Kovove Mater. 51 2013 283–289
DOI: 10.4149/km_2013_5_283

The effect of mass transfer between electrodes in the electrospark alloying process of titanium alloys with hard materials

K. Korkmaz*, A. V. Ribalko, O. Sahin

Department of Materials Science and Engineering, Gebze Institute of Technology, Gebze 41400, Kocaeli, Turkey

Received 16 January 2012, received in revised form 4 April 2012, accepted 4 June 2012

Abstract

In this study, electrospark alloying (ESA) method was employed to coat a titanium alloy with hard material (tungsten carbide). The role of titanium oxide film on the ESA process was investigated. Due to presence of the oxide film, the formation of unusual erosion and mass transfer mechanism in electrodes different from conventional ESA process were observed during the process. It was deduced that these cause some failure of deposited coating layer such as "washing away" and cavities formation in and/or under coating layer. To achieve a good quality coating, this study primarily focused on the electrical parameters of alloying process and then limiting time intervals of process were defined where there were failures of the coatings. Using electrical pulses with energy of 0.34 J (current amplitude of 200 A, pulse duration of 120 μs), it was possible to obtain a uniform coating layer with an average thickness of 52 μm.

Key words: coating, electrospark alloying, titanium, titanium oxide film

1. Introduction

The combination of high strength-weight ratio, good resistance to corrosion under normal conditions, excellent mechanical properties, relatively high melting point and biocompatibility makes titanium and its alloys to use as attractive materials. Their applications are found increasingly in aerospace, marine, chemical, petrochemical, sports and biomedicine industries because of their outstanding properties [1–3]. However, some poor tribological properties such as high and unstable friction coefficients, strong tendency to stick, low fretting wear resistance, etc., and poor corrosion resistance in some aggressive corrosive media such as hot chloride solutions limit to their extensive applications as engineering components [4–6]. But these properties could be improved by using some surface engineering methods such as ion implantation, thermal oxidation, chemical or physical vapor deposition (CVD, PVD) or duplex surface treatments [7–11]. However, most of these methods are very expensive for hard surface engineering. On the other hand, the electrospark alloying (ESA) process offers some unique advantages relative to other surface modification techniques [12]. This process could be a promising surface engineering technique to solve the problems mentioned above [12–14]. Hard material coating of titanium alloy by ESA method had been investigated from the point of view of deposition properties [15].

In this study, the ESA method was used to carry out a hard layer (WK-8) on the titanium alloy (BT31) substrates and to find out the important features of process ESA of the titanium alloys in connection with the presence of oxide film on its surface.

2. Experimental procedure

A special ESA machine was employed in the experiments. The ESA coating system was described in previous work [16]. Its power consumption was 180 W and the output of stabilized voltage was kept constant at 40 V. In the present investigation, the ESA process was conducted in air with a series of square pulses of certain duration of 100–1550 μs and with amplitudes of current 100–300 A. The pulse energies that correspond to these pulse parameters (pulse amplitudes-pulse durations) are given in Table 1.

---

*Corresponding author: +90-262-605-2666; fax: +90-262-653-8490; e-mail address: korkmazk@gyte.edu.tr

Table 1. Pulse parameters used in the experiments

	Amplitudes of current (A)			Energy of pulse (J)
	100	200	300	
Pulse durations (μs)	200	120	100	0.34
	400	220	180	0.72
	800	410	270	1.32
	1550	780	510	2.63

The system included a special oscilloscope (Tektronix TDS 220) to determine the energies of pulses. The main control parameter of the ESD process is the working current that corresponds to the average current of the pulse generator. The average pulse energy is determined by using current-voltage diagrams (at the oscilloscope monitor). The results of numerical integration of the oscillograms of current-voltage could satisfy the pulse energy. The details of ESA pulse energy measurement were given elsewhere [17, 18]. The amount of processing electricity was kept constant as 3 Coloumbs to compare experimental results with each other.

