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ELECTROLYTIC-PLASMA PROCESSING AND BORIDING OF VARIOUS SURFACES

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The results of electrolytic-plasma processing (EPP) of copper M2P substrates in 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl, brass L68 M2R EPP polished with 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl as well as steel 12X18N9T have been presented. Both anodic and cathodic treatment processes were used for EPP. Electrolytic-plasma boriding (EPB) was also used for surface strengthening and surface texturing of 12X18N9T stainless steel. After treatment with a borax solution, two additional peaks appear in the XRD patterns of the samples in addition to the Fe-α ferrite peaks. These peaks refer to iron borate $FeBO_3$ (hexagonal lattice) with lattice parameters a = 4.659Å; c = 14.601Å. It was shown that microhardness of the stainless steel of the 12X18H9T type after EPB processing increased from 130 to 500 kg/mm^2.

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INTRODUCTION

Electrolytic-plasma technology (EPP) is an environmentally friendly method of processing metal products and is an alternative to the traditional electrochemical method. This method can use alkali acids and low-concentration salts. In most cases, processing can be carried out in aqueous solutions of salts [1]. It is possible to process products from a large list of metals and even semiconductors. The list of those to be processed includes metal and semiconductor products made of stainless and carbon steels, copper and aluminum alloys, brass, zinc, titanium, and silicon. A distinctive feature of this technique is the short duration of the processing. The duration of the polishing process is 2…5 min when using 1…5% aqueous solutions of ammonium sulfate and ammonium chloride. Polishing of metals occurs in the range of voltages of 200…350 V and current densities of 0.2…0.5 A/cm^2 [2].

The polishing and etching process occurs in the presence of a vapor-plasma shell. Etching of microroughnesses is determined by a set of various parameters. These are the electrical characteristics of the circuit, thermal conditions, molecular and dynamic properties of the electrolyte in the near-electrode region. A multiphase metal-plasma-gas-electrolyte system arises near the anode during polishing. The strength of electric field reached of $10^4…10^5$ V/cm [3, 4]. Electric discharges destroy surface inhomogeneities.

The effects of etching, polishing or cleaning the surface of the product occur due to the synergistic effect of a chemically active environment and electric discharges in the range of a certain electrolyte temperature. It has been experimentally found that the metal removal rate and surface cleanliness are mainly influenced by the following factors. These are the voltage in the sample-electrolyte gap, the chemical composition of the electrolyte, its temperature, viscosity, electrical conductivity, exposure, as well as the properties of the material being processed.

The attractiveness of this method primarily lies in the short duration of the processing processes compared to traditional mechanical and electrochemical processing methods. Of course, the ecological side of the process should be mentioned.

Borated steels have fairly high corrosion and wear resistance due to the formation of solid iron borides. Diffusion saturation with boron also helps to increase the heat resistance and corrosion resistance of carbon steels. Boriding can be carried out in various environments.

Traditional methods include boriding in powder mixtures (electrolysis, liquid and gas) [5, 6]. Saturation with boron from the solid phase is carried out in powders of boron carbide, or amorphous boron. The duration of the process can be reduced by 2–3 times by using nano-sized amorphous boron powder [7].

In this regard, electrolytic plasma boriding (EPB) of metals and alloys, which has certain advantages. The treatment process takes minutes, does not require careful preliminary preparation of the surface to be treated, is easily combined with subsequent hardening in the same electrolyze and is carried out on inexpensive equipment without the use of toxic substances.

In this research electrolytic-plasma processing of materials made of stainless steel, brass and copper has been carried out. The steel samples were also processed by using electrolytic-plasma boriding treatment in a borax solution.

1. EXPERIMENTAL SETUP

Electrolytic-plasma polishing (EPP) is a special case of electrochemical machining which requires high voltage and uses an environmentally-friendly aqueous solutions of salts. A schematic diagram of the EPP process is shown in Fig. 1. sample is chosen as an anode connected to a DC energy source [8].

