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PULSE PLASMA NITROCARBURISING OF GAS SHOCK ABSORBER TUBES FROM STEEL W.No. 1.0116

NITROKARBURIRANJE CEVI PLINSKEGA BLAŽILCA IZ JEKLA W.No. 1.0116, V PULZIRAJOČI PLAZMI

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Gas shock absorber tubes from steel W.No. 1.0116 were pulse plasma nitrocarburised at 560 and 580°C in atmosphere containing carbon dioxide additions. Variations in compound layer structure, thickness, porosity, hardness-depth profiles and stability of the process were investigated. It was found that the formation of predominantly ε phase compound layer structure is promoted by high nitrogen atmosphere. The compound layer thickness was found to increase with increasing nitrogen content, temperature, and pulse as well as decreasing carbon dioxide content. The experiments showed that by use of high nitrogen atmosphere no pores appear in compound layers on steel W.No. 1.0116. Proper process control and the addition of carbon dioxide to the atmosphere with high content of nitrogen result in a reasonably thick compound layer from predominantly ε phase.

Key words: pulse plasma nitrocarburising, compound layer, structure, porosity, hardness-depth profile, thickness, stability of the process

Nitrokarburiranje cevi plinskega blažilca iz jekla W.No. 1.0116 v pulzirajoči plazmi je bilo izvršeno pri temperaturi 560°C in 580°C v atmosferi z dodatkom ogljikovega dioksida. Raziskali smo mikrostrukturo spojinske plasti, debelino, poroznost ter profil trdote nitrokarburirane plasti in stabilnost procesa. Ugotovili smo, da se lahko z uporabo atmosfere, ki vsebuje visok odstotek N_2, poveča tvorbo spojinske plasti, ki je pretežno sestavljena iz ε faze. Ugotovili smo, da debelina spojinske plasti raste z vsebnostjo N_2, temperaturo in frekvenco pulziranja ter z zniževanjem vsebnosti ogljikovega dioksida v atmosferi. Eksperiment je pokazal, da visoka vsebnost N_2 ne vpliva na nastajanje por v spojinski plasti, ki se tvori na jeklu W.No. 1.0116. Pravilno vodenje procesa ter dodatek ogljikovega dioksida v atmosfero z visoko vsebnostjo N_2 omogoča doseganje sprejemljive debeline spojinske plasti, ki je sestavljena pretežno iz ε faze.

Ključne besede: nitrokarburiranje v pulzirajoči plazmi, spojinska plast, struktura, debelina, poroznost, profil trdote, ponovljivost procesa

1 INTRODUCTION

Pulse plasma nitrocarburising has grown to a thermochemical heat treating process of particular technological and economic importance for improving the surface characteristics of components for mechanical engineering. The most important advantages are greatly improved wear, fatigue, and corrosion resistance. As a low temperature process it minimises distortion and volume change of parts treated. Pulse plasma nitrocarburising produces at the surface compound layer of a few micrometers in thickness consisting mostly of ε phase, and a significantly thicker diffusion zone. As opposed to conventional salt bath and gas processes, nitrocarburising in glow discharge pulse plasma affets several advantages. In addition to its increasingly important environmental acceptability, plasma nitrocarburising because of the possibility of freely selection at a wide variety of process parameters also makes it possible to match the properties of the layers to the specific load profile of the application.

In the present paper a short survey of theoretical aspects of pulse plasma nitrocarburising is given and its significance as industrial process is assessed. The experiments were carried out on two charges of gas shock absorber tubes with different load configurations and process parameters to produce at the surface an up to 10 μm thick compound layer consisting predominantly of ε phase.