In the present study, substrates (cathode electrode) with the dimension of $10 \times 10 \times 5\,\mathrm{mm}^3$ were prepared from a special titanium alloy (BT31) having the composition of Al (5.5–7.0 %), Mo (2.0–3.0 %), Si (0.15–0.40 %), Cr (0.8–2.0 %) including the impurities of Fe (0.2–0.7 %), Zr (0.5 %), O (0.18 %), N (0.05 %) and H (0.015 %). The treating electrode (anode) had a cross section of $2 \times 4\ \mathrm{mm}^2$ from tungsten carbide and cobalt (WK-8), WC (92 %) and Co (8 %).

Contact of electrodes is ensured by using an electrode holder with a frequency of 100 Hz during the forward and backward continuous sliding motion of the treating electrode on the surface of substrate. Thus, electrical discharges (as a result of contacting the micro roughness) and explosions of contacted points take place in a plasma channel in any instant of time, when the pulse current is applied. In result of the electrospark, a small part of melted electrode (anode) material is removed from the electrode and deposited to the substrate [12, 16, 18].

The mass change of electrodes, the mass loss of treating electrode and the mass gain of substrate were measured in time intervals of 30 s during 5 min of total processing time (one pass over the scanned area of $1\,\mathrm{cm}^2$ required approximately 30 s). For presenting the mass change of electrodes in each time interval (relative mass change), it was preferred to plot the experimentally measured mass differences between subsequent measurements rather than conventional presentation of mass change (cumulative mass change of electrodes as a function of processing time). Since this type of plot provides more information on dynamics of the mass transfer [16, 18, 19], the change in mass of the treating electrodes and substrates was measured by using a balance (Mettler Toledo 200) with the precision of 0.1 mg. Scanning electron microscope (Philips XL 30 SFEG) was employed for morphological and cross sectional analysis of coatings.

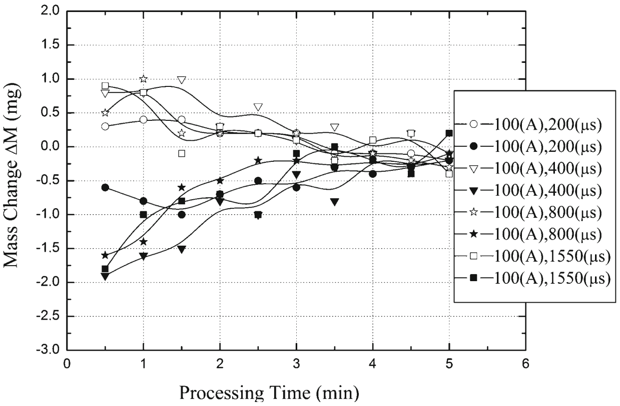

Fig. 1. Mass gain of the substrates and mass loss of the treating electrodes (solid dot) during processing by pulse current amplitude of 100 A with different pulse durations.

3. Results and discussion

3.1. *Electrospark alloying by pulse amplitude of 100 A*

Figure 1 shows the relative mass change of electrodes as a function of processing time. Both the mass loss of treating electrode and the mass gain of substrate decrease with processing time. As far as mass transfer from electrode to substrate concerns, this is the usual behavior of ESA in the most cases [16, 19]. Decreases in relative mass change of electrodes were due to a decrease in the amount of heat received by them as the coating process continued. As described below, this could only be possible when the temperature of plasma channel between electrodes decreased. At the beginning of an ESA, processing parameters, electrical pulse parameters, coating environment, and chemical composition of electrodes were fixed. After the first layer of ESA deposition, although other processing parameters stay as they are, the chemistry of substrate surface changes due to alloying by treating electrode. That is, for the chosen couple of electrodes, the amount of substrate material in erosive plasma will gradually decrease during processing. Therefore, the temperature of plasma, in turn, the amount of heat received by both electrodes, decreases. Consequently, decreasing erosion of treating electrode reduces the mass gained by the substrate.