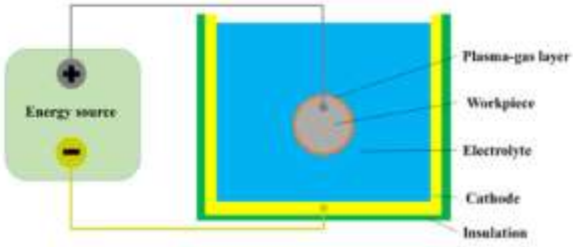

Fig. 1. A schematic diagram of the EPP process

The steel samples were taken for the studies after EPB treatment with a borax solution: First one of steel samples were without treatment; Second, samples were treated with 15% borax solution during t = 10 min; third, target treated with 20% borax solution during t = 10 min.

Electrolytic-plasma processing of copper M2P substrates in 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl, brass L68 M2R EPP polished with 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl as well as steel 12X18N9T has been carried out.

The XRD studies were carried out by using the X-ray diffractometer DRON-UM1 in copper Cu-Kα radiation using a Ni selectively absorbing filter. Diffracted radiation was recorded by a scintillation detector.

Qualitative phase analysis of the samples was carried out using the ICDD PDF-2 international database of crystallographic compounds.

2. RESULTS AND DISCUSSION

The images of original sample surface and after EPB treatment are shown in Fig. 2. XRD patterns of the samples before and after EPB are presented in Figs. 3, 4.

Fig. 2. The 12X18H9T stainless steel images before (left) and after EPB (right)

The initial sample is an austenite steel (see Fig. 3) with a Fe-α lattice parameter of a = 2.872Å. The steel is characterized by a coarse crystalline state and the presence of a moderate texture with (200) orientation.

After treatment with a borax solution, two additional peaks appear in the diffractograms of the samples (see Fig. 4,a,b) in addition to the Fe-α peaks. Most likely, these peaks refer to iron borate $FeBO_3$ (hexagonal lattice) with lattice parameters a = 4.659Å; c = 14.601Å. No other phases (including iron borides) were detected in the samples within the limits of sensitivity. The ferrite lattice parameter did not change after processing (within the measurement error).

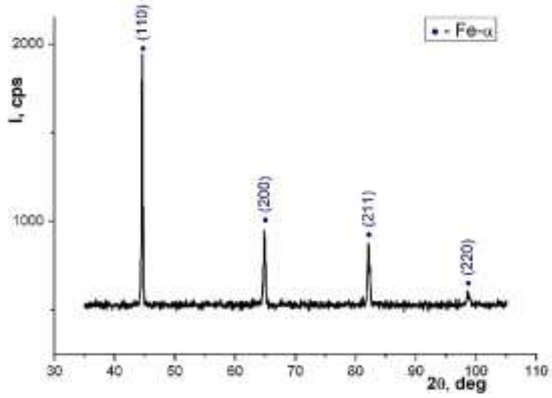

Fig. 3. XRD pattern from initial steel sample

It should be noted that the oxidation behavior of iron borides is a complex problem, due to the possibility of formation of different iron oxides (FeO, Fe_2O_3, Fe_3O_4), iron borates (Fe_3BO_5, Fe_3BO_6, $FeBO_3$, FeB_2O_4, FeB_4O_7) and boron oxides (B_6O, B_2O_3). At room temperature B_2O_3 becomes a non-crystalline structure, therefore it is difficult to detect this phase using XRD. Moreover, this phase at 973 K evaporates, and the formation of iron oxides and iron borates is preliminary. The increase in temperature and time of oxidation results in formation of different iron borates e.g., Fe_3BO_5, Fe_3BO_6, $FeBO_3$ and iron oxides e.g. Fe_2O_3.

