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Combined Plasma Surface Treatments for Wear and Corrosion Protection

Various diffusion and deposition technologies are applied to meet the requirements of mechanical, chemical and tribological properties of functional components made of steel. Nitriding, nitrocarburizing, carburizing, boriding and similar diffusion processes may be carried out in different working media that provide the active species for diffusion into surface zone of materials. Wear and corrosion resistant coatings of different chemical composition, texture and morphology may be grown onto the surface of industrial parts by various chemical, electrochemical, mechanical, thermal, plasma or combined processes. By combining the diffusion and deposition processes, the techniques that belong to the most advanced industrial surface treatments, a new quality surface structure may be obtained. It has been found that the excellent mechanical, tribological, corrosion and decorative behavior of steel components were produced by nitriding/nitrocarburizing followed by a post oxidation process. The combinations of gas nitriding, plasma cleaning and post-oxidation, as well as salt bath nitriding and post-oxidation were successfully applied and opened a new field of combined technology investigations. Principles, properties and some applications of combined technologies and pulse plasma were discussed.

***Keywords**: duplex technology, pulse plasma nitriding, plasma oxidation, extrusion dies, tool wear, tool life*

1. INTRODUCTION

Plasma surface engineering was successfully introduced in many industrial activities including microelectronics, sensors and actuators, mechanical engineering, biomedical engineering, energy conversion and similar. The functional components resistant to wear, fatigue and corrosion were produced by various diffusion and deposition technologies which combine the bulk and surface properties of materials in order to meet the requirements of so called high technology products. The quality-to-price relation is the most important factor for new technologies to enter and stay on the world market, esspecially during the slow down economy periods. Recently, in the field of plasma diffusion and deposition processes for surface treatment of materials, some technical solutions provided the step ahed towards the industrial applications.

The development of combined diffusion-deposition and plasma nitriding-plasma oxidation processes, as well as the introduction of pulse plasma are discussed.

2. DUPLEX TECHNOLOGY

Like in microelectronic, the surface treatment of some specific functional components in mechanical engineering requires more than one technology to be applied to satisfy the operational conditions. Usually two surface treatments are applied which is known in the literature as duplex technology or duplex surface treatment.

2.1 Combined diffusion and deposition

The possibility of using ionized gas as an active medium for diffusion and deposition surface treatment was invented by patents of Bernard Berghaus half century ago [1,2], but the combination of two technologies was strictly forbidden by leading coating companies due to low adhesion of so called hard coatings on plasma nitrided surfaces [3]. In the late eighties of the last century, the research performed at the Plasma Technology Center in Belgrade demonstrated for the first time the possibility of a successful combination of plasma nitriding and subsequent TiAlN coating deposition [4-8].

The basic idea of combining diffusion and deposition processes is illustrated in Fig. 1. The nitriding process was widely applied to broad range of steel

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grades and other ferrous materials, but the surface structure and properties were strongly related to the chemical composition of the substrate. Besides the improved tribological properties, the nitrided layer was also used to enhance the fatigue resistance and load bearing capacity of treated components. On the other hand, new developed hard coatings like TiN, TiAlN, CrN, ZrN and other nitrides carbides, oxides and borides of refractory elements were proved to have the excellent wear and corrosion resistance in many tribological couples. Unfortunately, the hard coatings performed well only on high quality and expensive substrates, which strongly limited their applications.