When a spark discharge takes place, the plasma

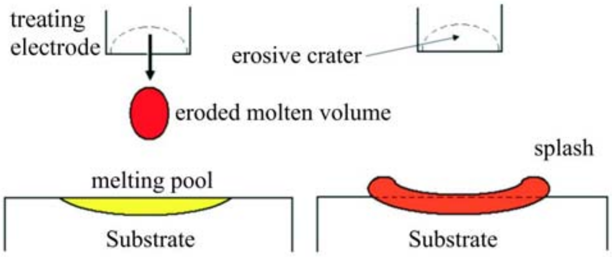

Fig. 2. The mass loss during mass transfer due to the ejection of relatively larger amount of liquid phase from the center of liquid splash towards its edges.

channel forms between a spot on the treating electrode and a corresponding spot on the substrate. At both ends of the plasma channel, i. e., just on the spots, the electrodes melt due to heat flow and so, a molten volume at the tip of treating electrode and a melting pool on substrate come into existence. The molten volume of treating electrode erodes away, but not all of it is transferred to the substrate. Unfortunately, the nature of ESA processing does not allow all the materials ejected from the treating electrode to solidify on the substrate [15, 16]. Therefore, the coefficient of mass transfer is always less than 1. Part of the eroded molten volume impinges on melting pool and mixes with the molten substrate material. The mixture solidifies on substrate within microseconds and has splash-like appearance. The mass loss during transfer is due to the ejection of relatively larger amount of liquid phase from center of liquid splash towards to its edges because of relatively high gas pressure squeezing liquid splash against the substrate ahead of solidification (Fig. 2). Ejected liquid phase was in the form of the tiny liquid particles, some of which after ejection fall on its own liquid splash and the rest fall on the outside range of splash boundary. Those of them fall on the outside range of splash boundary can not be welded to the cool solid substrate, and therefore solidify as free tiny particles. The liquid material splashed far away due to high gas pressure of plasma channel was named as washing away [19]. That is, during the first layer of deposition, substrate concurrently receives mass from treating electrode and looses mass due to washing away of molten pool of substrate spot caused by the intensive gas dynamics phenomena in plasma channel at the beginning of a spark discharge. The amount of mass washed away during deposition of the first layer is not easy to measure. Moreover, since its size is directly proportional to the size of molten spots on substrate and the strength of gas dynamics phenomena in plasma channel, for the upper layers of deposition it apparently may be negligible.

Depending on microscopic examination of interface between coating and substrate, it is concluded that washing away of liquid substrate material forms a non-flat substrate-coating interface. Especially, at the location of a spot, the concave pool was filled with anode material after washing away molten substrate.

After three to four minutes of alloying, the weight measurement showed that the substrates began to lose some mass for all of the pulse durations. Microscopic examinations of surface layer and its cross-section revealed that this could be related to occurrence of cavities (unusual mass loss) due to the evaporated material of substrate near the surface superheated as a result of spark discharges as shown in Fig. 3a,b. The mass lost by substrate during processing is a sign of the beginning of coating failure. Therefore, it is necessary to limit the alloying time by the beginning of evaporation in order to save the already deposited coating.

As it was experimentally shown in [19], the beginning of coating failure could be recognized by some distinctive characteristic of ESA parameters, such as stabilization of mass loss of the treating electrode; if the amount of mass gain of the substrate is zero or even negative. However, most precisely, the beginning of coating failure could be defined by a significant decrease in the value of the mass transfer coefficient after a maximum value. The mass transfer coefficient is the ratio of the mass gained by substrate to the mass lost by the treating electrode.

It should especially be noticed that, for 5 min of alloying with pulse duration of 1550 µs, an increase in weight of the treating electrode (that is, inverse polarity of mass transfer) was detected. Pulse parameters could not be the reason of this phenomenon, because it was not observed at the initial stage of alloying but revealed itself in the later stage of processing. The reason of this might be the cathodic flame. Part of the molten substrate material, due to overheated local volume, ejected and impinged with treating electrode.

