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# Improvement of Corrosion Resistance of Steels by Surface Modification

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## 1. Introduction

The corrosion of metals is a destructive process regarding to the basic modern constructional material with a great importance for the nowadays industry and in many cases represents an enormous economic loss. Therefore, it is not a surprise that the research on the corrosion and corrosion protection of metallic materials is developed on a large scale in different directions and a wide range of engineering decisions. For all that, the improvement of corrosion behaviour of metals and alloys still stays as one of the most important engineering problems in the area of materials application and it is one of the fundamental parts of modern surface engineering.

Special attention is usually focused on the corrosion behaviour of steels as the most commonly used engineering material, because of the limited corrosion resistance for many basic types of these alloys. In more cases they are selected not for their corrosion resistance and important properties are strength, easy fabrication and cost, but there are a lot of exploitation conditions requiring high corrosion resistance. For such a purpose is developed the special group of stainless steels which covers with a high level of certainty these requirements. The stainless steels have an excellent corrosion resistance, but it is not always attended with high strength, hardness and wear resistance. Together with the higher price of the high-alloy steels these are the main restriction for many applications and open up a wide field of opportunities for the surface modification as a method for combination of corrosion resistance along with high strength, hardness and wear resistance.

Surface modification in a wider sense includes all types of surface treatments and coatings that result in change in composition and microstructure of the surface layer. There are different methods for modifying the surfaces of structural alloys, dictated by the performance requirements of the alloy in its service environment. One of the approaches, traditional for the steels, is to modify the surface region of engineering alloys via diffusion of different elements and forming a layer with determinate chemical composition, microstructure and properties. These are the commonly used in practice methods for thermochemical treatment of metals which extended with the methods for physical vapor deposition and chemical vapor deposition form the basic modern techniques for surface engineering regarding to metals. Another approach involves coating of alloy surfaces via plasma spraying, electrospark deposition, modifying the surface by ion implantation or sputter deposition of selected elements and compounds, etc. In recent years a particular

attention is directed to the advance methods for surface modification of metals such as laser surface treatment, ion beam surface treatment and electrical discharge machining, which give a modified surface with specific combination of properties in result of nonequilibrium microstructural characteristics.

The obtained by all these methods surface layers can be classified in several ways. Based on the mechanism of the treating process, they can be categorized as:

- Overlay coatings;
- Diffusion coatings;
- Recast layers.

In the overlay coatings, an additional material is placed on the substrate by techniques such as physical vapor deposition (PVD), flame or plasma spraying, etc. The coating in these cases has a mechanical bond with the metallic surface, without much diffusion of the coating constituents into the substrate.

In diffusion coatings a chemical bond is formed with the metallic surface and is obtained a diffusion layer with modifying chemical composition in the depth of the layer. These coatings are formed generally at high temperatures and include such methods as thermochemical treatment and chemical vapor deposition (CVD). Thermochemical treatment is one of the fundamental methods for surface modification of metals and alloys by forming of diffusion coatings. The plain carbon steels and low-alloy steels are mainly treated by these methods to form on the surface layers with high hardness, wear resistance and corrosion resistance, but these methods are also often used to modify the surface of high-alloy steels, cast irons, nonferrous metals and for obtaining of layers with determinate chemical composition, structure and properties.

The recast layers are obtained after attacking the metallic surface with high energy stream such as laser, ion beam or electrical discharge for a very short time and pulse characteristics that involve local melting of the surface and after that rapidly cooling. The recast layer can be with the same chemical composition as the substrate, but with different microstructure and properties in result of nonequilibrium phase transformations during the rapidly cooling, or with a different chemical composition, microstructure and properties in result of attending diffusion process of surface alloying. In recent years of scientific and practical interests is the electrical discharge machining (EDM) for obtaining of recast layers with different characteristics and properties, mainly high hardness, wear resistance and corrosion resistance.

Typical cases of surface modification are diffusion coatings and recast layers, which will be the objectives of this chapter.

## 2. Diffusion coatings

The diffusion coating process is one of the most effectively and with a great practical application method for improvement of corrosion resistance together with wear resistance, hardness and working live of metals and alloys. This is very important for the carbon steels as the most widely used engineering material accounts more than 80% of the annual world steel production. Despite its relatively limited corrosion resistance, carbon steel has a wide application in whole nowadays industry and the cost of metallic corrosion to the total

economy is remarkable high. Because of that the carbon steels and in many cases low-alloy steels are the most used constructional metallic materials for surface engineering on the base of diffusion coatings.

The diffusion coatings are products of thermally activated high temperature processes, that form on the metallic surface chemically bonded layer with determinate chemical composition, structure and properties. For decades a variety of diffusion coatings have been developed and used to improve the properties of metallic surface. There are several kinds of coating methods among which the most commonly used and with the most widely industrial application is thermochemical treatment.

Thermochemical treatment technologies for surface modification of steels have been very well investigated and developed on research and industrial level. These are methods by which nonmetals or metals are penetrated into the metallic surface by thermodiffusion after chemical reaction and adsorption. By thermochemical treatment the surface layers change their chemical composition, structure and properties and in many cases this modified surface can work in conditions which are impossible for the bulk material. Carburizing, nitriding, carbonitriding, nitrocarburizing, boronizing, chromizing, aluminizing and zinc coating are the most popular methods for industrial application. Only carburizing from all these methods could not perform the requirements to form coatings on the surface with high corrosion resistance in the most cases of steel treatment. The other techniques often are used for improvement of the corrosion behaviour of steels by surface modification and more of them increase the wear resistance and hardness of the treated materials.

### **2.1 Diffusion coatings obtained by nitriding**

Nitriding is a thermochemical treatment in which nitrogen in atomic or ionic form is introduced by diffusion process into the metallic surface and in the case of steels is based on the solubility of nitrogen in iron (Davis, 2001, 2002; Pye, 2003). The unique of the nitriding process were recognized by the Germans in the early 1920s. It was used in the applications that required:

- High torque
- High wear resistance
- Abrasive wear resistance
- Corrosion resistance
- High surface compressive strength

Nitrided steels offer improved corrosion and oxidation resistance. The nitrided surface of an alloy steel or tool exhibits increased resistance to saltwater corrosion, moisture and water.

The treatment temperature is usually between 500 and 550 °C for periods of 1 to 100 h depending of the nitriding method, type of steel and the desired depth of the layer. Since nitriding does not involve heating the steel to austenitic temperatures and quenching to martensite is not required, nitriding can be carried out at comparatively low temperatures and thus produce diffusion coating with high quality without deformations of the workpiece.

This technique is of great industrial interest as it forms structures with hard nitride surface layers, so that the global mechanical performance, hardness, wear resistance and corrosion resistance of steels are greatly improved. In recent years new and innovative surface

engineering technologies have been developed to meet the rapidly increasing demands from different extreme applications, but gas and plasma (ion) nitriding remain as one of the most widely used techniques for surface engineering.

