IMPROVING THE CORROSION RESISTANCE OF COMPONENTS MADE FROM STRUCTURAL STEELS

POVEČANJE KOROZIJSKE ODPORNOSTI DELOV IZ KONSTRUKCIJSKIH JEKEL

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The corrosion resistance of structural steels can be enhanced considerably by using combined processing that consists of a chemical heat treatment followed by oxidation and an oil-bath immersion. Ferritic nitro-carbuirising, which forms a white compound layer on the surface, is the preferred method for the first processing step. The oxidation can be carried out either with water or N_2O, but water is the preferred oxygen donor, mainly for ecological reasons. As the final step, the components are immersed in an oil tank and cooled down to a room temperature.

This paper presents with the application of the process to improve the corrosion resistance of specimens of 41 Cr S4 V steel. The gaseous nitro-carbuirising was carried out in partially cracked ammonia combined with endo-gas. To form the oxide layer, water was added to the atmosphere for the final period of the treatment. Finally, the specimens were cooled down to 300 °C and immersed in an oil bath. The processing was optimised in terms of the optimum thickness and composition of the "white" compound layer as well as the oxide layer. The optimisation of all processing parameters led to an excellent corrosion resistance: more than 300 h in a salt-spray chamber before the first corrosion tracks appeared. This level of resistance is appropriate for applications in automotive industry.

Key words: nitro-carburising, oxidising, structural steels, corrosion resistance

Korozijsko odpornost konstrukcijskih jekel je mogoče zelo povečati z uporabo kombiniranega procesa s kemotermično obdelavo površine, oksidacijo in končno potopitvijo v oljno kopel. Feritna nitrocementacija, pri kateri na površini nastane bela plast, se največ uporablja kot prva stopnja procesa. Sledi oksidacija z vodno paro ali N_2O, vendar je zaradi ekoloških razlogov para primernejši vir kisika. V končni stopnji se deli potopijo v oljno kopel in ohladijo do sobne temperature.

V članku je predstavljena uporaba tega procesa za povečanje korozijske obstojnosti vzorcev jekla 41 Cr S4 V. Nitrocementacija je bila izvršena v delno razpadlem amonijaku, kombiniranem z endo plinom. Vodna para je bila dodana v zadnji fazi obdelave za oksidacijo. Na koncu so bili vzorci ohlajeni na 300 °C in potopljeni v oljno kopel. Obdelava je bila optimalna s stališča debeline in sestave belega spojinskega in oksidnega sloja. Z optimizacijo vseh parametrov obdelave je bila dosežena zelo dobra korozijska odpornost, in prvi sledovi korozije so se pojavili po več kot 300 h izpostave v komori s slano meglo. Ta nivo korozijske odpornosti je zadosten za uporabo v avtomobilski industriji.

Ključne besede: nitrocementacija, oksidacija, konstrukcijsko jeklo, odpornost proti koroziji

1 INTRODUCTION

Increased demands on the reliability of machine components, in particular in automotive industry, motivate the search for new technologies used for the processing of metallic materials. One of the most important properties of external automotive components is their corrosion resistance. These components often work in very difficult conditions – mostly in an environment of high humidity, combined with aggressive media like salt or other chemical constituents. These constituents increase the corrosion rate of steel parts significantly, and it is very difficult to preserve these parts for a sufficient length of time.

One of the possible ways to improve the corrosion, as well as wear resistance of machine components from iron alloys is nitro-carburising with a subsequent oxidation and oil immersion. Nitro-carburising is a widely used technique for improving the complex surface properties of structural steels. Normally, the process is carried out in a ferritic state, at a temperature in the range 560–620 °C for several hours, in an atmosphere consisting of partially cracked ammonia with addition of a carbon-containing constituent (endo-gas, propane). The preferred structure of the surface is a "white" compound layer of appropriate thickness – the optimum thickness is about 20 μm [1]. The desired phase and chemical compositions are represented by a homogeneous ε-phase on the surface and at least 8.6 % of overall N and C mass fraction content in this layer [2] when a corrosion resistance over 200 h has to be achieved. Finally, the diffusion intermediate region in between should have a thickness of 0.3 mm. However, opinions on how the optimum nitrided case has to appear are a little different, varying from author to author, **Table 1** [1–3], and probably depend on practical experiences.