Despite the fact that, while the pulse energy was increased approximately 8 times, only small differences in the amount of mass gained by substrate were observed, similar observation was also valid for mass loss of the treating electrode. Small mass transfer differences among various conditions of alloying caused some variations in the coating thickness and as a result an average coating thickness of 37 µm was obtained. It means that increasing pulse duration (pulse energy) did not change the average coating thickness.

Microscopic examination revealed that during processing three types of coating failure (or defects) formed: during the first layer of deposition, due to "washing away" (loss of molten substrate material due to gas dynamics phenomenon in plasma channel of a spark discharge, Fig. 3a,b), due to the evaporation by heat, accumulated in the overheated mass transferred from treating electrode, Fig. 3c,d, and due to the evaporation from substrate, Fig. 3e,f.

Now it is understood, that the cavities formation is one of major obstacles during ESA of Ti alloys. This

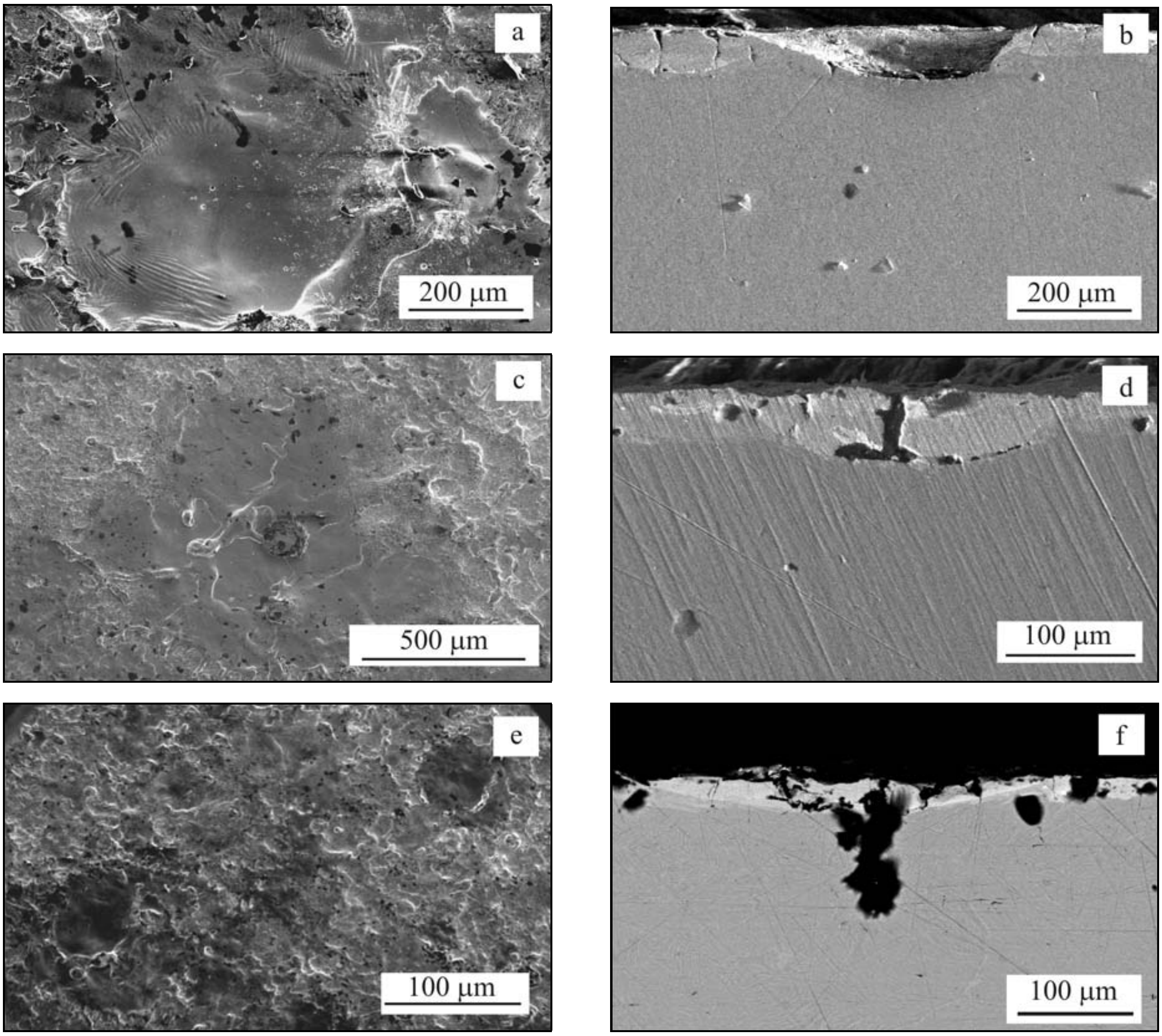