The case structure of nitrided steel depends on its type, concentration of alloying elements and particular conditions of nitriding treatment. The diffusion zone is the original core microstructure with the addition of nitride precipitates and nitrogen solid solution. The surface compound zone is the region where  $\gamma'$  ( $\text{Fe}_4\text{N}$ ) and  $\epsilon$  ( $\text{Fe}_{2-3}\text{N}$ ) intermetallics are formed. The corrosion resistance of steel varies with nitrided layer structure. The surface "white layer" can contain  $\epsilon$  nitride,  $\gamma'$  nitride or a two phase mixture  $\epsilon+\gamma'$ , below that is the diffusion zone. In acid solutions the iron nitrides corrode more slowly than iron and when the "white zone" is formed on the steel surface the improvement of the corrosion resistance is a fact. In Fig. 1 is shown the typical structure of nitrided plain carbon steel (Minkevich, 1965).

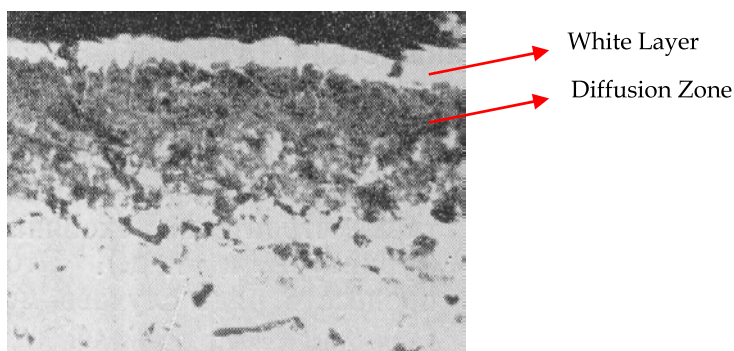


Fig. 1. Microstructure of nitrided GOST 10 steel ( $\times 340$ ).

The commonly used steels for nitriding are generally medium-carbon steels that contain strong nitride-forming elements such as aluminium, chromium, vanadium, tungsten and molybdenum. These alloying elements are beneficial in nitriding because they form nitrides that are stable at nitriding temperatures. Other alloying elements such as nickel, silicon and manganese are not so important for the characteristics of the nitrided diffusion coatings. Although these alloy steels are capable to form iron nitrides in the presence of nascent nitrogen, the properties of the nitrided layer are better in those steels that contain one or more of the major nitride-forming alloying elements.

Gas and plasma nitriding are the main methods for obtaining of nitrided diffusion coatings on steels with widely industrial application. The times of gas nitriding can be quite long, that is from 10 to 130 h depending on the application and the depth of the layer is usually less than 0.5 mm. Plasma nitriding allows faster nitriding process and quickly attained surface saturation on the base of the activated nitrogen diffusion. The process provides excellent dimensional control of the white-layer, its composition and properties.

Gas nitriding of steels (Davis, 2001, 2002; Pye, 2003; Smith, 1993) is a thermochemical treatment that takes place in the presence of ammonia gas which dissociates on the steel surface at the operating temperatures. The atomic nitrogen produced is adsorbed at the steel surface, and depending on the temperature and concentration of nitrogen, iron nitrides form at and below the steel surface. The patent for gas nitriding was first applied for by Adolph

Machlet and was for nitrogenization of iron and steel in an ammonia gas atmosphere diluted by hydrogen. Either a single-stage or a double-stage process can be used when nitriding with anhydrous ammonia. The temperature of the single-stage process is usually between 495 and 525 °C and it is produced a nitrogen-rich compound zone in a form of white nitride layer on the surface of the nitrated steel. For successful nitriding, it is necessary to control the gas flow so that there is a continuous fresh supply of ammonia at the steel surface. An oversupply of nitrogen may result in the formation of a thick layer of iron nitrides on the steel surface. Independently of some brittleness this nitride layer has a very good corrosion resistance. The principle purpose of double-stage nitriding is to reduce the depth of the white layer on the steel surface, but except for the reduction in the amount of ammonia consuming per hour, there is no advantage in using the double-stage process unless the amount of the white layer produced in the single-stage nitriding cannot be tolerated on the finished parts.

The gas nitriding for improvement of corrosion resistance of plain carbon steels and low-alloy steels can be carried out for shorter times at elevated temperatures (Minkevich, 1965). The purpose is to obtain on the steel surface non-etched nitrated layer without pores and thickness about 0.015 - 0.030 mm. In Table 1 are given the conditions of this process for some plain carbon steels and free-cutting steels.

Type of Steels (GOST)	Temperature, °C	Time, min	Dissociation of ammonia, %
08, 10, 15, 20, 25, 40, 45, 50, A12, A15, A20	600	60 - 120	35 - 55
	600	45 - 90	45 - 65
	700	15 - 30	55 - 75

Table 1. Gas nitriding process conditions for improvement of the corrosion resistance for plain carbon steels and free-cutting steels.

Plasma nitriding (ion nitriding) is a thermochemical treatment process in which nitrogen ions alone or in combination with other gases react at the workpiece surface to produce hardened and corrosion resistance surface on a variety of steels (Buchkov & Toshkov, 1990; Pye, 2003; Smith, 1993). The process is realized on the creation of gaseous plasma under vacuum conditions. The gases can be selected in whatever ratio to provide required surface metallurgy and the layer can consists of single phase, dual phase, or diffusion zone only. The surface metallurgy can be manipulated to suit both the application and the steel. Ion nitriding has many advantages and is appropriate to many applications that are not possible with the conventional nitrated techniques. The nitrated layer on the steel is of the order of 0.1 mm in depth and is harder than nitrated surface layers produced by gas nitriding. The process requires both hydrogen and nitrogen at the workpiece surface. The hydrogen makes certain that the surface of the steel is oxide-free and the chemical reaction takes place between the steel and nitrogen ions. The oxide-free surface enables the nitrogen to diffuse rapidly into the steel and sustains the nitriding actions. A major advantage of the plasma-nitriding process is the enhanced mass transfer of high-energy nitrogen ions to the surface of the steel under the action of an electrical field. The kinetics of the nitrogen ions into the bulk of the steel is controlled by the solid-state diffusion and nitride precipitation. Advantages of plasma nitriding include reduced nitriding cycles, good control of the  $\gamma'$  white iron nitride layer, reduced gas consumption, clean environmental operation, excellent surface quality

and reduced distortion of the workpiece. The white layer on the surface of the ion nitrided medium-carbon steel contains mainly from  $\gamma'$  iron nitride with a small amount  $\epsilon$  iron nitride. With the control of the process can be obtained layer from single  $\gamma'$  nitride phase. In Table 2 is made a comparison of the white layer structures of gas and ion nitrided GOST 10 steel (Buchkov & Toshkov, 1990).

Type of nitriding	Temperature, °C	Time, min	$\epsilon$ -nitride, %	$\gamma'$ -nitride, %
Gas	540	30	10	90
	540	300	10	90
	540	720	20	80
Ion	540	30	-	100
	540	300	-	100
	540	720	-	100

Table 2. Comparison of the white layer structures of gas and ion nitrided GOST 10 steel

Our investigations on the microstructure of ion nitrided EN 31CrMoV9 steel show that on the surface is formed nitrided white layer consists from  $\epsilon$ -nitride and  $\gamma'$ -nitride (Krastev et al., 2010) – Fig. 2. The thickness of the nitride white layer is 10 – 12  $\mu\text{m}$  and in depth follows 150 – 200  $\mu\text{m}$  diffusion zone with nitride precipitates – fig. 3.