The parameters of the oxidizing can be obtained in three basic ways. The first possibility is to use as oxidant N_2O, but this is associated with some problems, mainly with respect to processing regulations. The second, and preferred method, is the input of water into the furnace chamber during the last stage of the treatment. The third method is to input air into the furnace chamber during

Table 1: Examples of treatments for the formation of protective, corrosion-resistant layers. NH₃ – partially cracked ammonia, L – air, Endo – endo-gas, CₓHᵧ – hydrocarbon gas as a carbon-containing constituent [3]

Tabela 1: Primeri obdelave za pripravo varovalnih plasti, odpornih proti oksidaciji. NH₃ – delno razpadli amonijak, L – zrak, Endo – endo-plin, CₓHᵧ – ogljikovodik kot nosilec ogljika [3]

	Nitro-carburising at 580 °C for 4–5 h	Oxidizing (Temperature/time/Gas)	Cooling	Compound layer (μm)	Oxide layer (μm)	Corrosion resistance
1	NH_3 + Endo	520/60 min/Endo + L	furnace	19	3	112
2	NH_3 + Endo - C_xH_y	450/75 min/NH_3 + Endo + L	furnace	22	1.5	392
3	NH_3 + CO_2	450/75 min/NH_3 + L	furnace	24	1.8	400
4	NH_3 + Endo - C_xH_y	450/75 min/NH_3 + Endo + L	furnace	18	1.5	216

the last period of the processing. The preferred thickness of the oxide layer was reported to be 1–2 μm [1], and the layer has to consist only of magnetite (Fe_3O_4).

At the end of the treatment, the pieces must be immersed in an oil bath and cooled down to room temperature. The temperature from which the material is cooled is not fixed; it depends mainly on the practice of the hardening crew, but also on the type of oil, etc.

2 EXPERIMENTAL

Specimens and machine parts (front-axle ball joins) from the 41 Cr S4 V (0.38–0.45 % C, 0.9–1.2 % Cr, 0.05–0.08 % S) steel and heat treated to a hardness of 260–270 *HBW* 2.5/187.5 were surface processed. Before the processing, see Table 2 for details, the specimens and parts were polished. The surface treatment consisted of: nitro-carburising in a mixture of partially cracked ammonia and endo-gas, oxidizing in water vapour, furnace cooling down to 300 °C and then rapidly in an oil tank to room temperature.

The microstructure was assessed using light microscopy. The hardness depth profiles were measured with the Vickers method, using a load of 300 g (*HV* 0.3). For the evaluation of nitrogen, carbon and oxygen saturation of the surface, the GDEOs was used. X-ray diffraction was used for the analysis of the phase constitution of the compound layers as well as the oxide

layers. The corrosion resistance was investigated with salt-spray-chamber corrosion testing. The measure for the minimum corrosion resistance was a surface without any signs of corrosion after 240 hours.