Fig. 3. The surface morphology and cross-section of tungsten carbide coatings showing a cavity formed by evaporation of part deposited layer and substrate because of: overheating by a spark discharge through a thin high temperature surface layer of the already deposited coating (a, b), overheating by the heat accumulated in the mass transferred from the treating electrode (c, d), overheating by a spark discharge through the tiny hole in oxide film (e, f).

phenomenon is related to the surface properties of titanium, a thin titanium oxide film forms on the outer surface in air, especially, during the deposition (local high surface temperature). To perform proper ESA coating, this oxide film should be removed. Since it is impossible, the ESA should be ended, otherwise continuation of deposition destroys the deposited layer by forming cavities.

3.2. Electrospark alloying by pulse amplitude of 200 A

The mass transfer behavior given in Fig. 4 shows the absence of weight increment of the substrate and even loss of its weight for pulse duration of 120 μs, at the very beginning of alloying (first-third deposition layer). All the mass transfer curves have pos-

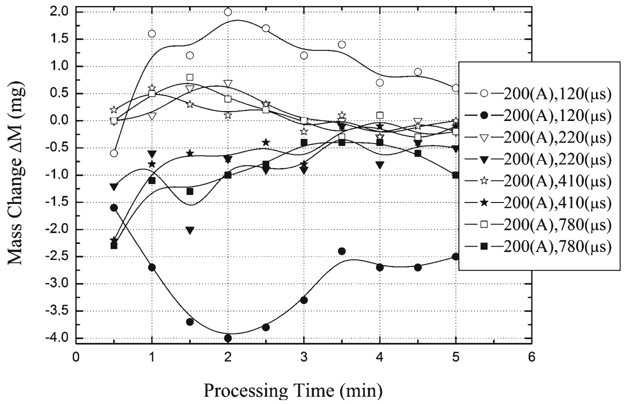

Fig. 4. Mass gain of the substrates and mass loss of the treating electrodes (solid dot) during processing by pulse current amplitude of 200 A with different pulse durations.

