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Changes in the CoCr alloys surface relief during plasma electrolytic treatment

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Abstract. Development of dentistry is strongly correlated with the new treatment method development and construction of metal, polymer and ceramic materials. Metal-ceramic crown is a common dental prosthesis. The aim of work was determination the causes of the ceramic coating spalling from the cobalt chrome metal frame. It is proposed to replace the standard sandblasting method to plasma electrolytic treatment. The burning of single microdischarges occurs during plasma-electrolytic process. The formation of the microwells and increasing surface roughness observed in cathode mode. This is due to local melting of the surface. The treated surface does not contain impurity elements that can cause the formation of microcracks.

Introduction

The work is devoted to the study the plasma-electrolyte surface treatment processes of cobalt-chromium alloys used in dentistry. The frame of the metal-ceramic crown is cast from these alloys. The metal frame is lined with dental ceramics, and thus we will get the construction of metal-ceramics. Before applying the ceramic coating, the surface of the frame must be treated with a sandblasting method to increase its roughness. The increase in the roughness parameters contributes to the increase in the adhesion of ceramics to the metal. The metal-ceramic crown is widely used because of its versatility. It is durable and can be used to restore posterior teeth. It is aesthetic and can be used by the smile line. Ceramics has a big palette of shades, which allows you to choose an individual color corresponding to the shade of the patient's teeth. The simplicity of the method of application of ceramics, which does not require special technical devices other than a conventional muffle furnace, and the above-mentioned advantages have caused a wide spread of the metal-ceramic crown. However, as statistic shows, there are cases of chipping ceramic coating from the surface of the metal frame. It was previously established [1] that one of the most likely reasons is the presence of nano-and micro-sized particles of electrocorundum, which is used in sandblasting. High-pressure steam generators are used to remove these particles, but this is not enough to remove electrocorundum particles. These particles are a source of internal stresses and microcracks, as they lie on the border of metal and ceramics. Therefore, the simplest solution is the



selection of a new simple non-mechanical method of microrelief formation. Non-mechanical treatment methods include electrophysical and electrochemical processes, laser and ultrasonic treatment. Another important requirement is the geometry of the processed frames, repeating the shape of the human tooth. Considering all the above methods, we can conclude the following:

- laser processing requires expensive equipment;
- electrophysical and electrochemical methods produce anodic dissolution over the entire surface, and the electroerosion process requires a counter-electrode, the control of which is very difficult;
- microplasma processing takes place in a vacuum condition and requires expensive equipment.

The solution to the problem can be found in the use of low-temperature atmospheric pressure plasma initiated from a conventional low-voltage power supply up to 300 V. One possible source of such plasma is gas discharges with liquid electrodes. This method of processing is carried out when the voltage is applied to the electrodes in the electrolyte solution, as a result, a vapor-gas discharge burns around one of the electrodes [2]. The peculiarity of this discharge is that it burns between the solid and the liquid. The solid electrode can be both anode and cathode. The combustion discharge on the cathode is cleaning and polishing workpiece, as under certain conditions it is possible to apply coatings [3]. The anode process on metals that have a tendency to form oxide protective film with high resistance during anodic polarization, anodic oxidation occurs in conjunction with the burning of micro-arcs, this process called micro-arc oxidation [4]. On metals that do not have this property, there is an erosion of the metal and its dissolution. The main difference of this method from the anode process of plasma-electrolyte treatment is that the treatment is carried out only by the interaction of plasma with the surface of the product, and anodic dissolution does not occur under the influence of electrochemical reactions.

The work is devoted to the study of physical and chemical processes of plasma-electrolyte treatment of cobalt chromium alloys, consists of the combination of two processes: the erosion of the metal and its anodic dissolution [5]. Erosion destruction occurs under the influence of a large number of independent micro-electric discharges, which are initiated at the boundary of the liquid and the metal electrode at different times and continue to develop independently of each other. Anodic dissolution of the metal is due to electrochemical reactions. It is necessary to determine the conditions under which the formation of the surface micro-relief happens.

Main part

The implementation of the plasma-electrolyte process can occur in two modes: anode or cathode polarization of the processed frame.

To study the process of plasma-electrolyte treatment, the appearance of micro-discharges and their effect on the surface of the processed metals was made an experimental setup, the functional scheme of which is shown in figure 1. It consists of a power supply system 1, the electrolytic bath 2, the fixing system of the electrode pattern 3, the oscilloscope 4, shunt, 5, voltmeter 6, ammeter 7, the thermocouple 8 and the specimen mounting 9.