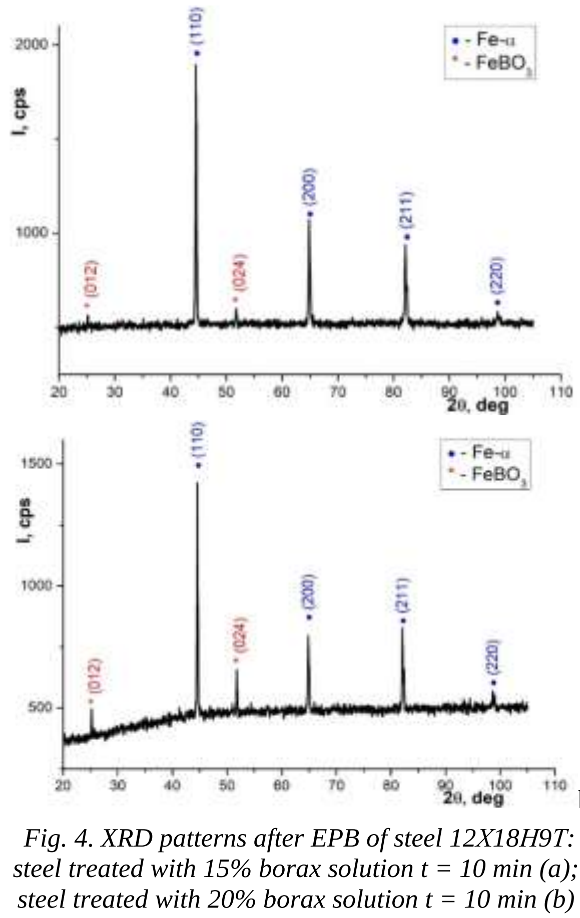

Fig. 4. XRD patterns after EPB of steel 12X18H9T: steel treated with 15% borax solution t = 10 min (a); steel treated with 20% borax solution t = 10 min (b)

The tendency for the formation of these phases results from the oxidation conditions (temperature, duration, atmosphere) and the phase composition of the borided layer. The presence of amorphous boride oxide at 773…873 K is responsible for formation of a glassy layer on the surface which protect the material from further oxidation.

The boriding atoms must have sufficient energy to overcome an activation energy barrier. The effect of temperature on chemical reaction rates (1) was arrived at by Arrhenius [9]. The relationship between the growth rate constant k, activation energy Q, and the temperature in Kelvin T, can be expressed by Arrhenius equation as

$$k = A \times \exp\left(-\frac{Q}{RT}\right), \qquad (1)$$

where A is the diffusion coefficient; Q is the activation energy (J/mol); R is the gas constant, and T is the absolute temperature (K). After a period of PEB time, the interface between the substrate and compact layer was saturated with boron. It was shown that microhardness of the stainless steel of the 12X18H9T type after EPB increased from 130 to 500 kg/mm^2.

In general, the EPP method can be used to process any conductive materials, but at the moment the method is used mainly for processing chromium-nickel steels. Chromium-nickel steels are in great demand in many industrial areas, and high demands are often placed on the surface quality of parts made of these alloys. EPP method is also used for steel dies and press molds made of carbon steels as finishing treatment.

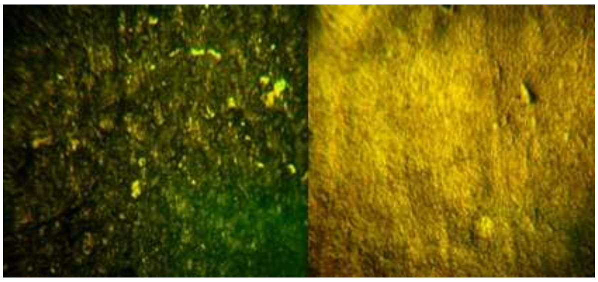

Fig. 5. Images of steel 12X18N9T surfaces before and after EPP in 2% solution $(NH_4)_2$ SO_4, anodic process (magnification ×160)

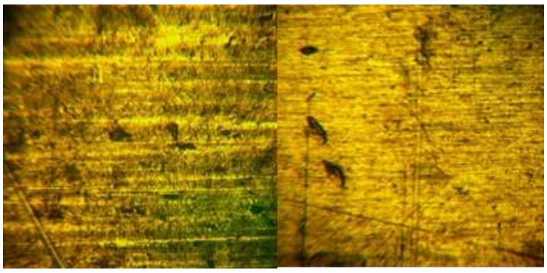

Fig. 6. Images of copper M2P before and after EPP in 2% solution $(NH_4)_2$ SO_4 + 0.5% NaCl, anodic process (magnification ×160)

The formation of plasma on the surface of anodic or cathodic substrate, which depends on the polarity of applied voltage, gives the capability to carry out anodic or cathodic EPP for various surface engineering. For the anodic EPP, it has been usually associated with surface passivation and coating, leading to oxidizing, carburizing, and/or nitriding of the electrode surface [10-16]. While the cathodic EPP has been used for preparing metal nanoparticles or depositing metallic coating [17-20].