3 RESULTS AND DISCUSSION

Figure 1 shows the microstructure of the surface region processed using processing route 1. On the surface there is a "white" compound layer with a thickness of 18 μm. The oxide layer is not clearly visible on the micrograph. The diffusion region with the presence of dispersed carbo-nitrides is located underneath. As shown in **Figure 2**, the oxide layer formed on the surface had a thickness of 1 μm. However, the compound ε-layer did not exhibit the recommended overall nitrogen and carbon concentration; this was a little below the limit of the mass fraction 8.6 %, which is recommended for achieving a suitable corrosion resistance. A slightly worse saturation of the surface is reflected in the hardness profile, **Figure 3**. As shown in this figure, the required nitriding case depth was not reached, but the difference between that and the real value is not significant. Although some of the parameters
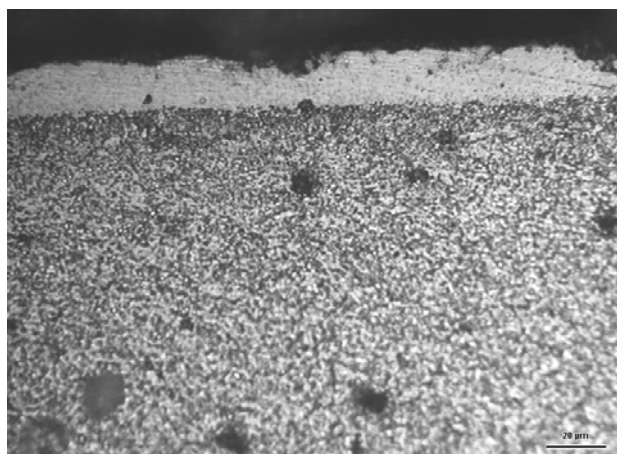
**Figure 1:** Microstructure of the surface after processing route 1
Slika 1: Mikrostruktura ob površini po obdelavi 1
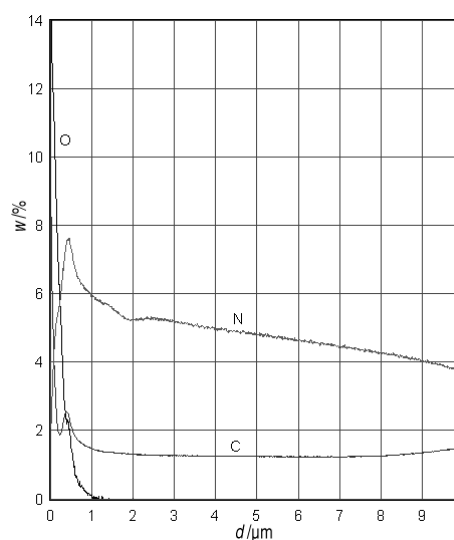
Figure 2: GDEOS depth profiles of the interstitials in the compound layer.
Slika 2: GDEOS globinski profil intersticijev v spojinski plasti

Table 2: Overview of processes and parameters. *Nitriding potential calculated according the formulas given by Somers [4]
**Tabela 2:** Pregled procesov in parametrov. *Nitridni potencial je izračunan po Somersovih [4] formulah

Nr.	Nitro-carburising+oxidizing
1	NH$_3$/Endo 1:1, overall 6 m^3/h/570 °C/*nitriding potential K_N = 1.7/300 min, for the last 90 min – 3.7 % propane addition + slow cooling down to 470 °C in the atmosphere NH$_3$/Endo 1:1 + 470 °C/nitriding potential K_N = 3.7/water input 1 l/75 min + cooling down and finally oil immersion
2	NH$_3$/Endo 3:2, overall 6 m^3/h/570 °C/nitriding potential K_N = 3.7/300 min, for the last 90 min – 3.7 % propane addition + slow cooling down to 470 °C in the atmosphere NH$_3$/Endo 3:2 + 470 °C/nitriding potential K_N = 5.3/water input 1 l/75 min + cooling down and finally oil immersion
3	NH$_3$/Endo 3:2, overall 6 m^3/h/590 °C/nitriding potential K_N = 1.7/300 min + 570 °C/ nitriding potential K_N = 3.0/150 min, with 3.7 % propane addition + slow cooling down to 490 °C in the atmosphere NH$_3$/Endo 3:2 + 490 °C/nitriding potential K_N = 9/water input 1 l/75 min + cooling down and finally oil immersion
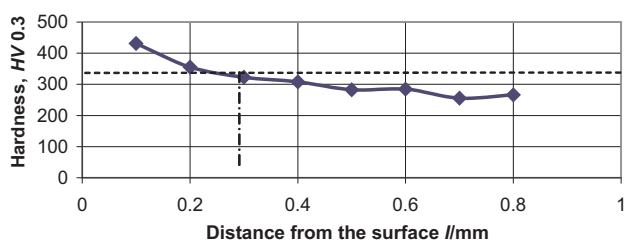
Figure 3: Hardness depth profile in the nitro-carburised region, processing route 1
**Slika 3:** Profil trdote v nitrocementirani plasti, obdelava 1

did not achieve the desired values, the corrosion resistance of the processed samples was 230 h, i.e., the main industrial parameter was achieved. Nevertheless, the limit was exceeded only slightly, and so it was decided to perform further experiments.