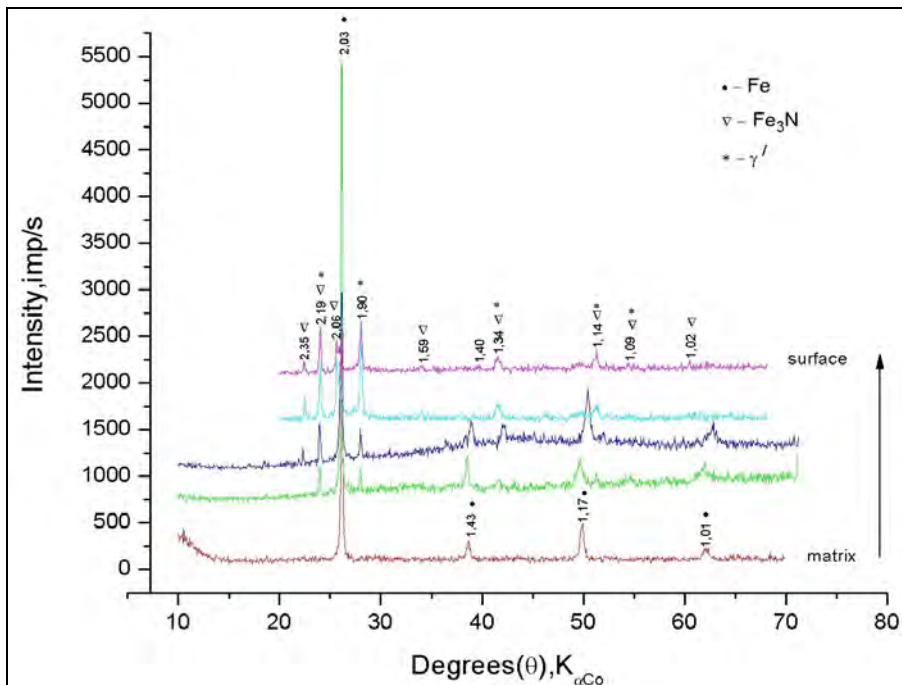


Fig. 2. X-ray diffraction patterns of ion nitrided surface layer on steel 31CrMoV9.

The microhardness of the nitride white layer is about 1050 – 1100 HV which together with the improve corrossions resistance provides high wear resistance.

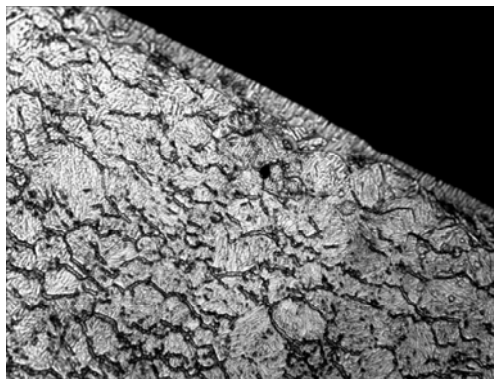


Fig. 3. Microstructure of ion nitrided surface of steel 31CrMoV9 (x600).

By contrast to plain carbon steels, the corrosion resistance of stainless steels can be reduced by nitriding, due to breakdown of the surface chrome oxide barrier to enable nitrogen diffusion into the steel. The stainless steels exhibit generally poor tribological properties, because of that treatments such as nitriding can enhance the surface hardness and improve the wear resistance. Plasma nitriding can be carried out for this purpose at temperatures from 350 to 500 °C (Castaletti et al., 2008). While giving significant improvement in wear resistance, the higher treatment temperatures tend to adversely affect on the corrosion performance of the stainless steels in result of formation of CrN. Improved corrosion resistance of plasma-nitrided layers on stainless steels are observed when the nitriding process is carried out at a lower temperature (400 °C) with presence in the layer of “S - phase”, which is supersaturated with nitrogen austenite. The expanded austenite layer in nitrided YB 1Cr18Ni9Ti steel has a good pitting corrosion resistance in 1 % NaCl solution and an equivalent homogeneous corrosion resistance in 1 N H<sub>2</sub>SO<sub>4</sub> solution, compared with the original stainless steel (Lei & Zhang, 1997).

## 2.2 Diffusion coatings obtained by boronizing

Boronizing or boriding is a thermochemical treatment that involves diffusion of boron into the metal surface at high temperatures (Davis, 2002; Liahovich, 1981; Minkevich, 1965; Schatt, 1998). The boriding process is carried out at temperatures between approximately 850 and 1050 °C by using solid, liquid or gaseous boron-rich atmospheres. Boronizing is an effective method for significant increasing of surface hardness, wear and corrosion resistance of metals. The basic advantage of the boronized steels is that iron boride layers have extremely high hardness values between 1600 and 2000 HV. The typical surface hardness of borided carbon steels is much greater than the produced by any other conventional surface hardening treatments. The combination of a high surface hardness and a low surface coefficient of friction of the borided layer provides also for these diffusion coatings a remarkable wear resistance. Boronizing can considerably enhance the corrosion-erosion resistance of ferrous materials in nonoxidizing dilute acids and alkali media and is increasingly used to this advantage in many industrial applications. It is also important that the borided diffusion coatings have a good oxidation resistance up to 850 °C and are quite resistant to attack by molten metals.



On the surface of the boronized steels generally a boron compounds layer is formed. It can be a single-phase or double-phase layer of borides with definite composition. The single phase boride layer consists of  $\text{Fe}_2\text{B}$ , while the double-phase layer consists of an outer phase of  $\text{FeB}$  and an inner phase of  $\text{Fe}_2\text{B}$ . The  $\text{FeB}$  phase is brittle and harder, forms a surface under high tensile stress and has a higher coefficient of thermal expansion. The  $\text{Fe}_2\text{B}$  phase is preferred because it is less brittle and forms a surface with a high compressive stress, the preferred stress state for a high-hardness, low-ductility case. Although small amounts of  $\text{FeB}$  are present in most boride layers, they are not detrimental if they are not continuous. Continuous layers of  $\text{FeB}$  can be minimized by diffusion annealing after boride formation. In Fig. 4 is shown the typical microstructure of borided layer on the surface of plain carbon steel (Schatt, 1998).

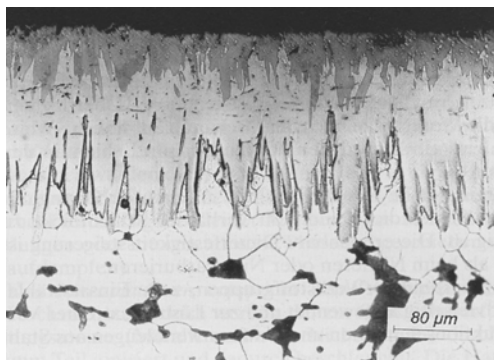


Fig. 4. Microstructure of borided layer on the EN C15 steel consisting of  $\text{FeB}$  (dark) and  $\text{Fe}_2\text{B}$  (light) phases.

Boriding can be carried out on most ferrous materials such as plain carbon steels, low-alloy steels, tool steels, stainless steels, cast irons and sintered steels. There are a variety of methods for producing of boride diffusion coatings on steel surface. Thermochemical boronizing techniques include:

- Pack boriding
- Paste boriding
- Liquid boriding
- Gas boriding
- Plasma boriding
- Fluidized bed boriding

Only pack and paste boriding from these methods have reached commercial success. Because of environmental problems gas and liquid boriding have a very limited application. Pack boriding is the most common boriding method with a wide development. The process involves packing the steel parts in a boriding powder mixture from ferroboration, amorphous boron or  $\text{B}_4\text{C}$ , fluxes and activators ( $\text{NaBF}_4$ ,  $\text{KBF}_4$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ ), and heating in a heat-resistant steel box at 900 to 1050 °C for one to twelve hours depending on the required layer thickness. The commonly produced case depths are 0.05 to 0.25 mm for carbon steels and low-alloy steels and 0.025 to 0.080 mm for high-alloy steels.