As a result of studying the morphology of the surface of steel, brass and copper after EPP, the presence of structural transformations and the formation of a modified layer 80…150 μm thick were established (Figs. 5-9).

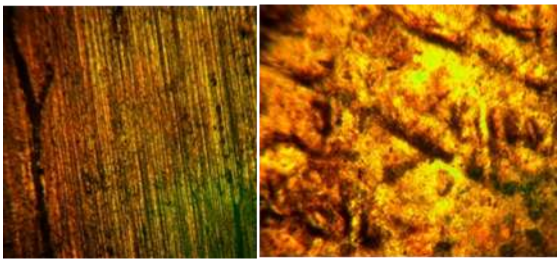

Fig. 7. Images of brass L68 M2R before and after EPP polishing with 2% solution $(NH_4)_2$ SO_4 + 0.5% NaCl, anodic process (magnification ×160)

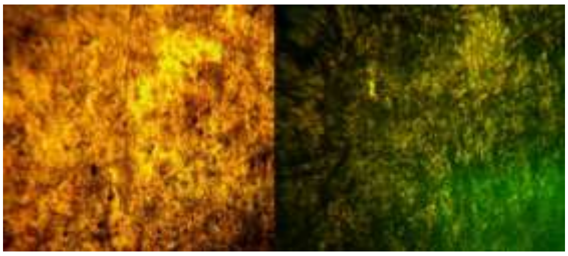

Fig. 8. Steel 12X18N9T EPP processed after the cathode process in which the sample melted anodic process (magnification ×160)

Fig. 9. Images of steel 12X18N9T before (left) and after (right) EPP anodic treatment

CONCLUSIONS

The possibility of both anodic and cathodic EPP polishing of various surfaces has been investigated. The results of electrolytic-plasma processing of copper M2P substrates in 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl, brass L68 M2R EPP polished with 2% solution $(NH_4)_2SO_4$ + 0.5% NaCl as well as steel 12X18N9T revealed decreasing of roughness of the treated samples as well as good polishing effect. Electrolytic-plasma boriding (EPB) was also used for surface strengthening and surface texturing of 12X18N9T stainless steel. After treatment with a borax solution, two additional peaks appear in the XRD patterns of the samples in addition to the Fe-α ferrite peaks. These peaks refer to iron borate $FeBO_3$ (hexagonal lattice) with lattice parameters a = 4.659 Å; c = 14.601 Å. It was shown that microhardness of the stainless steel of the 12X18H9T type after EPB increased from 130 to 500 kg/mm^2.

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ЕЛЕКТРОЛІТНО-ПЛАЗМОВА ОБРОБКА ТА БОРИДУВАННЯ РІЗНИХ ПОВЕРХОНЬ

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Представлено результати електролітно-плазмової обробки (ЕПП) мідних підкладок M2P у 2% розчині $(NH_4)_2SO_4$ + 0,5% NaCl, латуні L68 M2R EPP, полірованої 2% розчином $(NH_4)_2SO_4$ + 0,5% NaCl, а також сталі 12Х18Н9Т. Для ЕПП застосовувався як анодний, так і катодний процеси обробки. Для поверхневого зміцнення та текстурування поверхні нержавіючої сталі 12Х18Н9Т також використовували електролітно-плазмове боридування (ЕПБ). Після обробки розчином бури на рентгенограмах зразків з’являються два додаткових піки на додаток до піків фериту Fe-α. Ці рефлекси відносяться до борату заліза $FeBO_3$ (гексагональна решітка) з параметрами гратки a = 4,659Å; c = 14,601Å. Показано, що мікротвердість нержавіючої сталі типу 12Х18Н9Т після ЕПБ зросла від 130 до 500 $кг/мм^2$.