Therefore, the second processing was carried out using slightly changed conditions, as shown in **Table 2**. The main reason was to increase the nitrogen input into the material and to ensure a better and more stable corrosion resistance. The micrograph presented in **Figure 4** shows that the compound layer has a thickness of 21 μm.

The oxide layer on the surface had a thickness of 2 μm, **Figure 5**, and the concentration of nitrogen was also considerably higher than that achieved in the first
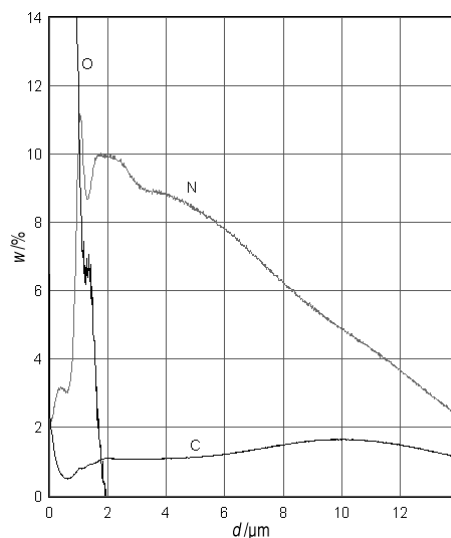
Figure 5: GDEOS depth profiles of the interstitials in the compound layer. Processing route 2.
Slika 5: GDEOS globinski profili intersticijev v spojinski plasti. Obdelava 2

process. The overall C+N content exceeded the mass fraction of 8.6 %, which is considered to be necessary to guarantee a high level of corrosion resistance, up to a depth of 7 μm. The oxide layer was formed mainly by
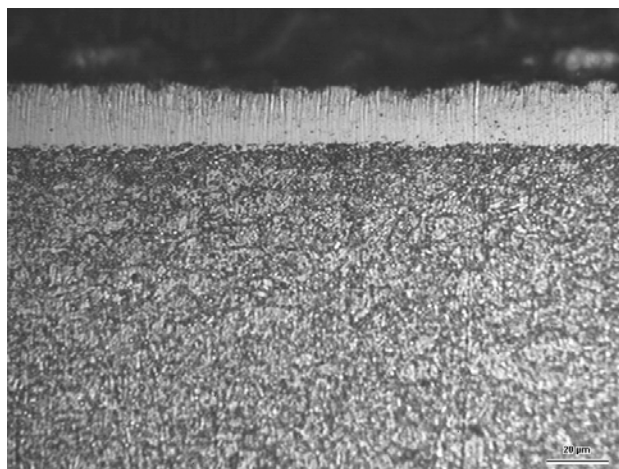
Figure 4: Microstructure of the surface from processing route 2
Slika 4: Mikrostruktura ob površini po obdelavi 2
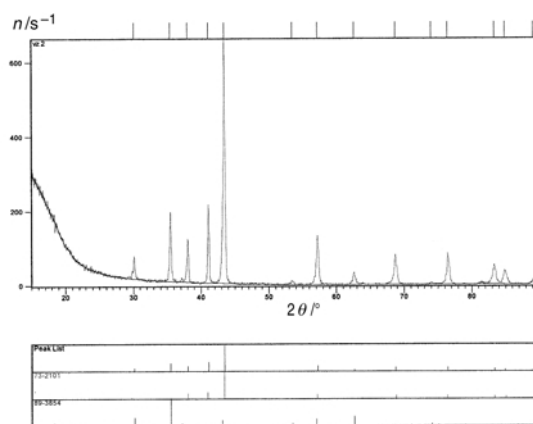
Figure 6: X-ray patterns obtained from the specimen after carbo-nitriding and oxidizing
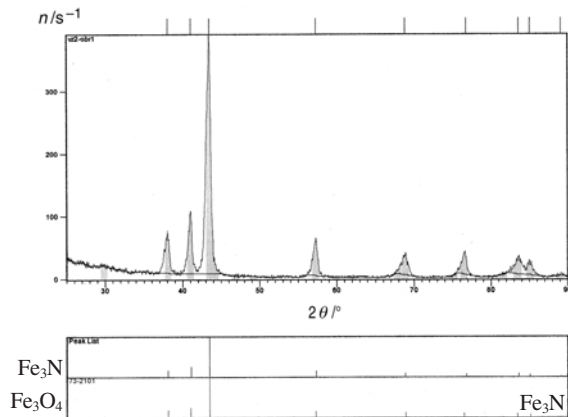**Slika 6:** Rentgenski spektri po nitrocementaciji in oksidaciji

