EFFECT OF CATHODE MATERIAL ON MICROSTRUCTURE STATUS OF THE COATING FABRICATED USING AN ELECTRO-THERMAL AXIAL PLASMA ACCELERATOR

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Abstract. The pulsed-plasma coatings were fabricated by electro-thermal axial plasma accelerator applying the cathodes made of graphite, tungsten, steel AISI 1020, steel T1 and 28 wt.%Cr cast iron. The coating thickness increases as the melting point of the cathode decreases. The usage of Cr (W)-rich cathode results in high amount of retained austenite leading to cracks under the coating crystallization.

Key words: Pulsed-plasma deposition, coating, microstructure.

1. INTRODUCTION

Surface engineering is a key approach to control the service life and reliability of the machine parts [1–3]. Pulsed-plasma treatment is applied for the alloys surface hardening through the structural modification [4–7] and for the coating deposition [8–10]. Surface structural modification is a result of the different plasma-related factors such as (a) quenching caused by plasma-induced super-fast heating [4, 11–14], (b) detonation strengthening under the dynamic pressure of plasma jet [4, 15–17], (c) radiation-stimulated doping by the plasma components (atoms, ions) [18, 19]. The plasma pulses are also used to strengthen the previously coated overlays [20, 21]. There are different plasma-accelerating devices which are used for pulsed-plasma processing [22–24]. Among them, an electro-thermal axial plasma accelerator (EAPA) stands out for its simplicity and ability to work in atmospheric conditions [25, 26]. EAPA’s working principle is a high-current discharge inside the EAPA chamber leading to a very fast release of accumulated energy with a consequent formation of a plasma flux directed to the target surface [25]. The material of the EAPA’s cathode is of great importance since it controls the structure and functionality of the coating. This is because the EAPA cathode is exposed to intensive erosion under
high-current discharge manifesting in its evaporation and melting with further micro-droplets ejecting out of EAPA. Thus, the pulsed-plasma coatings consist of the products of high-current erosion of the electrodes of the plasma accelerator and sublimation of the material of the walls of the accelerator inner chamber [25, 27, 28].

Typically, the plasma accelerators used in plasma processing technologies include the cathodes made of refractory metals such as tungsten ($T_{\text{Liq}} = 3422^\circ\text{C}$) or molybdenum ($T_{\text{Liq}} = 2623^\circ\text{C}$) [29]. Graphite ($T_{\text{Liq}} \sim 3700^\circ\text{C}$) is also used as the electrode for electric arc surface treatment [30]. The use of refractory materials is caused by the need to increase the electrodes’ erosion resistance under the multiply discharge sparks inside the accelerator. This approach is beneficial for pulsed-plasma surface modification. However, when pulsed-plasma processing is used for the protective coating deposition then another approach should be used to intensify the cathode erosion. Within this approach, an appropriate cathode material should have a low melting temperature to facilitate the cathode erosion in order to produce an increased fraction of the liquid micro-droplets. In this regard, the main objective of the present work was an assessment of the effect of the cathode material on the microstructure and properties of the plasma coating deposited on the metallic surface employing an electro-thermal axial plasma accelerator.

2. EXPERIMENTAL PROCEDURE

The pulsed-plasma processing was conducted using an electro-thermal axial plasma accelerator, the design and operation principle of which is described in detail in [25, 26]. The EAPA is a paper-bakelite tube crimped on both sides with steel shells. A channel (inner discharge chamber) with a diameter of 8 mm is positioned inside the EAPA coaxially. The cathode is a rod of 5–6 mm diameter inserted into the channel. The opposite steel shell serves as an anode. The distance between the cathode tip and the exit of the EAPA is 50 mm. The power source of the accelerator is a 1.5 mF capacitive energy storage which enables to store the voltage of 2–5 kV to be applied to the electrodes in order to generate a high-current discharge inside the accelerator chamber [26]. The discharge time of 0.6–1.0 ms allows to release the energy of approximately 10 kJ resulting in temperature inside the chamber up to 10 thousand K [28]. This leads to the evaporation (melting) of substances present inside the chamber (including the surface of the electrodes and the chamber), followed by the atoms ionization and plasma formation. The liquid micro-droplets are caught by the plasma flux from the cathode surface to be further transferred to the target surface.