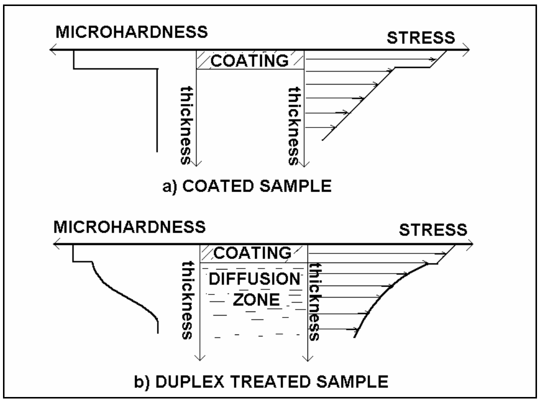
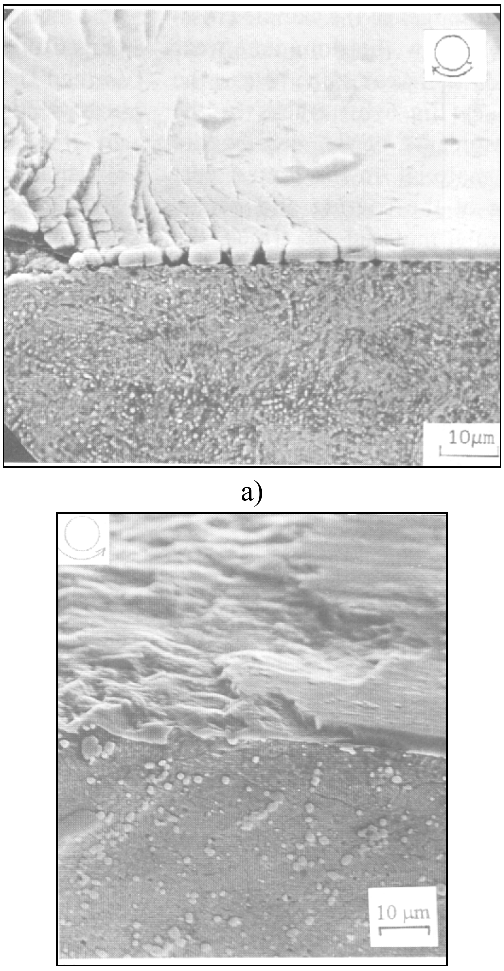


Figure 1. Mechanical properties of a) coated and b) duplex treated sample

The microhardness distribution over the cross section of only coated substrate is a step function, as shown at the left side diagram of Fig. 1a. When exposed to the strain, a large mechanical stress discontinuity is present at the coating to substrate interface of coated sample caused by the Young modulus difference. This my lead to the coating delamination (Fig. 1a right side diagram). In addition, a soft substrate has no load bearing capacity to support a hard overcoating, that will be destroyed under the action of a normal force.

The microhardness distribution over the cross section of nitrided and then coated substrate is given on the left side of Fig. 1b. The enhanced surface microhardness before coating provided a better substrate load bearing capacity and more continuous stress distribution (right side diagram of Fig. 1b).

The properties of combined surface structure were excellent. The most critical parameter, the coating-to-substrate critical load for adhesion exceeded the maximum level known in the literature [8]. New quality tribological properties were obtained and the field of plasma surface engineering applications was enlarged [9-13].



a)

b)

Figure 2. Wear of a) coated and b) duplex treated surface layer [9]

The mechanism of hard coating degradation was also changed. Instead of cracking, flaking, delamination and detachment of only coated HSS substrate (Fig. 2a), layer by layer wear of TiN coating deposited on plasma nitrided surfaces was found (Fig. 2b), which increased the service life of duplex treated components [14]. Today, combined nitriding-deposition technology offers “Highest industrial benefit…” [15].

2.2 Pulse plasma nitriding and oxidation

Salt bath, gaseous or plasma nitriding were applied to enhance the wear, corrosion and fatigue resistance and combined diffusion-deposition duplex technology to improve tribological properties and corrosion resistance of tools and different steel products. Some coatings, such as galvanic and hard chromium, are very effective in suppressing the action of the aggressive surroundings, but suffer from the environment pollution. Combined diffusion-deposition technology, which gives the excellent wear and corrosion resistant surface structure, is non convenient for complex geometry workpieces and relatively expensive for mass production of low price components. Plasma nitriding can improve the corrosion resistance of some steel grades to the level that is not sufficient for example for hydraulic parts.

In order to enhance the performance of industrial components used under combined corrosive and mechanical wear several surface treatments which combine nitriding and oxidation were developed such as NITROTEC, TENIFER QPQ, SURSULFOXYNIT, NIOX, NITROTEC and similar [16].

A post-oxidation process applied to salt bath nitrocarburized parts producing a single phase carbonitride overlayer ε-Fe_{2-3}(N,C) was found to be very effective against both wear and corrosion, but due to the application of toxic components like cyanides, serious environmental problems were produced [17,18]. The efforts were also made to produce a monophase ε carbonitride layer by plasma techniques. Plasma nitrocarburizing usually results in formation of a mixed $\gamma' + \varepsilon$ compound zone inferior in tribological applications related especially to impact loads, but plasma nitrocarburized samples may be post-oxidized to obtain a magnetite superficial layer with enhanced wear and corrosion resistance [19-22].

The parameters of an oxidation process determine the oxygen concentration gradient at the oxide-nitride interface, the growth and structure of the superficial oxide layer, the micro pore concentration and the oxide zone phase (Fe_3O_4, Fe_2O_3, FeO) and thickness.