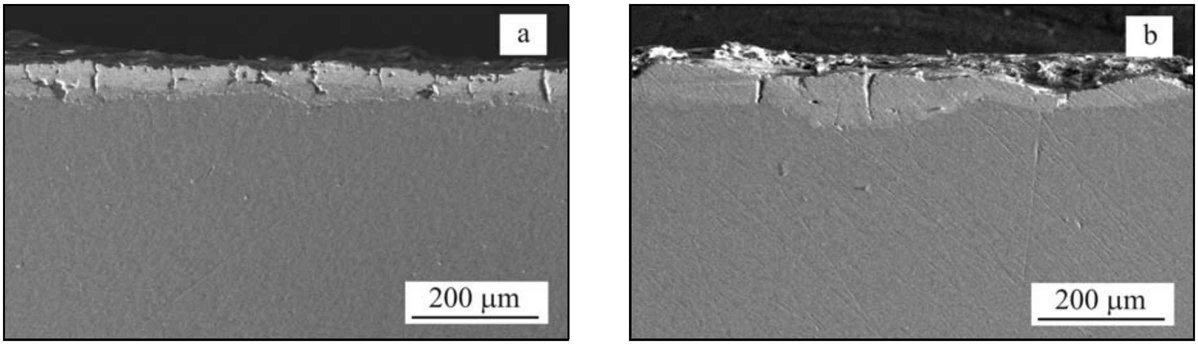

Fig. 5. The cross-sectional images showing the nonuniformity of layers after processing by pulse current amplitude of 200 A and duration 120 μs (a) and 780 μs (b) which have the same average thickness.

itive slopes, which are not common in ESA [16, 19].

However, as it was found out from the cross sectional metallographic analysis of specimens, the mass transferred from the treating electrode clearly ensured the formation of a tungsten carbide deposition layer. Therefore, it should be concluded that increasing of pulse current amplitude causes intensive evaporation of the substrates due to presence of thin oxide film and "washing away" of molten substrate material. In other words, for some cases, the mass loss of the substrate was more than the mass received from the treating electrode.

Further alloying, about 1.5 min, was still accompanied by the mass loss of the substrate. However, its intensity was lower than that in the initial stage of alloying. The mass gain of the substrates increased, despite of decreasing erosion behavior of the treating electrode (except pulse duration of 120 μs). After 2 min of processing, both the mass loss of the treating electrodes and mass gain of the substrates decreased. Comparing the case of alloying by pulse amplitude of 100 A, for this set of experiments significant differences in the amount of mass transferred to the substrate by the employment of various pulse duration were not present (except the pulse duration of 120 μs). After 3 min of alloying, for pulse durations of 220 μs, 410 μs and 780 μs, in spite of incoming mass from the treating electrode, substrate mass loss was observed.

The mass loss behavior of the treating electrode and the weight gain behavior of the substrates for pulse duration of 120 μs were essentially different than those of others. So, the mass loss of the treating electrode increased in time of coating and reached a maximum 4 mg at the end of 2 min of alloying. Increasing of mass loss of treating electrode during ESA is unusual for conventional processing. Unusual increment of the erosion of the treating electrode was probably related to the significant increase in heat flow density at the treating electrode-plasma channel interface. Probably, the main reason of additional heating of treating electrode and destruction of its surface is the cathodic plasma flame, formed as a result of intense substrate evaporation.

It is natural, that the amount of mass received by substrate correlates with the coating thickness. For the case of ESA with pulse amplitude of 200 A (except the case 120 μs), the mass gained by substrate had small variation in quantity from one pulse duration to another, so the average thickness was about 52 microns. The amount of variation in thickness with respect to average value increased if pulse duration increased. The level of variation is defined by not only the surface profile of coating but also by the profile of coating-substrate interface, because the interface looses its initial flatness due to the "washing away" molten substrate, during deposition of first layer (Fig. 5).

Increasing of pulse duration up to 220 μs and above formed many cavities due to substrate evaporation. The substrate material was ejected through the deposition and solidified on it like randomly distributed particles of different forms. The rate of deposition of the first layer of coating and amount of mass transfer decreased despite of increasing pulse energy. It was probably related with increasing the thickness of oxide film, which could form easily by increasing heat, in turn, increasing pulse energy.

3.3. Electrospark alloying by pulses amplitude of 300 A

In Figure 6, the processing time dependence of the mass change of electrodes is given for alloying by pulses of different durations. After 30 s of processing, the mass loss of the substrate was more intensive than that of ESA with pulse current amplitude of 200 A. However, the deposition of a tungsten carbide layer was achieved. For this time, the diameters of cavities were larger than those of cavities formed by ESA with pulse amplitude of 100 A and 200 A.