Pulse-plasma treatment was carried out with the following parameters: accumulated voltage is 4 kV; distance between electrodes is 50 mm; current amplitude is up to 18.5 kA, the number of the plasma pulses is from 3 to 18. The tip of the cathode was a rode of 5 mm diameter made of different materials namely graphite,
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3. RESULTS AND DISCUSSION

According to [28] the pulse-plasma treatment using EAPA is advised to be carried out at a discharge voltage of 4 kV, while at least six pulses should be applied to obtain a coating of several tens of micrometers. The use of such a treatment mode caused the destruction of the graphite cathode just after the first pulse due to the low strength of graphite, which could not withstand the shock-wave pressure in the accelerator chamber under the discharge. In this regard, the voltage was lowered to 2 kV while increasing the number of 9–18 pulses.

As a result of nine pulses, a weakly etched «white» discontinuous layer of a non-uniform thickness (less than 15 μm) appeared on the surface (Fig. 1a). The «white» layer referred to a modified microstructure of cast iron resulting from high-speed quenching of the near-surface layer, which proceeded through the successive phase-structural transformations in the matrix phase, specifically «Pearlite» → «Austenite» → «Martensite».
As shown in [26] when the plasma flux ejected from the EAPA reaches the metallic target it may cause the ultra-fast heating of the surface with a heating rate of about \((4-5) \times 10^6\) K/sec. As a result, the surface temperature may rise up to the melting point leading to surface melting. After the heating, the cooling occurs with
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The cooling rate of \((3.7–5.5)\times10^6\) K/sec [26] which enables the martensite transformation from the liquid state. Under microscope observation, the chromium carbides were not detected within the «white» layer meaning that they partially dissolved in the melt to saturate the matrix with chromium thus increasing its resistance to etching. Since the «white» layer had a small thickness, the measurement of its microhardness was not possible. After applying 18 pulses, there was no significant change in the «white» layer thickness, however, it became more uniform with fewer discontinuities since the places of ruptures were filled with copper. The appearance of copper can be explained by the fact that, due to the high electrical resistance of graphite, the arc spot was displaced inside the accelerator from the cathode surface to the copper cathode mount. The mount melting resulted in the transfer of the liquid copper micro-droplets to the cast iron surface making the copper coating of up to 30 μm thickness.

Figure 1b shows the coating formed as a result of pulse-plasma processing using a tungsten cathode (six pulses with a voltage of 4 kV). As can be seen, the processing resulted in a “white” layer of 10–20 μm thicknesses without the discontinuities. The outer edge of the layer was uneven reflecting the mechanism of the transfer of the micro-droplets of the electrode material. Such droplets are seen as the large globules shown by the arrows in Fig. 1b.

The usage of the cathode made of a steel AISI 1020 (4 kV, 6 pulses) significantly changed the status of the «white» layer towards a sharp increase in its thickness. The total thickness of the layer reached 70–95 μm. After the etching, a uniformly white structure turned to a non-uniform structure (Fig. 1c). As seen, the outer periphery of the layer (about 2/3 of the thickness) was etched more intensively than the layer adjacent directly to the substrate. Thus the etched coating gained a stripped structure consisted of alternating white and dark areas oriented along the surface (Fig. 1c). The dark stripes performed a structure of acicular martensite (see the insert to Fig. 1c). It should be noted that there were no cracks in the coating and there was no clear boundary between the layer and the cast iron, which indicated a strong metallurgical bond between the coating and the substrate.

About similar coating thickness was obtained when using the cathode of steel T1. Non-etched «Steel T1 cathode»-coating is shown in Fig. 1d to reveal its thickness of about 85–105 μm. Notably, the coating contained the pores and the cracks oriented perpendicular to the “coating/substrate” interface and propagated into the substrate to the depth of 30–40 μm. When 28 wt.%Cr cast iron was used as the cathode, the coating’s thickness has increased even more to 110–150 μm performing the cracks as well (Fig. 1e). After the etching both «Steel T1 cathode»-coating and «28 wt.%Cr cathode»-coating had a layered white/black structure (Fig. 1f). Within the black strips, the structure exhibited the carbide network surrounding the matrix grains of 0.2–2.0 μm in size (see the insert to Fig. 1f).

The coatings, fabricated using steel T1 and 28 wt.%Cr cast iron were studied by EDS (the corresponded EDS-spectra and the local chemical composition are
presented in Fig. 2). According to the spectra, the «Steel T1 cathode»-coating contained 18.41 wt.% W and 4.30 wt.% Cr which were close to the nominal chemical composition of steel T1. Accordingly, 27.06 wt.% Cr and 1.50 wt.% Mn were found on the «28 wt.%Cr cathode»-coating to be coherent to the chemical composition of the cast iron. These data revealed that the mentioned coatings were formed of the cathode material transferred by plasma flux.