2 SOME THEORETICAL ASPECTS OF PULSE PLASMA NITROCARBURISING

The pulse plasma nitrocarburising process is characterised by a glow discharge surrounding the workpieces surface, which appears at low pressures when a voltage is applied between the workpieces and the furnace wall. The workpieces are held at a negative potential (cathode) while the furnace bell is positive (anode). The furnace must initially be pumped down to a low pressure and subsequently refilled with a suitable gas mixture to a pressure of ~1-10 hPa. A voltage of 200-1000 V is then applied, whereupon the gas species in the reaction vessel becomes ionised. By controlling the power input the workpieces can be heated to the nitrocarburising temperature, but better control of the magnitude and uniformity of the temperature is obtained with auxiliary convection heating. Another way to control the heat input to a greater precision is to apply a pulsating voltage and supply the furnace with heating elements. In this manner the workload temperature can be controlled with the retention of a high degree of glow discharge control. The problems with arc formation, local overheating, and

the hollow cathode effect can thus be minimised. The pulse frequency that could be used ranges between DC and 33 kHz. To obtain uniform nitriding depths and uniform compound layer thickness it is important to emphasise that process parameters - applied voltage, pulsing frequency, load configuration, etc.- must be selected empirically. Load configuration is very important. If components are placed too close together the hollow cathode effect can cause severe problems.

The compound layer structure and the depth of the diffusion zone can be controlled by varying the gas mixture, pulsing frequency and temperature. Normally the compound layer contains only the γ phase. To achieve a compound layer consisting of ε phase on steels a gas mixture of nitrogen, hydrogen and carbon dioxide is used.

The base for understanding the events during the formation of the compound layer and the diffusion zone is provided by the ternary Fe-N-C phase diagram. The two significant binary systems making up the sides of the ternary system, Fe-C and Fe-N[1], are well known. However, many observations are in disagreement with this diagrams. These deviations are often explained in terms of kinetics or orientational relations between the lattices of the various phases prevailing over the pure thermodynamic equilibrium in the formation of these phases. For these reasons a new ternary phase diagram has been proposed by J. Slycke et al.[2]. This diagram eliminates all ambiguity regarding the interpretation of how structures have evolved, since all observations can be explained by the local equilibrium approach. The major difference between the new diagram and that published by Naumann et al.[1] is that it allows the frequently observed direct contact between ferrite (α) and ε phase. The new Fe-N-C phase diagram shown in **Figure 1** is characterised by two

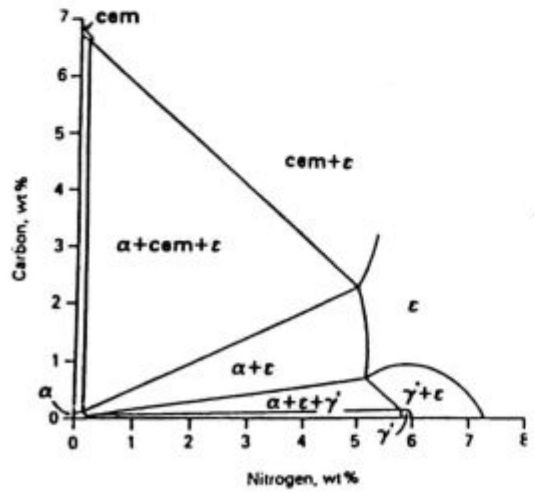

Figure 1: Schematic ternary Fe-N-C phase diagram at ~580°C suggested by J. Slycke et al.[2]

Slika 1: Shematski ternerni Fe-N-C fazni diagram pri ~580°C po J. Slycke et al.[2]

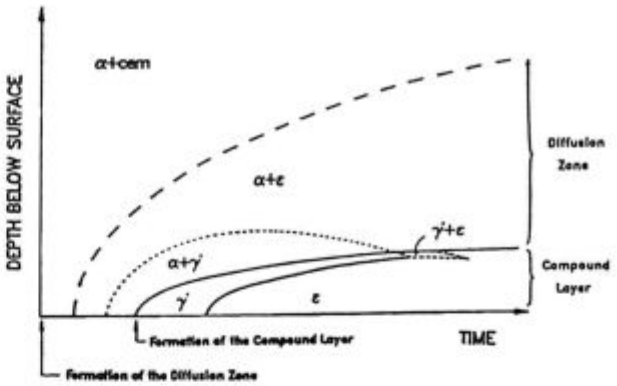

Figure 2: Schematic illustration of the evolution of the diffusion zone and compound layer during nitrocarburisig of carbon steels[3]

Slika 2: Shematska ponazoritev razvoja difuzijske in spojinske plasti pri nitrikarburiranju ogljikovih jekel[3]

three phase equilibrium (α + ε + γ and α + Fe_3C + ε) and one ternary two phase field (α + ε).