Paste boriding is an attractive technique for producing of boride diffusion coatings on steels surface because of lower cost and less difficulty in comparison with pack boriding. It is carried out usually in a paste from  $B_4C$  as a boriding agent,  $Na_3AlF_6$  as an activator, fluxes, and binding agent for the paste formation. The temperature of the process is from 800 to 1000 °C and heating is mostly inductively or resistively. A layer in excess of 50  $\mu m$  thickness may be obtained after inductively or resistively heating to 1000 °C for 20 min. The relationship between the boride layer thickness and time for iron and steel boronized with  $B_4C-Na_2B_4O_7-Na_3AlF_6$  based paste at 1000 °C is shown in Fig. 5 (ASTM Handbook, 1991).

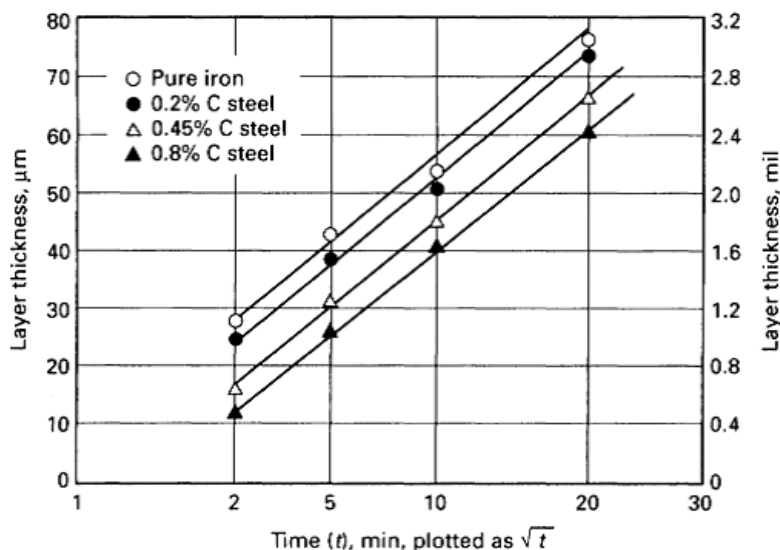


Fig. 5. Relationship between the boride layer thickness and time for iron and steel boronized with  $B_4C-Na_2B_4O_7-Na_3AlF_6$  based paste at 1000 °C.

Gas and plasma boriding are carried out in  $B_2C_6-H_2$  or  $BCl_2-H_2$  mixtures which are high toxic and also there are problems with the explosiveness of the gaseous atmosphere. As a result these techniques have not gained commercial acceptance. Plasma boriding has some advantages, mainly the lower temperature of the thermochemical process of about 650 °C and reduction of the duration.

Fluidized bed boriding is the recent innovation on the area of boriding technologies. It is carried out in special retort furnace and involves a bed material of coarse silicon carbide particles, a special boride powder and oxygen-free gas atmosphere from nitrogen-hydrogen gas mixture. The process offers several advantages, can be adaptable to continuous production and has low operating costs due to reduced processing time and energy consumption for mass production of boronized parts.

Our investigations on pack boriding show that it is possible to change the traditional type and amount of activator, and provide a successful diffusion process with high quality of obtained boride layers. The compositions of powder mixtures were from 55 %  $B_4C$ ; 1 to 3 %  $NaBF_4$  or  $Na_3AlF_6$  and diluter  $Al_2O_3$ . The thermochemical treatments are carried out with

EN C60 steel at 950 °C and time from two to six hours. The results show that it is possible to exchange the traditional for the process  $\text{NaBF}_4$  with the inexpensive  $\text{Na}_3\text{AlF}_6$  as an activator, and amount of 3 % is enough to provide boride layer with the required thickness, structure and hardness. In Fig. 6 are given the structures of borided surface of steel C60 obtained for 2 and 6 h in powder mixture containing 3 %  $\text{Na}_3\text{AlF}_6$ . The XRD analysis shows that the boride layers consist mainly from  $\text{Fe}_2\text{B}$  with a small amount of  $\text{FeB}$ . The microhardness of the boride diffusion coatings is 1600 - 1800 HV.

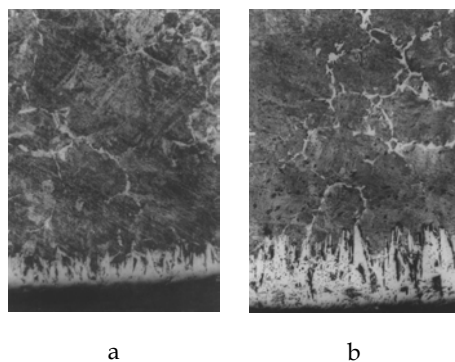


Fig. 6. Microstructure of boride layers on C60 steel obtained for 2 (a) and 6 (b) hours pack boriding at 950 °C in powder mixture containing 3 %  $\text{Na}_3\text{AlF}_6$  (x150).

The borided steels have a higher corrosion resistance together with the high hardness and wear resistance. In Fig. 7 is given a comparison in the corrosion resistance of 0.45 % C plain carbon steel before and after boronizing (ASTM Handbook, 1991).

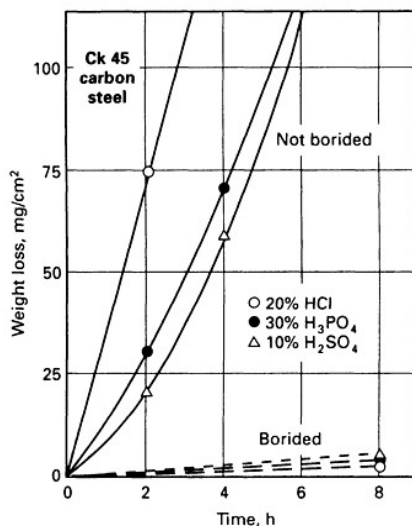


Fig. 7. Corroding effect of mineral acids on boronized and unboronized Ck45 steel.

After boronizing, the corrosion rate of boronized low carbon steel AISI 1018 is about 100 times lower than the corrosion rate of unboronized one based on the electrochemical measurement (Suwattananont, 2005). The boronized high strength alloy steel AISI 4340 and austenitic stainless steel AISI 304 have corrosion rate about several times lower than the corrosion rate of unboronized steels. The comparison of the tafel plots between boronized and unboronized AISI 1018 steel is shown in Fig. 8.