XRD allowed to evaluate the phase status of the coating. As seen in Fig. 3, the coating obtained by the «Steel AISI 1020 cathode» consisted of $\alpha$Fe, $\gamma$Fe and cementite carbide ($M_3C$). Taking into account the ratio of the intensities of the peaks $(111)_{\gamma Fe}$ and $(110)_{\alpha Fe}$ alpha-iron prevailed in matrix while austenite volume fraction was 12.7 vol.%. Attention is drawn to the pronounced peak of $(200)_{M3C}$, indicating the presence of a significant amount of cementite carbide. In contrast, the XRD pattern for the «28 wt.%Cr cathode»-coating showed the significantly increased intensities of the peaks $(111)_{\gamma Fe}$ and $(200)_{\gamma Fe}$ meaning an increased amount of austenite with volume fraction of 83.2 vol.%. At the same time, the cementite peak was much weaker as compared to the «Steel T1 cathode»-coating.

Figure 3b shows the distribution of microhardness over the cross-section of the coatings. As seen, in the case of a tungsten cathode, the microhardness of the «white» layer at the very surface (10 µm) was about 600 HV$_{50}$. At a depth of ~20 µm, the microhardness rises to 870–900 HV$_{50}$, after which it begins to decrease deeper into the sample to stabilize at a depth of over 40 µm at about 550 HV$_{50}$. In the case of using a steel AISI 1020 cathode, the average microhardness of the subsurface layer was 750 HV$_{50}$. The sharp spike in microhardness (up to 1010 HV$_{50}$) corresponded to a narrow (~10 µm width) «white» layer, directly adjacent to the substrate. At greater depth, the microhardness decreased to about 600 HV$_{50}$, which corresponds to the initial microhardness of cast iron. The curve for «Steel T1 cathode»-coating repeated the above profile with the differences that at the very surface the microhardness
was close to 600 HV\textsubscript{50}, and the highest microhardness value near the boundary with the substrate was 930 HV\textsubscript{50}. The microhardness profile for the «28 wt.% Cr cathode»-coating is not shown in Fig. 3b since it is almost superimposed on the profile for «Steel T1 cathode»-coating.

It should be noted, that the coating formed by the steel AISI 1020 electrode has unusually high microhardness. Since the cathode was made of low-carbon steel (containing less than 0.2 wt.% C), the hardness of the coating in the quenched state should not exceed 400 HV\textsubscript{50}. Actually, however, the microhardness was 750–800 HV\textsubscript{50}, which corresponds to a 2.5–3 times higher carbon content (0.5–0.8 wt.% C) than that in steel AISI 1020. This finding allows to presume that the micro-droplets transferred from the cathode to the target surface were somehow considerably enriched with interstitial elements which lead to the distortion of \(\alpha\text{Fe}\) lattice. This enrichment might take place due to contact of the micro-droplets with a plasma flux containing C, N, O atoms evaporated from the dielectric EAPA walls under the arc discharge inside the EAPA chamber [25]. The superfast crystallization of (C, N, O)-rich micro-droplets resulted in high-carbon martensite formation as follows from the XRD pattern (the presence of about 13 vol.% of retained austenite supports the speculation of high carbon content in the coating).

The coating obtained by pulsed-plasma processing with a “Steel AISI 1020”-cathode has a heterogeneous structure: it was characterized by a darker contrast of the outer layers and a light contrast of the inner ones. As it was assumed, the inner layers of the coating were formed during the first plasma pulse under high heating/cooling rates and high structural stresses, which sharply refined the crystals, increased the density of defects providing a “structureless” state close to amorphous [32]. This has resulted in a low etching rate of the inner layers. During the subsequent pulses, the coating was formed under the lower heating/cooling velocities since the heat from the previous pulses was retained in the coating. This caused a coarsening of martensite to be distinguishable under the microscopic observation (Fig. 1c). Due to heat accumulation, the tempering took place in outer
layers resulted in cementite carbide precipitation (proved by XRD) and increased propensity for etching.