The ε phase field extends towards lower nitrogen contents with increasing carbon content as consequence of the stabilising effect of carbon on the ε phase, which can exist at a lower nitrogen content (~5% N) than the γ phase (5.9% N).

The different sequences during the nitrocarburising process of low carbon steels[3] are shown schematically in **Figure 2**. During this process ε phase and γ' phase are formed within the evolving diffusion zone, followed by the formation of γ and ε phases in the fully developed and growing compound layer.

3 EXPERIMENTAL PROCEDURE

3.1 Material and process of pulse plasma nitrocarburising

The gas shock absorber tubes ϕ 28 x 175 mm used in the present work are from steel W.No. 1.0116 with the chemical composition given in **Table 1**.

Table 1: Chemical composition of steel W.No. 1.0116, (in wt-%)
Tabela 1: Kemijska sestava jekla W.No. 1.0116 (v ut.%)

	C	Si	Mn	P	S	Cr	Mo	Ni	Al	Cu
WNr 1.0116	0,15	0,013	0,53	0,011	0,008	0,023	0,006	0,019	0,049	0,031

The pulse plasma furnace used was a GP 1000/80 M nitriding unit manufactured by Metaplas-Ionon GmbH, **Figure 3**. The furnace is equipped with a convection heating system and with an internal gas/water heat-exchanger for quick cooling.

The gas shock absorber tubes in load configuration as shown in **Figure 4** were pulse plasma nitrocarburised at 560 and 580°C at 5,2 hPa and 2,8 hPa pressure, using a total gas flowrate of 100 and 67 l h^{-1}. The gas shock ab-

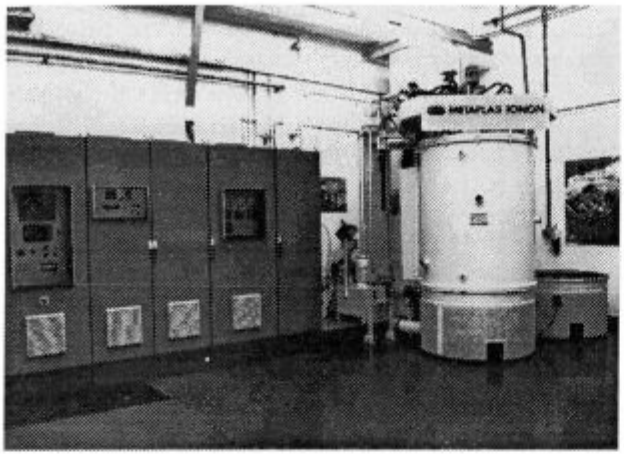

Figure 3: Pulse plasma nitriding furnace GP 1000/80 M
Slika 3: Peč za nitriranje v pulzirajoči plazmi GP 1000/80 M

sorber tube's temperature was measured with two chromel-Alumel termocouples embedded in a tubes on two different levels (top and bottom) in the first and the third circuit.

Gas atmospheres with nitrogen contents 70,5 and 87%, carbon dioxide contents 2,5 and 2% and hydrogen contents 27 and 11% respectively, were employed. The pulse frequency used was 2 and 2,5 kHz, respectively. Convection and plasma heating to process temperature took appr. 4h and the isothermal treatment lentghs were 10 and 4 hr respectively, followed by forced cooling in a flow of nitrogen.

4 RESULTS AND DISCUSSION

4.1 Compound layer structures

In pulse plasma nitrocarburising, the large number of freely definable treatment parameters make it possible to control precisely the structure, composition, and growth characteristics of the compound layer without impairing the formation of the diffusion layer.

The tubes nitricarburised for 10 and 4 hr in the pulsed plasma mode, considering the 0,480 ms glow-on time, 0,020 ms glow-of time, the 0,200 ms glow-on time, and 0,200 ms glow-of time, respectively were transversally sectioned at the middle, metallographically prepared, and etched with 3% nital for the determination of the thickness of the compound layer on an optical microscope. The thickness of the compound layer was taken by averaging five measurements for each tube.