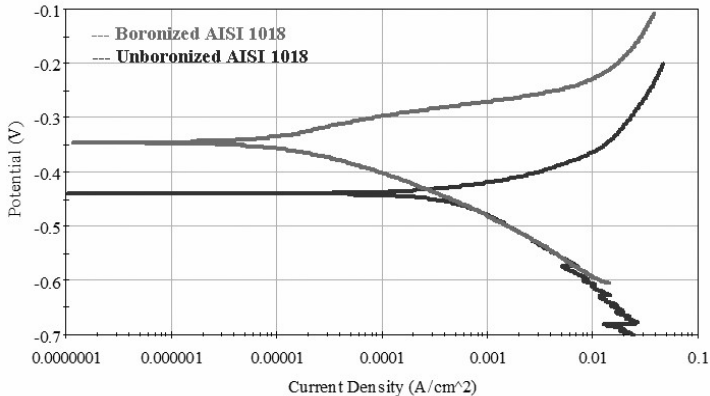


Fig. 8. Tafel plots of boronized and unboronized low carbon steel AISI 1018.

After boronizing the steel becomes nobler and has lower corrosion rate than the unboronized one which proves that the corrosion resistance of the boronized steels is improved.

### 2.3 Diffusion coatings obtained by carbonitriding and nitrocarburizing

Carbonitriding and nitrocarburizing are those thermochemical treatments which involve diffusional addition of both carbon and nitrogen to the surface of steels for production of diffusion coatings with determinate structure and properties (ASTM Handbook, 1991; Chatterjee-Fischer, 1986; Davis, 2002). Carbonitriding is a modified form of gas carburizing rather than a form of nitriding. The modification consists of introducing ammonia into the gas carburizing atmosphere to add nitrogen to the carbonized case as it is being produced. Nascent nitrogen forms at the steel surface by the dissociation of ammonia in the furnace atmosphere and diffuses simultaneously with carbon. Typically, carbonitriding is carried out at a lower temperatures and shorter times than is gas carburizing, producing a shallower case than is usual in production carburizing. The temperature range for the process is normally 750 – 950 °C and the properties of the obtained diffusion coating are similar with those obtained by carburizing. After the next heat treatment they have high hardness and wear resistance, but the corrosion resistance enhance is unessential. For the improvement of corrosion behaviour of steels the carbonitriding should be carried out at lower temperatures of about 700 °C for obtaining on the surface a carbonitride compound layer. In this case the thermochemical process transforms into nitrocarburizing. Nitrocarburizing, as definition, is thermochemical treatment that is applied to a ferrous object in order to produce surface enrichment in nitrogen and carbon which form a

compound layer. This technique has a wide application in the industry and is carried out as gaseous, plasma and liquid process. There is a tendency for limitation of the liquid process because of its toxicity and environmental problems. Based on the temperature range of the thermochemical treatment, nitrocarburizing can be classified as:

- Ferritic nitrocarburizing
- Austenitic nitrocarburizing

Ferritic nitrocarburizing is this thermochemical treatment which is realized at temperatures completely within the ferrite phase field. The primary object of such treatments is usually to improve the anti-scuffing characteristic of ferrous engineering components by producing a compound layer in the surface which has good tribological characteristics. In addition, the fatigue characteristics can be considerably improved, particularly when nitrogen is retained in solid solution in the diffusion zone beneath the compound layer. This is normally achieved by quenching into oil or water from the treatment temperature, usually 570 °C. The obtained at these temperatures compound white layer provided the enhancing of the corrosion resistance of the nitrocarburized surface. The compound layer produced by ferritic nitrocarburizing consists mainly from  $\epsilon$  carbonitride because of low carbon solubility in  $\gamma'$  nitride. In Fig. 9 is shown the typical microstructure of nitrocarburized surface of low carbon steel (Chatterjee-Fischer, 1986).



Fig. 9. The microstructure of nitrocarbonized EN C15 steel at 570 °C for 2 hours.

On commercial basis post nitrocarburizing oxidation treatments have been used to enhance the aesthetic properties of gaseous nitrocarburized components. However it is proved that these additional techniques improve the fatigue, wear and corrosion resistance of steel surface and can be successfully combined for this purpose.

When the treatment temperature is such that partial transformation of the matrix to austenite occurs through enrichment with nitrogen, than the treatment is referred to as austenitic nitrocarburizing. With austenitic nitrocarburizing the subsurface is transformed to iron-carbon-nitrogen austenite, which is subsequently transformed to tempered martensite and bainite, with hardness in the range of 750 to 900 HV. The keeping of compound layer from  $\epsilon$  carbonitride on the nitrocarburized steel surface together with the transformed subsurface after the nitrocarburizing process at temperatures of about 700 °C provide enhance of the fatigue resistance of treated parts together with high corrosion and wear

resistance. Typical transformed austenite case thicknesses are in the range 50 to 200  $\mu\text{m}$ . However, much deeper cases can be achieved by employing a precarbured treatment prior to nitrocarburizing.

#### 2.4 Diffusion coatings with high corrosion resistance on metals basis

The diffusion coatings on metals basis for improvement the corrosion resistance of steels have a wide industrial application. The main aim of the thermochemical treatment in this case is to form on the steel surface a layer from metals with high corrosion resistance, their solid solution in the metal matrix, or their compounds. The metals that are usually used for this thermochemical treatment are chromium, aluminium and zinc.

Chromizing is a surface treatment process of developing a chromized layer on metals and alloys for heat-, corrosion-, and wear resistance (Davis, 2001; Liahovich, 1981; Minkevich, 1965). The technique is applied principally for different types of steels and cast irons, but it is also of interest for surface modification of nickel, molybdenum, tungsten, cobalt and their alloys. Chromized steels offer considerably improved corrosion and oxidation resistance of the surface and can work successfully in complicated conditions combining wear, high temperature, corrosion, erosion and cavitation. If the plain carbon or alloy steel for chromizing contains carbon more than 0.4 %, a corrosion and wear resistant compound layer from  $\text{Cr}_{23}\text{C}_6$  and  $\text{Cr}_7\text{C}_3$  with thickness 0.01 – 0.03 mm will be formed on the surface. On steels with low carbon content compact chromium carbides layer cannot be formed, but because of high solubility of chromium in iron it will be formed on the steel surface a solid solution with chromium content up to 60 % which provide the high corrosion resistance of the diffusion layer. There are a variety of methods for producing of chromium diffusion coatings on steel surface, such as gaseous, liquid, pack and vacuum chromizing, but only vacuum and pack processes are developed as thermochemical treatment technologies with a wide industrial application.

The pack chromizing is often preferred because of its easily process conditions and low cost. The components to be chromized are packed with fine chromium powder and additives. A typical chromizing mixture consists of 60 percent chromium or ferrochromium powder, up to 2 percent halide salt as an activator and about 38 percent aluminium oxide as inert filler. The process is carried out at 900 – 1050  $^{\circ}\text{C}$  for 6 to 12 hours.

The aluminizing pack-cementation thermochemical treatment has also the most widely industrial application for production of aluminium diffusion coatings. The process is commercially practiced for a wide range of metals and alloys, including plain carbon steels, low-alloy steels and high-alloy steels, cast irons, nickel- and cobalt-base superalloys. Sample aluminide coatings have high corrosion resistance and resist high-temperature oxidation by the formation of an aluminium oxide protective layer and can be used up to about 1000  $^{\circ}\text{C}$ . The powder mixture for pack aluminizing usually consists from about 50 % aluminium or ferroaluminium powder, 1 to 2 %  $\text{NH}_4\text{Cl}$  as an activator and about 48 % aluminium oxide as inert filler. As the other processes of pack-cementation, the aluminizing technique consists of packing the steel parts in the powder mixture and heating in a heat-resistant steel box at 800 to 1100  $^{\circ}\text{C}$  for three to fifteen hours, depending on the alloy type and required layer thickness. The aluminized diffusion coatings on plain carbon steels and low-alloy steels are usually about 0.05 – 0.8 mm thick and represent a white layer with a complicated

composition from iron aluminides ( $\text{Fe}_3\text{Al}$ ,  $\text{FeAl}$ ,  $\text{FeAl}_2$  and  $\text{Fe}_2\text{Al}_5$ ) with high corrosion and oxidation resistance and solid solution of aluminium in  $\alpha$ -iron (Davis, 2001; Liahovich, 1981; Minkevich, 1965; Springer et al., 2011).