The main studies were carried out on samples of cast cobalt-chromium alloy firm Starbond CoS with the following composition and characteristics: Co - 59%, Cr - 25%, W - 9%, Mo - 3.5%, Si - 1%, other components (C, Fe, Mn, N) - maximum 1.5; the limit of the tensile strength (Rp 0.2) Of 650 MPa, a tensile strength of 910 MPa, ultimate elongation 8, the modulus of elasticity of 200 GPa, the Vickers hardness of 280 HV 10, a density of 8.8 g/cm³, solidus-liquidus interval 1305 - 1400°C, the temperature of the casting 1500 - 1550°C, the thermal expansion coefficient of 14.0 μm/m °C. The frameworks of metal-ceramic crowns in dentistry are made from this type of alloy. The electrolytic bath is filled with electrolytes of the required concentration and composition. As a working fluid were used the aqueous solutions of NaCl, Na₂CO₃, the concentration of which was 1 - 5% by weight.

The electrical power system is a DC (direct current) power supply with a continuously adjustable voltage. The power supply consists of a diode bridge and a laboratory autotransformer adjustment type 1M with a voltage range from 1 to 240V, 50 Hz. Also was used pulsating current source obtained after a two-half-period rectification. The change of the current and voltage form at the

moment of discharge ignition was determined using an oscilloscope FLUKE 105 SCOPEMETER SERIES II, time scan varied from 5 NS to 60 seconds. Relative measurement errors did not exceed 0.025%. To prevent changes in the size of the anode area, a dielectric protective cover was put on, which leaves open only a strictly defined part of the electrode. The area of the electrode on the surface of which was initiated the process of burning plasma was 0.8 cm^2 , the area of the counter-electrode 34 cm^2 .

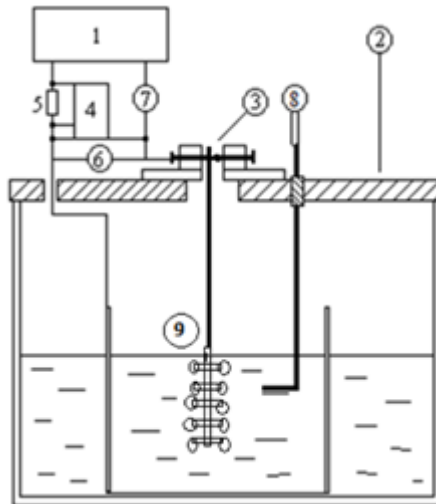


Figure 1 - Experimental setup

The main working parameters of the plasma-electrolyte process are: voltage on the electrodes, discharge current and current density on electrodes.

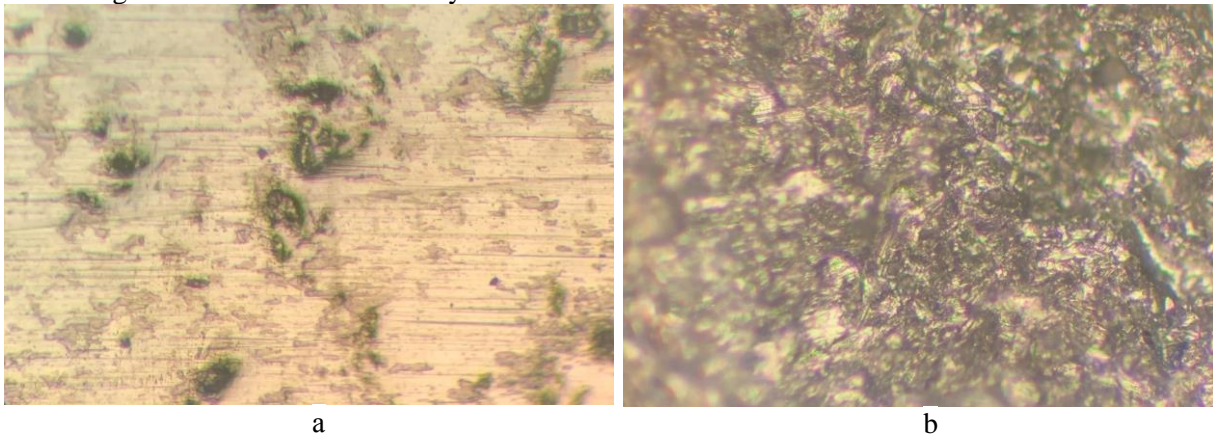


Figure 2 - Image of the surface with magnification $\times 20$: a - after machining with a mill, b - after sandblasting.

Voltage measurement at the anode was carried out using a digital universal measuring device APPA 105, the relative measurement error is 0.1%. With a digital multimeter, APPA 305 was carried out the temperature measurement of the electrolytic cathode with the help of the chromel-copel thermocouple. The electrolyte temperature was measured by a mercury thermometer.