Figure 7: X-ray patterns obtained from the specimen after carbo-nitriding and oxidizing, removed 0.01 mm from the surface.
Slika 7: Rentgenski spektri po nitrocementaciji in oksidaciji ter odvzemu 0,01 mm debele plasti s površine

Figure 9: Microstructure of the surface from processing route 3
Slika 9: Mikrostruktura ob površini po obdelavi 3

Fe_3O_4 (magnetite), **Figure 6**. This is in a good agreement with the requirements written in the introduction. What is also very important is that the "white" compound layer was only formed by the ε-carbo-nitride, **Figure 7**. Favourable results from the structural investigations were also reflected in the hardness profile; it is evident that the surface hardness as well as the nitriding case depth of were acceptable levels, **Figure 8**. Also, the corrosion resistance was significantly better, the first signs of corrosion only appeared after 450 h, see **Table 3**.

The second step led to all of the required surface parameters being achieved. The third step, therefore, focused on investigations into what happens when the parameters of the layer are exceeded. To achieve this the processing was significantly prolonged, and also the temperatures used for some periods were slightly extended, see **Table 2**, processing route 3.

Figure 9 shows a micrograph of the compound layer formed on the surface. The total thickness of the "white" layer was 34 μm. The oxide layer on the surface is also clearly visible, and according to the measurements in **Figure 10**, its thickness was of 1.7 μm. The overall C+N content easily exceeded the mass fraction of 8.6 %, mainly in the region close to the surface. Further away, however, the nitrogen content drops down dramatically. It seems that the higher treatment temperature applied
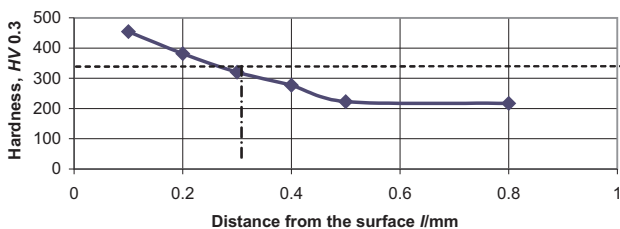

Figure 10: GDEOS depth profiles of the interstitials in the compound layer. Processing route 3.
Slika 10: GDEOS profili intersticijev v spojinski plasti, obdelava 3

for a long time, during the first period of the nitro-carburising, promotes the diffusion of nitrogen atoms into the core material. That portion of nitrogen is then absent in the region that is closer to the surface. The increased nitrogen content in the near-surface layer can,