For each pulse duration, the mass loss of the treating electrode and mass gain of the substrate start to increase from the beginning of coating and reach a maximum between 1.5 and 2.5 min of processing. High

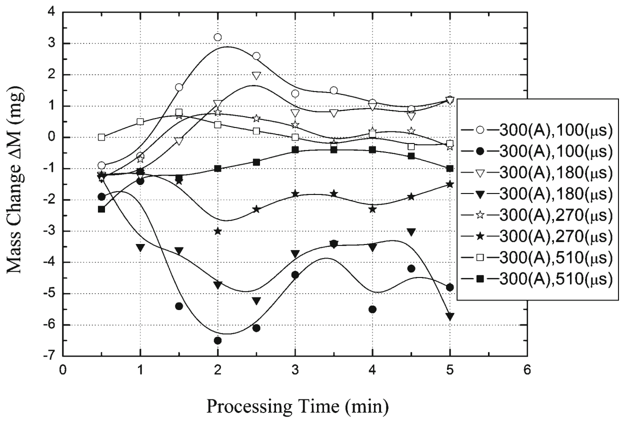

Fig. 6. Mass gain of the substrates and mass loss of the treating electrodes (solid dots) during processing by pulse current amplitude of 300 A with different pulse durations.

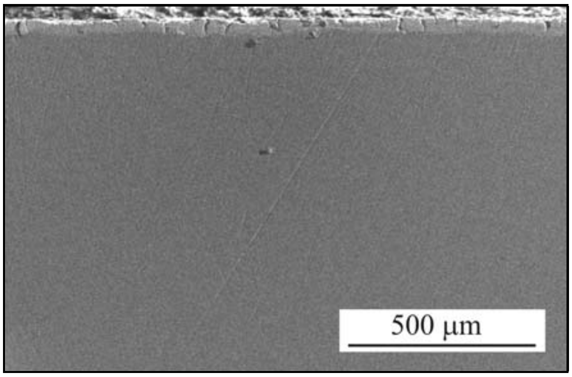

Fig. 7. A general cross-sectional view of coating obtained by the application of pulse energy of 0.34 J.

mass loss of the treating electrode could be due to the extreme effect of cathodic plasma flame.

Despite the major differences in the amount of mass transfer for different alloying modes, e.g., various pulse duration, the average thickness of coating was 50 µm (Fig. 7). It is necessary to note that the ESA of titanium alloy usually arises low mass transfer coefficient. For example, for the alloying by pulse duration of 100 µs, which was the case of maximum mass transfer, it was 0.49.

4. Conclusions

In the present study, tungsten carbide (WK-8) electrode material was deposited on titanium alloy (BT3) substrate by using the electrospark alloying (ESA) method. During the process, the ESA behavior of titanium alloy and the role of oxide film in development spark discharge were investigated.

The results of experiments have indicated that the presence of oxide film influences essential features on the surface modification of titanium alloys with ESA process. The mass transfer mechanism, the erosion behavior of electrodes, and the formation of deposit layers were considerably different than the conventional ESA process using different couple of electrodes.

Presence of oxide film effected the development of spark discharges and led to longer development of them than usual. Thus, it caused higher density of thermal stream and heat accumulation on the substrate material. Increasing heat and pressure resulted in "washing away" failure on the molten substrate material. Therefore, unusual mass changes were observed at the substrate and the treating electrode. As a result, the curves of mass change in electrodes (substrate and treating electrode) had positive slopes at the beginning of ESA. In addition to this, high temperature skin layer on its surface was another reason of failure of ESA coating during the process. It does not melt under discharge, however, the transferred heat to the volume underneath evaporated and destroyed the coating due to overheating. Finally, some cavities in the coating took place.

Presence of rare cavities in the coating is attributed to the ESA processing of titanium alloys in atmosphere. In order to reduce their number and increase some technological parameters of ESA, it is necessary to concentrate on the electrical parameters of alloying process. Thus, it is possible to judge that the ESA coating of titanium alloy from the very beginning of the process is accompanied by evaporation of substrate and cavity formation on the substrate surface in the presence of oxide film that is attributed to the ESA technology of titanium alloys in air.