Current-voltage characteristics were measured as follows. The voltage on the electrodes was increased stepwise from 0 to 240-250 V with a step of 5-10 V and exposure for 5 seconds with continuous recording of the voltage between the electrodes, the current and the electrolyte temperature.

The temperature of electrolyte reached 970°C for two minutes and didn't change.

After plasma-electrolyte processing, the samples were examined using an optical microscope Leica EZ4D, which allows to obtain images of opaque objects, as well as to produce microphotography of these surfaces. The survey was conducted at three points of the sample.

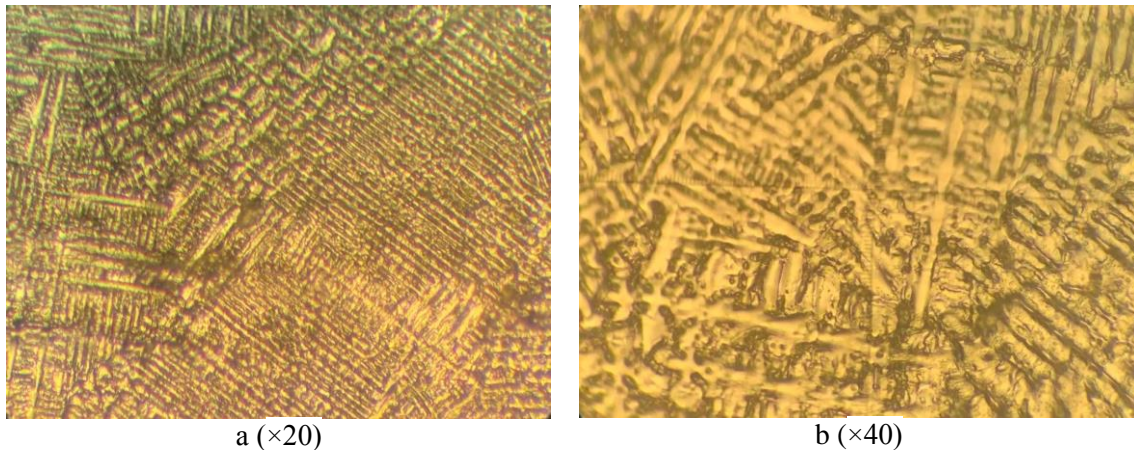


Figure 3 - The image of the cobalt-chromium alloy surface after plasma-electrolyte treatment at anode mode: a – $\times 20$ magnification, b – $\times 40$ magnification.

Consider the anode mode of plasma-electrolyte treatment, the current-voltage characteristic of which is shown in figure 4 a. The use of two different polarizations showed that in the anode mode when the electrolyte temperature is above 70°C , anode dissolution of the electrode prevails, and power of discharge is not enough to form local irregularities and grooves. Figure 3 shows the images obtained on an optical microscope, where we can observe the dendritic structure of the alloy. Similar images are obtained by chemical etching of samples for metallographic analysis. At small processing times, the use of "cold" electrolyte temperature 22°C and the value of the applied voltage $U = 230\text{ V}$ observed the formation of local depressions and holes, under the action of single water hammer formed by micro-discharges. However, intensive heating of electrolyte under the action of gas discharges leads to an increase of temperature, which in turn leads to the disappearance of water hammer. Thus, the anode mode of plasma-electrolyte treatment is inefficient for the formation of the micro-relief surface of cobalt-chromium alloys. This mode of plasma polishing will be effective for reducing the roughness of clasp dentures.