Figure 8: Hardness depth profile in the nitro-carburised region, processing route 2
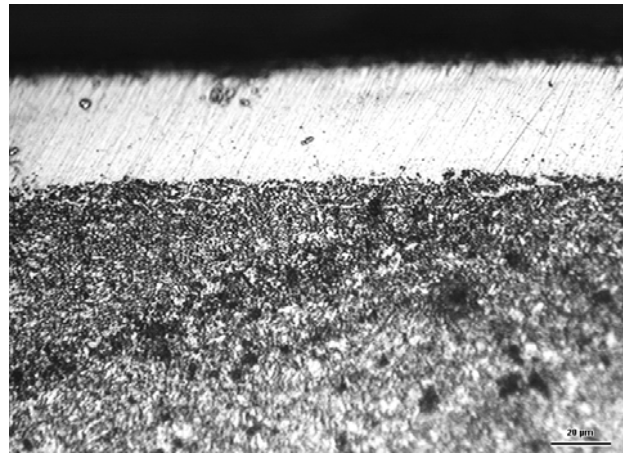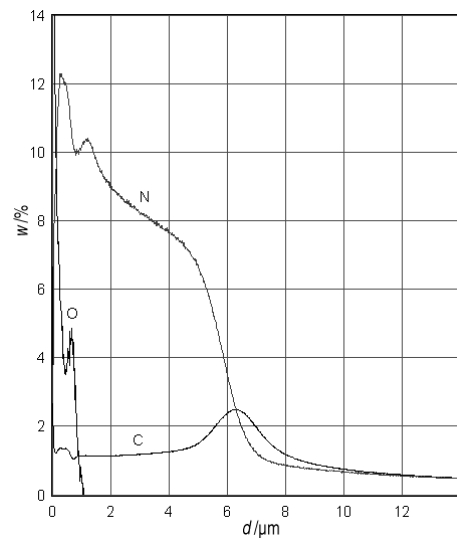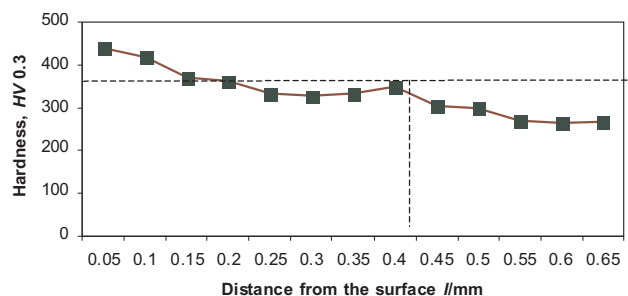**Slika 8:** Profil trdote nitrocementirane plasti, obdelava 2

Figure 11: Hardness depth profile in nitro-carburised region, processing route 3
Slika 11: Profil trdote v nitrocementirani plasti, obdelava 3

thus, be attributed to an increased nitriding potential in the periods carried out at lower temperatures (570 and 490 °C). The deeper diffusion of nitrogen is also reflected in an increased hardness in the region far away from the surface, compared to the samples treated using the processing routes 1 and 2, **Figure 11**. Finally, the corrosion testing indicated that no significant improvement in the corrosion resistance was achieved, **Table 3**. In connection with a longer processing time, it is clear that the processing leading to a compound layer that is too thick is not desirable for economic reasons and cannot be recommended.

Table 3: Summary of the structural parameters and the corrosion resistance achieved using processing routes 1, 2 and 3
Tabela 3: Pregled strukturnih parametrov in korozijske odpornosti, doseženih po obdelavah 1, 2 in 3

Processing route	"White" layer (μm)	Oxide layer (μm)	Corrosion resistance (h)
1	18	1	230
2	21	2	450
3	34	1.7	450

4 CONCLUSIONS

1) The experimental treatment confirmed that it is possible to form a "white" compound layer of a desired thickness and composition.
2) Also, a thin and continuous oxide layer of an acceptable thickness up to 2 μm, containing magnetite, can be produced.
3) The optimum treatment led to the achievement of the combined layer, increasing the corrosion resistance up to 450 h.
4) Exceeding the optimum thickness and other parameters does not lead to an improvement in the corrosion resistance and cannot be recommended, mainly for economic reasons.

5 REFERENCES

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