Based on high chemical potential of plasma state, in recent years the investigations were carried out with the aim to develop an effective, envi-ronment clean, plasma post-oxidation process.

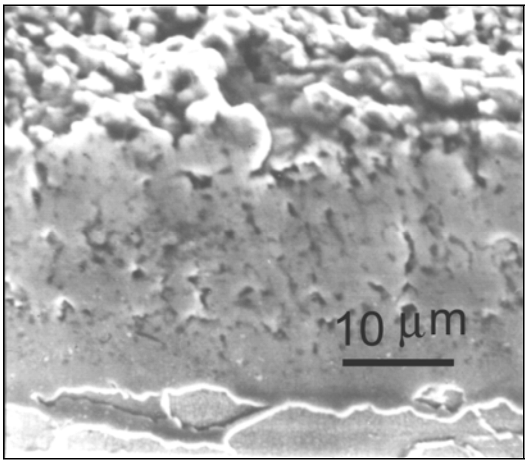
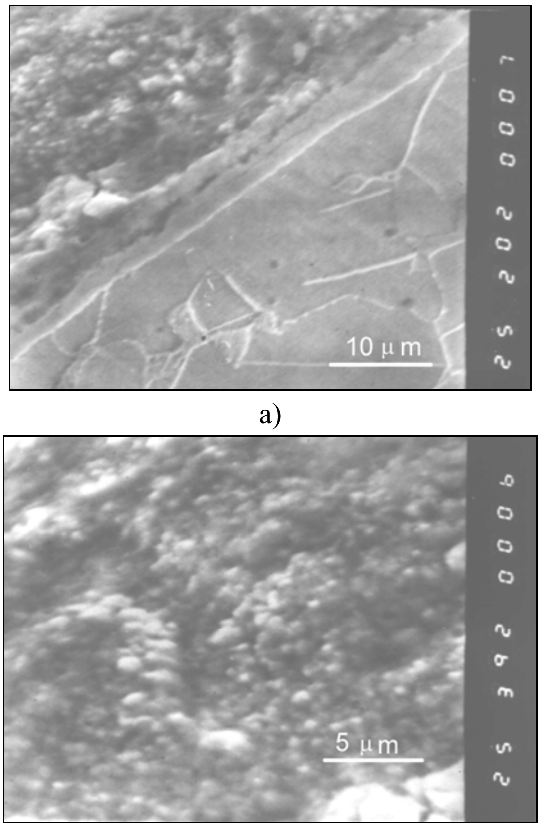


Figure 3. SEM micrograph of salt bath nitrided compound layer cross section [23]



a)

b)

Figure 4. SEM micrographs of plasma nitrocarburized samples treated in 4.3% oxygen gas: a) cross-section b) surface

The SEM micrograph of the cross section of salt bath nitrided sample by TENIFER process is given in Fig. 3. Onto diffusion zone a compound layer was formed with the thickness over 30 µm. The XRD examination revealed the existence of a ε carbonitride layer with no indices of γ' phase, which is usual for the salt bath processes. The porosity of compound zone is more evident at the outer part of the layer, so that the existence of a thin γ' phase at the interface cannot be excluded.

Salt bath nitriding followed by oxidation process was proved to give a surface structure of enhanced corrosion resistance superior to corrosion properties of 20 µm thick hard chromium galvanic coating, but still there are some difficulties in reproducing similar structure by plasma processes [17].

The structure of the surface zone of the sample treated in 4.3% oxygen containing atmosphere is given in Fig. 4a and Fig 4b. It steams from SEM analysis that a complex compound zone is formed on nitrocarburized and post-oxidized specimens. On γ' compound layer an oxide layer was formed (Fig. 4a) with a palisade structure clearly visible from Fig. 4b.

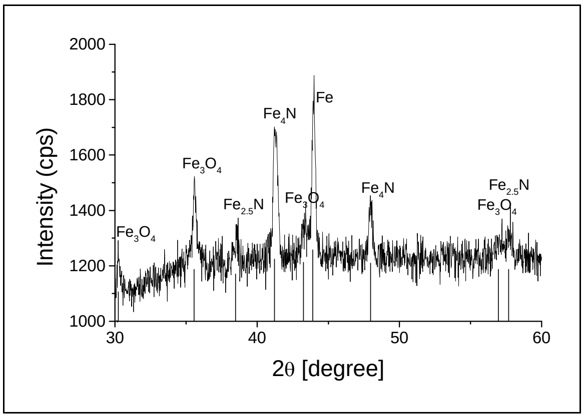


Figure 5. XRD spectum of plasma nitro-carburized samples oxidized at 14.4% of oxygen in the gas discharge

The XRD investigations of plasma nitrocarburized sample (Fig. 5) revealed that beneath the magnetite layer, the γ' phase was transformed to the ε phase after post-oxidation in 14.4% oxygen containing hydrogen/nitrogen mixtureThe surface zone consisted of Fe_2O_3 overlayer, ε sublayer at the Fe_2O_3-γ' interface and the diffusion zone beneath.It was demonstrated that plasma processing can be used to combine nitrocarburizing and oxidation.

