of the analysed microstructure. The nitro-oxidation process caused an enormous increase of the surface layer microhardness (6,5 times) in comparison to the base material. This increase was observed only in ε-phase layer, whereas the microhardness of the other part of the compound layer as well as the diffusion zone exhibited the values similar to the base material. Enhanced surface hardness positively influences tribological properties of the material treated by nitro-oxidation [6].

## 5 CONCLUSIONS

The nitro-oxidation treatment is mostly used with the tools, constructions and final products without further processing. Nitro-oxidation performed in fluid environment is more environmental friendly than nitro-oxidation process carried out in salt baths.

Applying this process on thin deep-drawing steel sheets, a valuable construction material capable of further processing can be obtained.

The results of analyses proved the presence of nitride and oxide layers on the surface, which significantly influenced the base material characteristics. After nitro-oxidation treatment, the material showed enhanced corrosion resistance and improved certain mechanical properties.

In order to obtain a continuous surface layer important for good corrosion resistance, precise control of the process parameters is necessary. Plasma nitro-oxidation also known as PLASOX process presents a competitive technology to nitro-oxidation in fluid environment. This process should provide a porous-free

surface layer, which will be the subject of further research into the possibility of further technological processing following nitro-oxidation.

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