The coatings obtained using steel T1 and 28 wt.% Cr cast iron were highly enriched with the alloying elements, as follows from EDS analysis (Fig. 2). Since Cr, W, Mn decrease the Mₘ temperature [33] these coatings comprised a higher amount of retained austenite (seen in XRD for the steel T1) resulting in lower microhardness as compared with «Steel AISI 1020 cathode»-coating. It is noteworthy, the structure of the above coatings did not include Cr-based carbides or W-based carbides which are characteristic for high-Cr cast iron or tool steel T1 [25]. Instead, the presence of cementite carbide (M₃C) was revealed in the XRD pattern (Fig. 3a). This fact allows to presume that the coating crystallization proceeded by the non-equilibrium path with the formation of metastable carbide with the retention of alloying elements inside the lattice. The cementite network emergence (Fig. 1f) was driven by the over-saturation of the austenite with carbon, the precipitation of this network was stimulated by the repeated heating under plasma pulses. The formation of metastable carbide (cementite) instead of carbides M₆C and M₂C («Steel T1 cathode»-coating) or M₇C₃ and M₂₃C₆ («28 wt.% Cr cathode»-coating) was kinetically favourable since it did not require the long-distance diffusion of tungsten (chromium) atoms. All the coatings were characterized by the same pattern of the microhardness profile with a sharp spike at the boundary with the substrate. This spike was associated with the plasma-modified layer of the substrate (cast iron). This layer actually was a transitional layer providing a good bonding between the coating and the bulk substrate.

As follows from Fig. 4, the coating thickness is in inverse proportion to the melting temperature of the cathode materials (the data for melting tempering of the steel T1 and 28 wt.% Cr-cast iron are adopted from [25]). This finding allows to control the coating thickness by means of selecting the proper alloys for the EAPA’s cathode. In this context, the eutectic alloys are perspective candidates for the cathode materials due to its lower melting temperature [34, 35] (both steel T1 and cast iron belong to eutectic-containing alloys).

The cracks occurrence in the coating is an important issue controlling coating performance. As seen, the usage of steel T1 and 28 wt.% Cr-cast iron resulted in cracks formation in the coating while other cathodes (steel AISI 1020 and tungsten) ensured the cracks’ absence. The possible reason is the coating contraction under crystallization. When crystallizing the coating volume decreases leading to tensile stress occurrence [36]. The temperature-dependent volume decrease might be compensated by the phase FCC → BCC transformation under the cooling which leads to the specific volume increase [37]. The more austenite retains under the cooling the less increase in specific volume occurs causing the crack initiation. That is why W-rich and Cr-rich coatings with a higher amount of retained austenite were prone to cracking while Fe-rich coating (“Steel AISI 1020-cathode”) with mostly BCC structure was free of cracks.
Fig. 4 – The correlation between the cathode melting temperature and the average coating thickness.

The results obtained showed that the cathode material is a key factor greatly affecting the pulsed-plasma coating thickness, defectiveness, and the properties. The metallic materials with lower melting points are favourable for the formation of thick coating while the materials with BCC lattice ensure the cracks’ absence.

4. CONCLUSIONS

1. Pulsed plasma treatment using an electro-thermal axial accelerator with the arc discharge voltage of 4 kV provides a surface modification of high-chromium cast iron to the depth of 10–15 μm with a microhardness of 950–1010 HV50, and also leads to the formation of a coating due to the transfer of the cathode materials by plasma flux. The thickness of the coating increased as the melting point of the cathode material decreased. The thickest coatings (85–150 μm) studied in this work were obtained after using the cathode materials (steel T1 and 28 wt.% Cr-cast iron) containing in their structure a carbide eutectic with a lower melting temperature. In these cases the coatings were mostly built by the micro-droplets taken by plasma flux from the cathode’s surface.

2. When a low-carbon steel AISI 1020 was used as the cathode, the coating had a structure of high carbon martensite with the microhardness of 870–900 HV50. The possible reason of such behaviour was the enrichment of steel AISI 1020 micro-droplets by interstitial elements (C, N, O) through the contacting with a plasma flux.

3. The coatings obtained using the “Steel T1-cathode” or “28 wt.% Cr-cast iron-cathode” had a structure consisting of αFe, γFe, and cementite carbide. Their distinctive feature was an increased volume fraction of retained austenite and the absence of Cr(W)-based carbides (M7C3, M23C6, M6C, M2C).

4. Phase FCC→BCC transformation inhibited the cracks initiating during the coating formation. The coatings containing predominantly austenitic matrix were prone to cracks occurrence while the coating with αFe-based matrix was free of cracks.
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