3. PULSE PLASMA

Plasma surface treatment of small diameter holes and complex shaped parts like bearing openings of aluminium alloy extrusion dies is very difficult. Both, a local overheating due to hollow cathode effect and low penetration depth of plasma processing may limit the applicability of plasma treatment. In addition, glow-to-arc plasma insta-bility is very common in continuous d.c. discha-rges. Pulse plasma offers an excellent solution to the cited problems. Pulse plasma is much more stable then continuously operated discharge. The hollow cathode effect my partially be controlled and plasma penetration depth into the small diameter holes is enhanced [24].

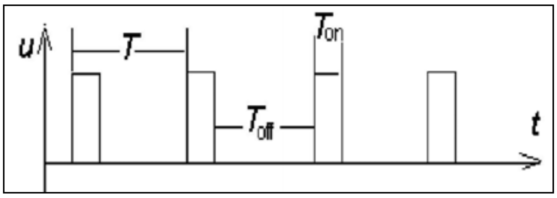


Figure 6. Voltage pulses of pulse plasma generator

New process parameters were introduced such as frequency and duty cycle or pulse duration T_{on} and pulse pause T_{off} (Fig. 6). The typical shapes of voltage (negative) and current pulses versus time are given in Fig. 7 that illustrates the rise of current due to glow to arc transition and the electronic fast breaker switch off the supply power [25].

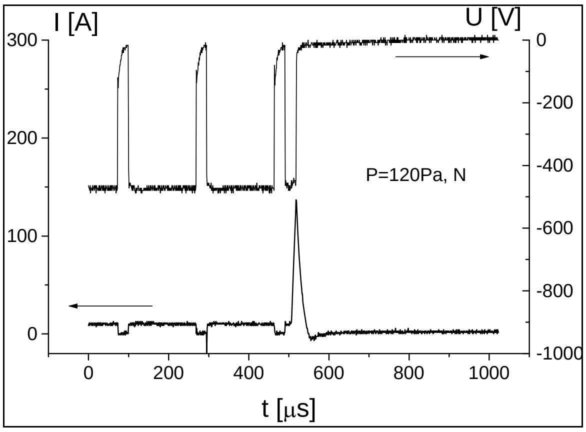


Figure 7. Voltage and current at arc ignition [25]

The pulse plasma penetration depth in the small diameter opening was tested by plasma nitriding the specimen shown schematically in Fig. 8.

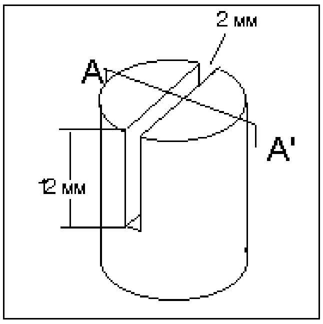


Figure 8. Sample for testing plasma penetration

Pulse plasma was used with T_{on}=57 μs, and T_{off}=3 μs. After nitriding, the sample was cut along the vertical axes of symmetry (plane A-A') and the microhardness distrubution was measured at several places inside the opening. The microhardness distribution measured at the sample surface and 6 mm deep in the opening revealed an excellent plasma penetration ability (Fig. 9).

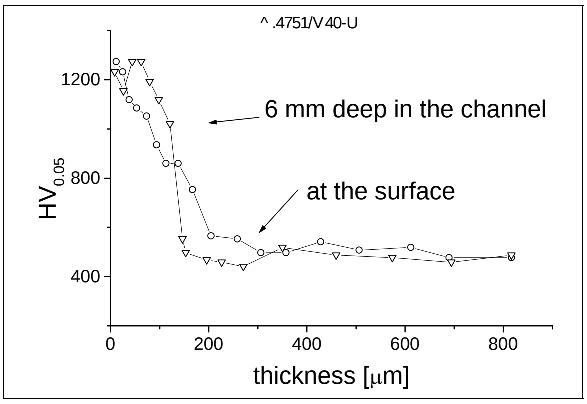


Figure 9. Microhardness distribution inside the openings

The additional important conclusion is that hollow cathode effect is not so pronounced as to produce a local overheating and softening of tool material.