Figure 5 shows the microstructure of the nitrocarburised layer on the outer surface of the 5 tubes taken from the third circuit from 5 different levels of the charge no.1 (560°C). The charge no.1 contain 685 tubes in 5 circuits with 20 mm intercircuit distance, processed for 10 hr in pulsed plasma mode, considering the 0,480 ms glow-on time and 0,020 ms glow-of time. The compound layers thickness appears to be 5 to 8 µm and the growth rate 0,5 to 0,8 µm/hr. Metallographical analysis (**Figure 5**) indicates that the compound layer on tubes on the top and bottom (sample 1 and 5) obtained by the above pulse plasma nitrocarburising parameters mainly consisted of γ' phase - $Fe_4(N,C)_{1-x}$. While the compound layers of the tubes between two (samples 2 - 4) consisted beside of γ' phase also of ε phase- $Fe_{2-3}(N,C)_{1-x}$ and carbide particles. In the compound layers grain boundaries are parallel to the diffusion direction and thus perpendicular to the surface. Under compound layers of these same tubes (samples 2 - 4) a 15 to 25 µm thick fringe of pearlite is found, while this fringe is not found under the compound layer on top and bottom tubes (samples 1 and 5).

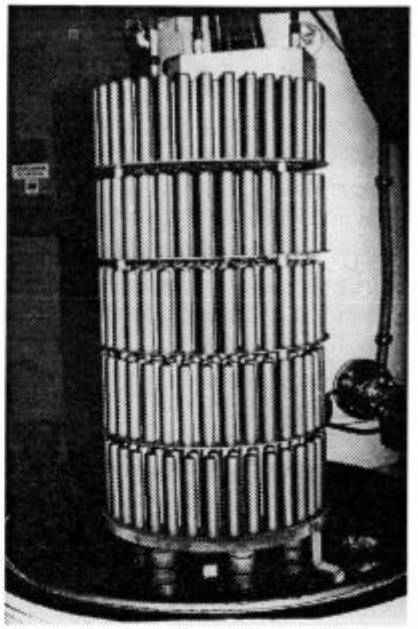

Figure 4: Gas shock absorber tubes in load configuration
Slika 4: Razporeditev cevi plinskega blažilca v sarži

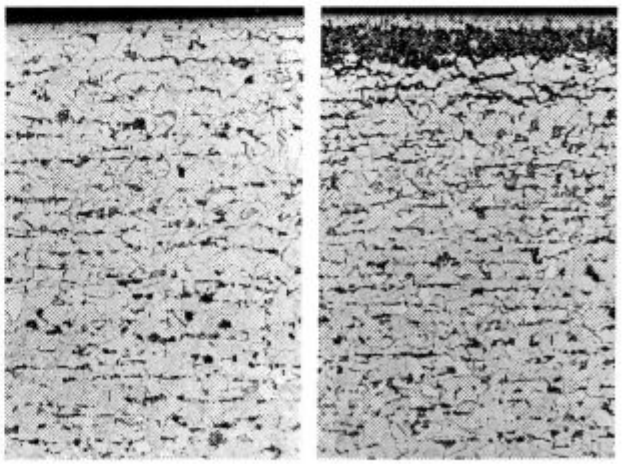

Figure 5: Microstructure of the nitrocarburised layer at the outer surface of tubes (200x)
Slika 5: Mikrostruktura nitrokarburirane plasti ob zunanji površini cevi (200x)

From the obtained microstructures it is possible to conclude that the temperature within the charge was not equalised or the distribution of gas mixture because of charge configuration was not fulfilled. The analysis of the process parameters actually shows that in spite of the relative high pressure (5,2 hPa) the temperature difference between the two thermocouples was too large (~25°C), because of the hollow cathode effect caused local overheating. This effect called the hollow cathode can occur when the cathode drops to a dimension equal to the distance between tubes.

Nitrocarburising depth on 5 tubes from top to bottom is shown in **Table 2.**

Table 2: Metallographically determined nitrocarburising depth on tubes from charge no.1

Tabela 2: Metalografsko določene globine nitrokarburirane plasti na ceveh iz sarže 1

No. of tube	Nitrocarburising depth in mm
1	0,43
2	0,48
3	0,46
4	0,43
5	0,47

Microhardness profiles HV0,3 of the nitrocarburised layers for the same 5 tubes (top and middle of the tube) are shown in **Figure 6.**

From the **figures 5 and 6**, it can be seen that the microstructure and hardness of diffusion layer on tubes from different levels are affected by the hollow cathode efffect, which causes also the irregular thickness and the type of compound layer which is also too thin.