Our research group has been carried out investigations on high-temperature corrosion and abrasive resistance of chromium and aluminium diffusion coatings on EN C45 steel as parts of sintering machine in an agglomeration process of iron ores. The specimens are produced by pack-cementation process at the optimal characteristics for the both heat treatment techniques. The structure of the obtained diffusion coatings is given in Fig. 10. The comparison shows that better behaviour in these work conditions have the chromium diffusion coatings despite of their smaller thickness.

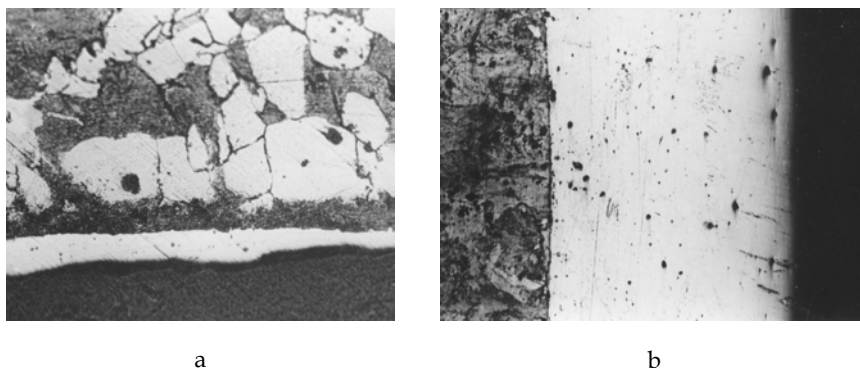


Fig. 10. Diffusion coatings on C45 steel produced by chromizing (a) x150, and aluminizing (b) x250.

Zinc diffusion coatings are traditional method for corrosion protection of steels with a great practical importance and a wide industrial application (Proskurin et al., 1988). Zinc has a number of characteristics that make it a well-suited corrosion protective coating for iron and steel products in most environments. The excellent field performance of zinc coatings results from its ability to form dense, adherent corrosion product films and a rate of corrosion considerably below that of ferrous materials. Many different types of zinc coatings are available and each has unique characteristics, which affect not only on the applicability, but also on the relative economics and expected service live. Hot-dip galvanizing and sherardizing are the main thermochemical treatment techniques for producing of zinc diffusion coatings on steel surface.

The hot-dip galvanizing process, also known as general galvanizing, produces a zinc coating on iron and steel products by immersion of the material in a bath of liquid zinc. Before the coating is applied, the steel surface is cleaned to remove all oils, greases, soils, mill scale, and rust. Galvanized coatings are used on a multitude of materials ranging in size from small parts such as nuts, bolts, and nails to very large structural shapes. The process is usually carried out at 440 to 470 °C for 1 to 10 minutes and in result is obtained zinc diffusion coating which consists of a series of zinc-iron compound layers from  $\text{FeZn}_{13}$  ( $\xi$ -phase),  $\text{FeZn}_7$ - $\text{FeZn}_{10}$  ( $\delta$ -phase),  $\text{Fe}_5\text{Zn}_{21}$  ( $\Gamma_1$ -phase) with a surface layer of solid solution of iron in zinc ( $\eta$ -phase) or pure zinc.

Sherardizing is a diffusion process in which the steel parts are heated in the presence of zinc dust or powder in inert medium. Aluminium oxide or sand in amount of 20 % is added to the zinc powder as inert filler and 1 to 2 % halide salts are used as activator. The thermochemical treatment can be carried out in retort, rotated drum or as a pack-cementation process at 350 to 500 °C for three to twelve hours. The structure of the obtained layer is the same as the structure on steel surface after hot-dip galvanizing with a thickness about 50 – 400 µm.

### 3. Recast layers

The recast layers on metals and alloys are created by treating the surface with high energy stream such as laser, ion beam or electrical discharge for a very short time and pulse characteristics. The high energy attack on the surface involves local melting and in many cases vaporizing of metal microvolumes. After the cooling, on the treated metal surface a recast layer with different structure and properties from the substrate is formed. This recast layer can be with the same chemical composition as the substrate or with different one if in the thermal process suitable conditions for surface alloying are created. When the recast process is not controlled there are on the surface microcracks and pores which have negative influence on the surface properties and the recast layer must be removed. In the controlled recast processes it is possible to produce surface layer with determinate chemical composition, thickness, structural characteristics and properties, which are unique for the material with the very high hardness, corrosion- and wear resistance. The basic techniques that give opportunities in this direction are laser surface treatment and electrical discharge machining.

Laser surface treatment is widely used to recast and modify localized areas of metallic components. The heat generated by the adsorption of the laser light provides a local melting and after controlled cooling is obtained a recast layer on the metal surface with high hardness, wear resistance and corrosion resistance. The laser surface melting is based on rapid scanning of the surface with a beam focused to a power density scale of  $10^4$  W/cm<sup>2</sup> to  $10^7$  W/cm<sup>2</sup>. Quench rates up to  $10^8$  -  $10^{10}$  K/sec provide the formation of fine structures, the homogenization of microstructures, the extension of solid solubility limits, formation of nonequilibrium phases and amorphous phases or metallic glasses, with corrosion resistance 10–100 time higher compared to crystalline (Bommi et al., 2004). Laser surface melting is a simple technique as no additional materials are introduced, and it is especially effective for processing ferrous alloys with grain refinement and increase of the alloying elements content in solid solution. In fact the process has been employed for improving the cavitation erosion and corrosion resistance of a number of ferrous alloys.

The laser surface melting can be combined with a simultaneous controlled addition of alloying elements. These alloying elements diffuse rapidly into the melt pool, and the desired depth of alloying can be obtained in a short period of time. By this means, a desired alloy chemistry and microstructure can be generated on the sample surface and the degree of microstructural refinement will depend on the solidification rate. The surface of a low-cost alloy, such as low carbon steels, can be selectively alloyed to enhance properties, such as resistance to wear and corrosion (Davis, 2001).

Electrical discharge machining is a thermoelectric process that erodes workpiece material by series of discrete but controlled electrical sparks between the workpiece and electrode



immersed in a dielectric fluid (Asif Iqbal & Khan, 2010). It has been proven to be especially valuable in the machining of super-tough, electrically conductive materials, such as tool steels, hard metals and space-age alloys. These materials would have been difficult to machine by conventional methods, but EDM has made it relatively simple to machine intricate shapes that would be impossible to produce with conventional cutting tools. In EDM process, the shapes of mold cavities are directly copied from that of the tool electrode, so time-consuming preparation work must be done on the fabrication of the corresponding tool electrode.