4. SOME APPLICATIONS

Introduction of duplex technology and pulse plasma provided a significant step ahead in plasma surface engineering. New applications are continuosly developing and new products constructed based on excelent surface structure produced by combining plasma diffusion and deposition processes. The excellent examples are the surface treatment of gear cutting hobs [6], alluminium extrusion dies [26], forging dies [26] and dies for casting Al alloys [27].

As an illustration of pulse plasma nitriding application the treatment of aluminium extrusion dies is described.

The aluminium alloy AlMgSi0.5 (AA 6063) with the composition 0.20 - 0.60 Si; Max 0.35 Fe; 0.45 - 0.90 Mg was extruded. The die and extrudate were preheated to the temperature of 470^0C and 490^0C respectively. Due to friction the temperature of extrudate at the die inlet is between 500^0C and 510^0C at the extrusion rate of 10-15 m/min.

The photo of a part of the die bearing is given in figure 10. The 1.2 mm die-bearing slit has to be surface treated. The dies were conventionally plasma nitrided and pulse plasma nitrided for the purpose of comparison. The results of the production tests of the tool service life are shown in Table 1.

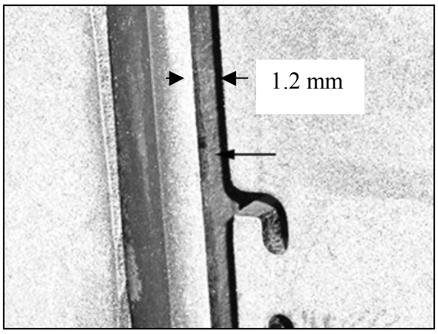
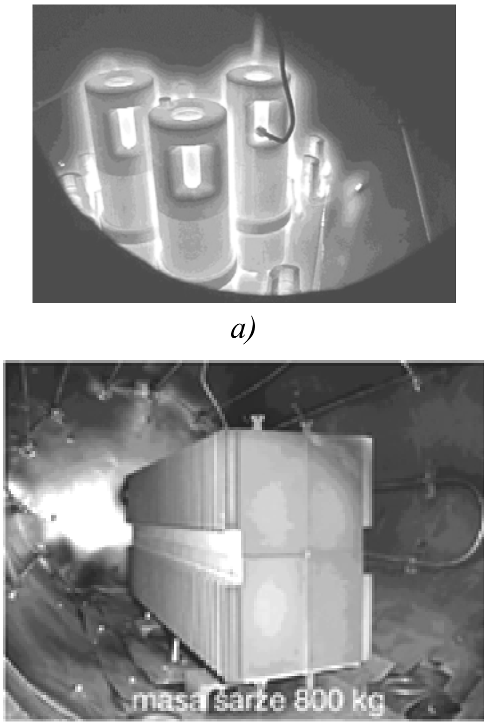


Figure 10. The bearing configuration of the die U1P1a

The service life of pulsed plasma nitrided dies was found to be 1.9 to 3.87 times longer compared to conventionally plasma treated tools.

Two additional applilcations of pulsed palsma are illustrated in fig 11. The parts of Al casting in pulse plasma during surface treatment are shon in Fig 11 a, while Fig 11b is a photo of 800 kg mass sharge of special linear gears after pulse plasma treatment.



a)

b)

Figure 11. a) Die casting dies and b) linear gears in pulse plasma

5. ENVINROMENT IMPACT

The advantage of applying plasma processing instead of salt bath nitriding followed by post oxidation is clearly evident when environment pollution is considered [17]. Compared to serious problem of cyanides storage, plasma nitriding and post oxidation are practically completely non-polluting processes.

Table 1. Service life of conventionally and pulse plasma nitrided extrusion dies

1. Die label	Conventional plasma process			5. Pulse plasma Number of extrusions	6. Tool life factor 5/4
	2. Number of nitriding	3. Number of extrusion	4. Average No of extrusions		
K2040	2	112	56	136	2.43
K4040	3	135	45	174	3.87
U1P1A	6	397	66	125	1.92
TMF2.1				118	

6. CONCLUSIONS

In recent development of plasma surface treatment of tools and functional components some important steps ahed are evident. The contribution to plasma surface engineering of combined diffusion-deposition treatment, plasma nitriding followed by plasma oxidation and pulse plasma were described.

ACKNOWLEDGMENT

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