As mentioned above the goal of the present work was to obtain at the surface of the gas shock absorber tubes a compound layer consisting predominantly of ε phase with a thickness of ≥ 10 µm. In the case of the gas shock absorber tubes the thickness of diffusion zone is not so very important. Such compound layer produced by pulse plasma nitrocarburisig process improves corrosion and wear resistance and after fine polishing one can obtain also satisfactory level of decorativeness. In order to avoid the hollow cathode effect causing local overheating of tubes it was necessary to rearrange the load configuration in such a way that the distance between tubes and each next circuit is appr. 1,3 time the distance between tubes. With new load configuration charge no. 2 processed at 580°C contains 552 tubes in 6 levels.

The thickness of the compound layer produced at 580°C with a 4 h treatment depends not only on the nitrogen and carbon dioxide levels in the treatment atmosphere, but also on the pulse frequency used. The results indicate that increasing the pulse frequency and the nitrogen level in the atmosphere an increased compound layer thickness ≥ 10 and a surface hardness in excess of 320 HV1 are obtained. The growth rate becomes greater than 2,5 µm/hr. This tendency is mostly due to the increased nitrogen "activity" in the plasma.

Figure 7 shows the typical microstructure of the nitrocarburised layer on the outer surface of the shock absorber tubes which consists predominantly of ε phase - $Fe_{2-3}(N,C)_{1-x}$. The compound layer at the surface consists of 2 µm thick monophase range of ε - $Fe_{2-3}(N,C)_{1-x}$, and it is followed by a two-phase field (ε + γ') up to 6 µm thick. In the compound layer grain boundaries are parallel with the diffusion direction and thus perpendicular to the surface. The diffusion zone below the compound layer consisted of the eutectoid constituent braunit (α + γ') from the binary Fe-N[1] system and some islands of pearlite and needles of γ'. The present experiments have confirmed that the use of high nitrogen atmospheres produces no pores in the compound layers developed on steel W.No. 1.0116.

4.2 Reliability survey

The reproducibility of the process is shown in **figure 8**, which presents the results of the processing of 23

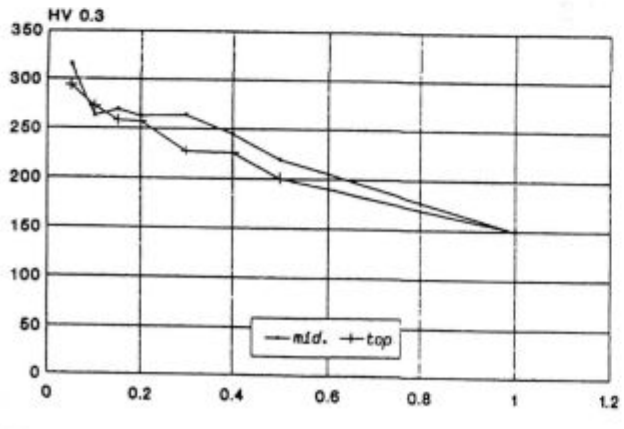

Figure 6: Microhardness profiles HV0,3 of the nitrocarburised layers
Slika 6: Profil mikrotrdote HV0,3 nitrokaburirane plasti

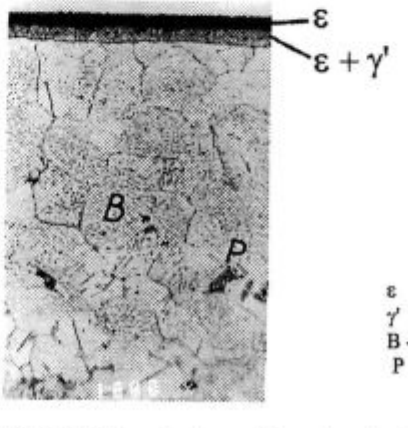

Figure 7: Microstructure of the nitrocarburised layer on the outer surface of the shock absorber tubes
Slika 7: Mikrostruktura nitrokarburirane plasti na zunanji površini cevi plinskega blažilca