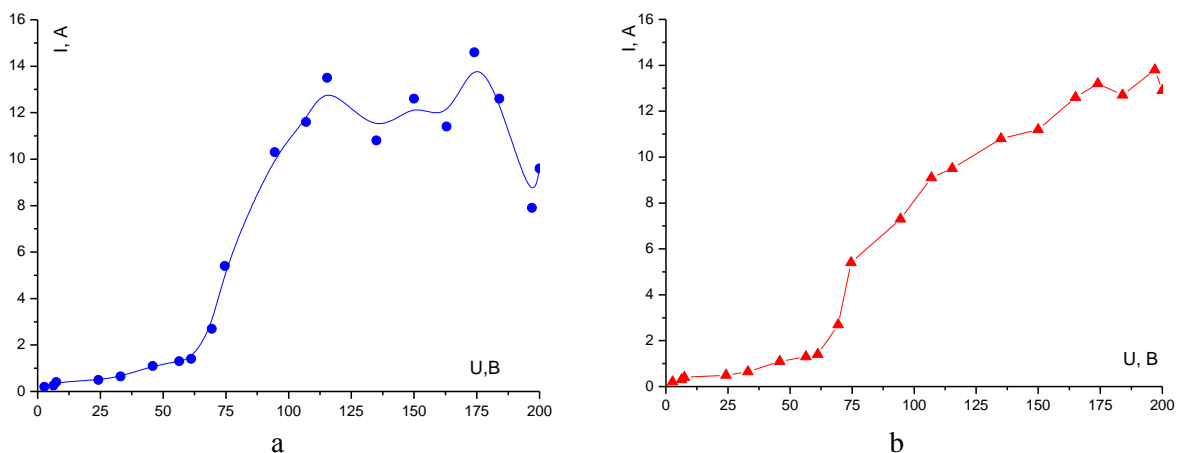


Figure 4 - CVC of the plasma-electrolyte process: a – anode mode, b – cathode mode.

Consider the cathode mode of plasma-electrolyte treatment, the current-voltage characteristic of which is shown in figure 4 b. In the cathode mode is observed more intense of the light effect of single micro-discharges. The thermal energy released by micro-discharges is sufficient to melt the active electrode. Therefore, an important task was the need to select the values of voltage and discharge current for local melting of the surface at which the formation of micro-holes and increase the surface roughness will occur. The lack of a process of dissolution of the electrode during the

cathodic polarization eliminates polishing effect observed in the anodic regime. Figure 5 shows surface images obtained at $U = 194$ V, $I = 12.6$ A, processing time 40 seconds.

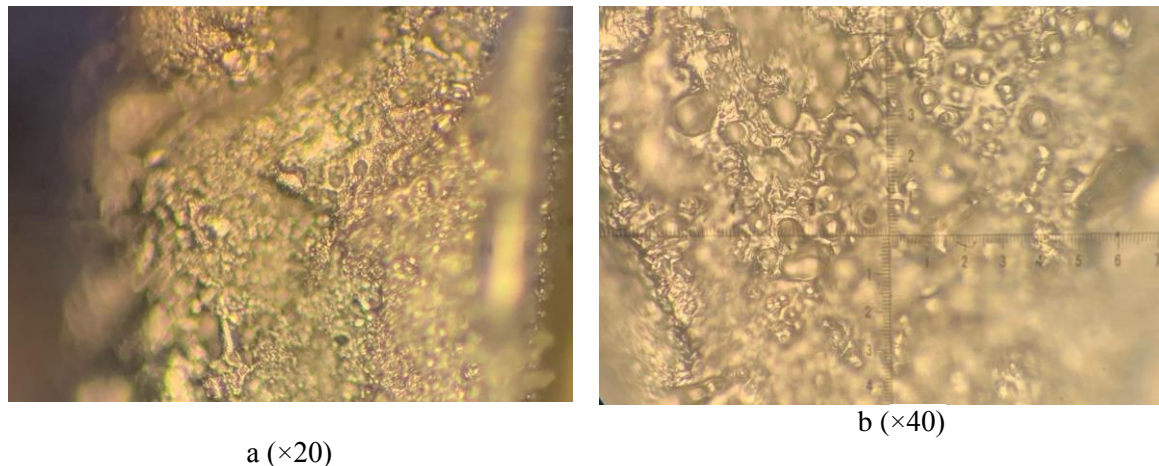


Figure 5 - Image of the cobalt-chromium surface after plasma-electrolyte treatment at the cathode mode: a – $\times 20$ magnification, b – $\times 40$ magnification.

Under these conditions, local melting of the surface and the formation of micro-holes and grooves ranging in size from 40 to 120 microns were observed. This microrelief is suitable for subsequent application of a ceramic coating. The analysis of the volt-ampere characteristics of the two modes shows that the anode mode is characterized by the presence of a maximum in the region of 130 V, fixed fluctuations in the amplitude of the current in the range from 110 to 180 V should be also noted. In the case of the cathode regime, there is a smooth increase in volt-ampere characteristic (VAC) with the presence of an inflection zone in the region of 60 – 75 V. This area is characterized by the beginning of the combustion of micro-discharges.

Conclusion

On the basis of the conducted researches, it is established that the formation of microholes is observed at the cathode mode, as a result of local melting from single micro-discharges. A comparison of anode and cathode modes showed the advantages of using the latter. This is due to the lack of anodic dissolution of the surface and a higher rate of electrical erosion. However, a more intense heat without control of the surface temperature may lead to the electrode melting. In the future, it is necessary to investigate the thermal effect on the cobalt-chromium alloys microstructure under these conditions. In general, we can conclude that this new method effectively solves the problem of replacing the sandblasting method for processing metal frames of dental prostheses. The obtained data can be used to create specialized dental equipment.

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