The basis of EDM can be traced as far back as 1770, when English chemist Joseph Priestly discovered the erosive effect of electrical discharges (Ho & Newman, 2003). In 1943 Russian scientists Boris Lazarenko and Natalya Lazarenko (Satel, 1956) applied the destructive effect of electrical sparks for manufacturing and developed a controlled process of machining difficult-to-machine metals by vaporizing material from the surface. At the recent years the research interests and practice are directed to the novel application of electrical discharge machining in the area of surface modification.

### 3.1 Surface modification by EDM

The electrical discharge machining uses electrical discharges to remove material from the workpiece, with each spark producing temperature of about 8000-20000 °C. This causes melting and vaporizing of small volumes of the metal surface and after cooling in the dielectric fluid the melted zones are transformed in recast layer with specific structure. The EDM modified surface consists from two distinctive zones (Kumar et al., 2009; Ho & Newman, 2003):

- Recast layer
- Heat affected zone

The recast layer is also named white layer and it crystallizes from the liquid metal cooled at high rate in the dielectric fluid. The depth of this top melted zone depends on the pulse energy and duration. Below the top white layer is the heat affected zone with changes in the average chemical composition and possible phase changes. In Fig. 11 is shown the typical microstructure of EDM modified steel surface.

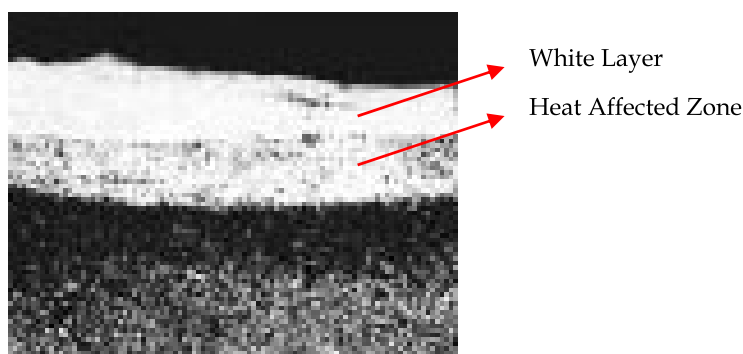


Fig. 11. Microstructure of EDM modified steel surface.

The recast white layer as well as the other discussed white layers can not be etched and has very high hardness, corrosion resistance and wear resistance. The phenomenon of surface modification by EDM has been observed for over four decades. Under the high temperature of the discharge column, the white layer can dissolve carbon from the gases formed in the discharge column from the hydrocarbon dielectric and receives higher carbon content than the base material and hence show increased resistance to abrasion and corrosion. Moreover electrode material has been found in the workpiece surface after machining with conventional electrode. Better surface properties have been obtained by machining with powder metallurgy electrodes containing alloying elements which diffuse in the workpiece surface. Fine powders mixed in the dielectric offer another way for achieving desirable surface modification. All this determines the three main directions for surface modification by electrical discharge machining (Kumar et al., 2009):

- Surface modification by conventional electrode materials
- Surface modification by powder metallurgy electrodes
- Surface modification by powder-mixed dielectric

In the EDM process with conventional electrode has been observed material transfer from the electrode to workpiece surface which is a function of the various electrical parameters of the circuit. The high energy machining results in lower surface deposition, but there is more diffusion in depth. Also it is found that the negative polarity is desirable for increase of material transfer from the tool electrode. The improvement of the surface integrity, wear- and corrosion resistance of the workpiece material can be realized by surface alloying during sparking, using sintered powder metallurgy electrode. With the alloying there is a potential to increase workpiece hardness from two to five times and significant enhance the corrosion resistance that of the bulk material. It is possible remarkable to increase the corrosion resistance of carbon steel by using of composite electrodes containing cooper, aluminium, tungsten carbide and titanium. The material from the electrode is transferred to the workpiece and the characteristics of the surface layer can be changed significantly. The same results can be achieved with the addition of metallic and compound powders in the dielectric. In this case are used Ni, Co, Fe, Al, Cr, Cu, Ti, C (graphite), etc.

### **3.2 Surface modification by electrical discharge treatment in electrolyte**

Such a method as EDM is the electrical discharge treatment in electrolyte, where the modification goes by a high energy thermal process in a very small volume on the metallic surface, involving melting, vaporisation, activation and alloying in electrical discharges and after that cooling of this surface with high rate in an electrolyte. The high energy process put together with the nonequilibrium phase transformations in the metallic system causes considerable modifications of the metallic surface and obtaining of layers with finecrystalline and nanocrystalline structure (Krastev at al., 2009; Krastev & Yordanov, 2010). The metallic surface after electrical discharge treatment in electrolyte has a different structure in comparison with the metal matrix which determines different properties. It is observed remarkable increasing of hardness, strength and corrosion resistance related to the nonequilibrium phase transformations and the obtained finecrystalline microstructure. The investigations show that obtained on tools layers have higher hardness, wear resistance, tribocorrosion resistance and corrosion resistance, which give better performance, considerable increasing of working life and wide opportunities for industrial application.

For the electrical discharge treatment in electrolyte is developed a laboratory device, shown in Fig. 12, giving opportunities for treatment of cylindrical workpieces with diameter up to 20 mm. The electrolyte 3 is in active movement by mixing from a magnetic stirrer 4. After passing of electric current with determinate characteristics through the electrolyte between the workpiece 1 and electrode 2 starts an active sparking on the workpiece surface. The sparking characteristics depend on different factors such as parameters of the electric current, type and composition of the electrolyte, movement of the workpiece and electrolyte.

The workpieces are made from high speed steel HS 6-5-2 with structure after the typical heat treatment for tools of this steel and hardness about of 950 HV. The choice of high-alloy steel is founded on the opportunity for higher effectiveness of treatment on structure and properties of modified surfaces after the nonequilibrium phase transformations from liquid state.

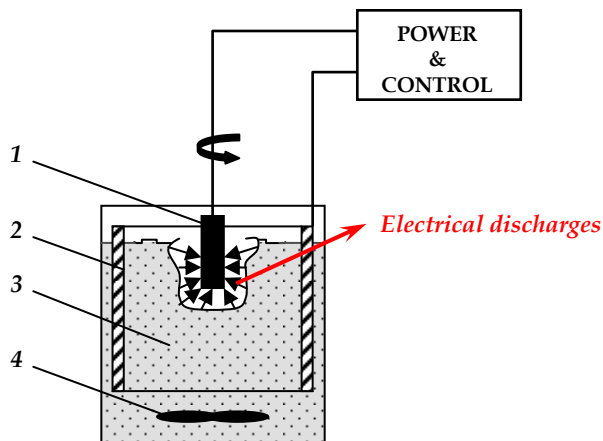


Fig. 12. Installation for electrical discharge treatment in electrolyte: 1 – workpiece, 2 – electrode, 3 – electrolyte, 4 – magnetic stirrer.

The principle changes that occur on the modified steel surface by the high speed quenching from liquid state in the treatment process can be described as:

- Expansion of the solubility in solid state
- Grain refinement with possibilities for obtaining of nanocrystalline structure
- Formation of metastable phases
- High concentration of crystalline imperfections

Some studies at similar conditions show significant increasing of solubility of carbon in steel up to 2 % in the martensite and 3.5 % in austenite which is a precondition for high strength of the treated surface.