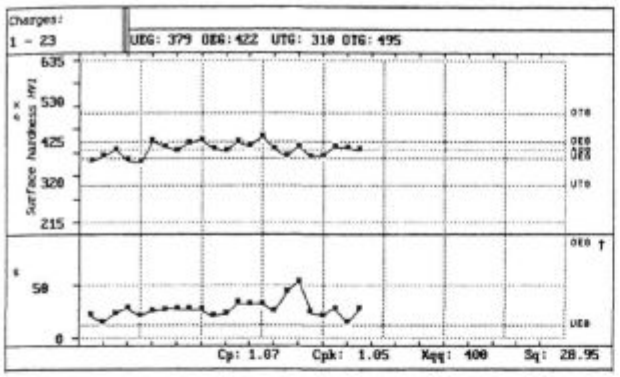

Figure 8: Reproducibility of the pulse plasma nitrocarburising process on 23 charges
Slika 8: Ponovljivost procesa nitrokarburiranja v pulzirajoči plazmi pri 23 saržah

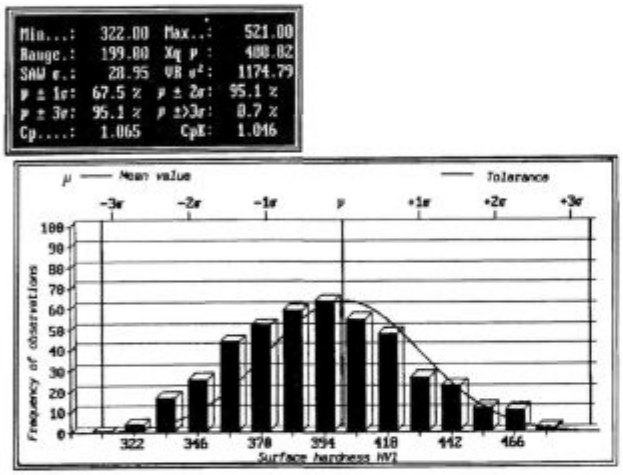

Figure 9: Statistical consideration of surface hardness HV1 data on 23 charges
Slika 9: Statistična obdelava podatkov površinske trdote HV1 pri 23 saržah

charges. A typical charge may contain up to 552 tubes with a net weight of around 94 kg.

Statistically confirmed quality control data for surface hardness HV1 are shown in **figure 9**.

These distributions satisfy customer's ± 3σ (standard deviation) quality requirements, that mean 95% of all pulse plasma nitrocarburised tubes have to meet this specification. However, it should be pointed out that fluctuations in the hardness of the core materials, i.e. 150-230 HV1 and used UIC (Ultrasonic Contact Impedance) hardness testing method[4] can affected the nitrocarburising results and are not taken into account in the statistical control. Clearly, improved control over the variations experienced in core hardness would be expected to reduce the amount of scatter observed in the nitriding results. Fortunately, the quality requirements are already satisfied to such an extent that these effects may be disregarded.

5 CONCLUSIONS

On the basis of the present experiments, it is confirmed that the atmosphere consisting of 87% N_2 + 2% CO_2 + 11% H_2 and increased pulse frequency are required in the glow discharge to produce a compound layer thickness ≥ 10 μm without pores and with a predominantly ε phase structure.

From the results is evident that higher nitrogen content in atmosphere, higher temperature and increased pulse frequency strongly influenced the compound layer growth rate which is by the second charge nearly three times higher than in by the charge no. 1 processed in a less suited atmosphere. With a new load configuration charge no. 2 and increased pulse frequency the phenomenon called the hollow cathode effect, which causes local overheating among the tubes, was also avoided.

Beside this, it is very important that pulse plasma nitrocarburisig quickly overcomes its sometimes still unfavourable image and that this modern and progressive technology is recognised as a reliable case hardening process. What good are all the remarkable technical, economical and environmentally clean properties of the process if it cannot be justified in practical use under industrial conditions? The results presented in this work prove that such a demand can be fulfilled.

6 REFERENCES

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