In this study, to achieve an excellent quality coating, pulse currents with amplitudes and duration times ranging from 100 to 300 A and from 100 to 1550 µs, respectively, were employed. Using electrical pulses with energy of 0.34 J (current amplitude of 200 A, pulse duration of 120 µs), a uniform coating layer with average thickness about 52 µs was obtained without any cavities.

References

[1] Standard specification for titanium and titanium alloy bars and billets, ASTM B348-83.
[2] Leyens, C., Peters, M.: Titanium and Titanium Alloys: Fundamentals and Applications. Weinheim, Wiley-VCH Verlag 2003. doi:10.1002/3527602119
[3] Froes, F. H., Jones, R. H.: In: Fourteenth International Titanium Application Conference and Exhibition, Light Metal Age, USA, *57*, 1999, p. 117.
[4] Budinski, K. G.: Wear, *151*, 1991, p. 203. doi:10.1016/0043-1648(91)90249-T
[5] Bell, T.: In: Proceedings of the first Asian International Conference on Tribology. Eds.: Tsinghua Uni-

versity, By the State Key Laboratory of Tribology, Beijing, *2*, 1998, p. 421.

[6] Shoesmith, D. W., Noel, J. J.: Corrosion of Titanium and Its Alloys, Shreir's Corrosion. In: Corrosion and Degradation of Engineering Materials, Elsevier 2010, p. 2042. PMid:20532290

[7] Alonso, F., Ugarte, J. J., Sansom, D., Viviente, J. L., Oñate, J. I.: Surf. Coat. Tech., *83*, 1996, p. 301. doi:10.1016/0257-8972(96)02767-3

[8] Liu, Y., Ye, Z., Yang, D., He., S.: Adv. Tribol., 2010, p. 614.

[9] Beguin, J. D., Adrian, D., Petit, J. A.: In: Proceedings of the 20th International Conference on Surface Modification Technologies. Eds.: Sudarshan, T. S., Stiglich, J. J. Materials Park, AMS International 2006, p. 59.

[10] Bell, T., Dong, H., Sun, Y.: Tribol. Int., *31*, 1998, p. 127. doi:10.1016/S0301-679X(98)00015-2

[11] Dong, H., Sun, Y., Bell, T.: Surf. Coat. Tech., *90*, 1997, p. 91. doi:10.1016/S0257-8972(96)03099-X

[12] Johnson, R. N., Sheldon, G. L.: J. Vac. Sci. Technol., *4*, 1986, p. 2470. doi:10.1116/1.574093

[13] Korkmaz, K., Bakan, H. I.: Kovove Mater., *48*, 2010, p. 153. doi:10.4149/km_2010_2_153

[14] Frangini, S., Masci, A., Bartolomeo, A.: Surf. Coat. Tech., *149*, 2002, p. 279. doi:10.1016/S0257-8972(01)01450-5

[15] Parkansky, N., Beilis, I. I., Rapoport, L., et al.: Surf. Coat. Tech., *108–109*, 1998, p. 253. doi:10.1016/S0257-8972(98)00652-5

[16] Ribalko, A. V., Korkmaz, K., Sahin, O.: Surf. Coat. Tech., *202*, 2008, p. 3591. doi:10.1016/j.surfcoat.2007.12.037

[17] Ribalko, A. V., Khamurari, V. I.: Sov. Surf. Eng. Appl. Electrochemistry, *6*, 1988, p. 26.

[18] Korkmaz, K., Ribalko, A. V.: Kovove Mater., *49*, 2011, p. 265. doi:10.4149/km_2011_4_265

[19] Ribalko, A. V., Sahin, O.: Surf. Coat. Tech., *201*, 2006, p. 1724. doi:10.1016/j.surfcoat.2006.02.044