By the investigations were obtained layers on the workpiece surface with approximately equal thickness, depending of the electrical current characteristics and time of treatment. The modified surfaces can be observed as a light layer on the workpieces. The melted and resolidified layer during this process can be also referred as a “white layer”, since generally no etching takes place in these areas at the metallographic preparation because of its high

corrosion resistance which is one of the important characteristics of nanocrystalline structures.

The electric discharges generate an enormous amount of heat, causing local melting on the workpiece surface and thereupon it is rapidly quenched from the liquid state by the electrolyte. This recast area has a specific structure which is composed of several microscopic metallurgical layers, depending of machining conditions. In Fig. 13 is shown an optical micrograph of the modified surface of high speed steel obtained by electrical discharge treatment in electrolyte.

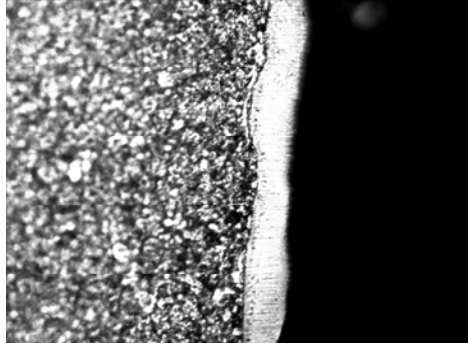


Fig. 13. Microstructure of recast layer obtained by electrical discharge treatment in electrolyte of HS 6-5-2 steel, x800.

The high rate of the recasting process gives opportunities for formation of metastable phases and considerable decreasing of grain size. The electrolyte type is of great importance for the chemical composition, microstructure and properties of the modified layer. By these experiments the electrolyte is on water basis and contains boron or silicon compounds. At short times of treatment it is not observed diffusion of elements from the electrolyte in the modified surface, but it is available diffusion process inside the workpiece between the white layer and the matrix - Table 3. The strong carbide-formed elements such as Mo, W, and V diffuse from the white layer to the matrix and Cr, Co in the opposite side.

Chemical element	Matrix of workpiece	White layer
Si	<0.01	<0.01
Mo	5.58	4.87
V	2.30	1.63
Cr	4.25	4.52
Co	<0.01	0.19
Ni	<0.01	<0.01
W	8.34	5.75

Table 3. EDS analysis of modified workpiece from HS 6-5-2 steel

The thickness and integrity of obtained recast white layer on the steel surface by electrical discharge treatment in electrolyte depend on the electrical current characteristics and time duration of the treatment. At higher voltage are observed thicker white layers by equal

durations of the treatment. In Fig. 14 are shown the light microscopy micrographs of steel workpiece surfaces, modified for two minutes at 80 V and 100 V. The optical measured thicknesses of the layers are 0.01 mm and 0.02 – 0.03 mm respectively.

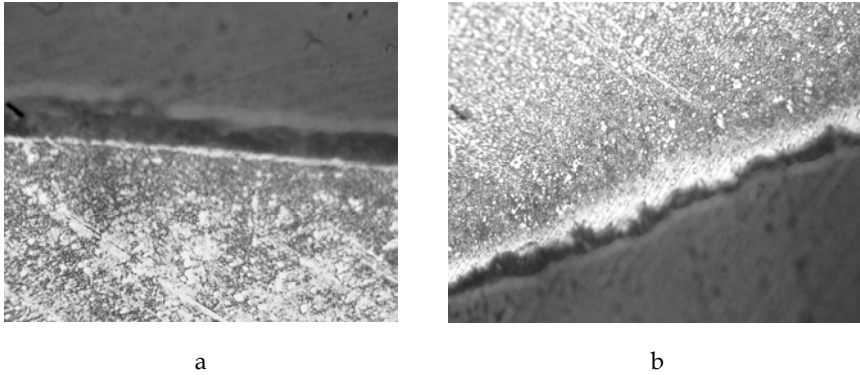


Fig. 14. Microstructure of layers, obtained for 2 min at 80 V, and for 2 min at 100 V (b) x800.

At higher voltage and longer duration of the treatment it is observed increasing of roughness of the white layer surface which is illustrated with SEM micrographs in Fig. 15.

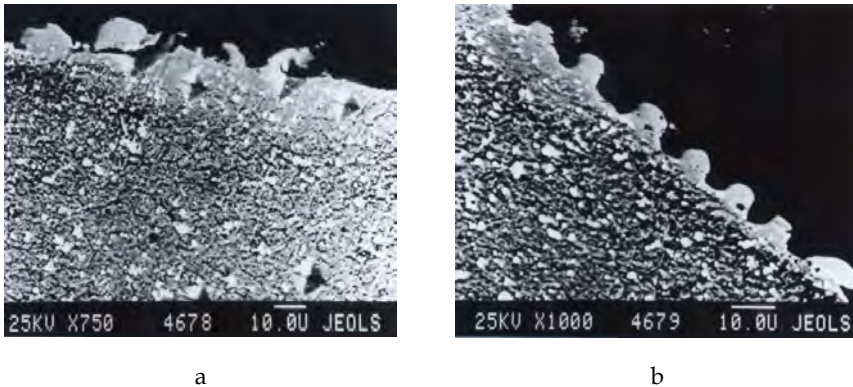


Fig. 15. SEM micrograph of modified steel surface by duration of 2 min (a) and 3 min (b) at 100 V.

The fine structures of modified layers with specific etching are shown after SEM investigation on Fig. 16. By modification on the workpiece surface can be observed two specific zones:

- White zone
- Phase transformations zone

The “Phase transformations zone” has different structures depending on the temperature and cooling rate. When the temperature of the steel surface is above the melting point and

cooling rate is lower a zone with dendritic structure is formed – Fig. 16a. In the other case (Fig. 16b), when the temperature is in the austenitic region and the cooling rate is higher than the critical one a martensite is formed.

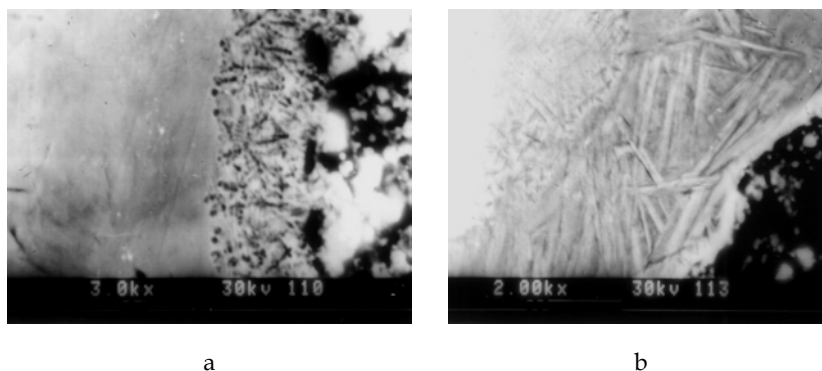


Fig. 16. SEM images of different microstructures of the modified layers on HS 6-5-2 steel surface: a - dendritic microstructure in the phase transformations zone, b - martensitic microstructure in the phase transformations zone.

The hardness of the modified layers can vary considerably and depend of the treatment conditions, electrolyte composition and microstructure, but in principle it is higher than the hardness of the typical microstructure of this steel. The microhardness of the modified layers is measured by Hanneman test and shows values after the different treatments up to 1600 HV which are very higher than the microhardness of HS 6-5-2 steel microstructures after the typical heat treatment. The experiments show that tools with such surface hardness have higher wear resistance and working capacity.

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