Electron beam surface alloying of carbon steel by aluminium followed by micro-arc oxidation

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Abstract. A composite coating was produced using e-beam formation of surface alloy followed by micro-arc oxidation technique. The Al-Steel surface alloy was formed directly on steel substrate in vacuum by alternating processes of Al thin film deposition followed by a pulsed electron-beam mixing of deposited film and a top layer of the substrate with further formation of the MAO coating from the surface alloy. The microstructure of the coatings including surface morphology, phase and element composition was studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The final ceramic coatings have a typical morphology for MAO coatings and consist of Al\textsubscript{2}O\textsubscript{3} and some amorphous Al\textsubscript{2}O\textsubscript{3} phases.

1. Introduction

It is well known that micro-arc oxidation (MAO) technology is widely used for growing ceramic-like coatings with high hardness, good corrosion, and wear resistance. The MAO is considered as an advanced form of anodic oxidation and primarily applied to valve metals such as aluminum, magnesium, titanium, zirconium and their alloys \cite{1-3}. These valve metals set as anodes are directly oxidized to form the hard and compact ceramic coatings of Al\textsubscript{2}O\textsubscript{3}, MgO, TiO\textsubscript{2}, and ZrO\textsubscript{2} oxides during plasma electrolytic oxidation. But, it is difficult using conventional MAO method to obtain a thick compact coating on a non-valve metal, iron for example. Jiang and Wang grew a MAO coating on Q235 steel set as an anode in a mix solution of sodium aluminate and sodium dihydrogen phosphate \cite{4, 5}. This MAO coating consisting was porous and not very compact. However, MAO coatings on steel substrates can be obtained if the aluminum high adhesion layer previously applied. Such a highly adhesive coating, or rather a surface alloy, can be obtained by surface alloying with a low-energy, high-current electron beams (LEHCEB).

In this work aluminum-steel surface alloy was produced directly on steel substrate in vacuum by alternating processes of Al thin film deposition followed by a pulsed electron-beam mixing of deposited film and a top layer of the substrate with further formation of the MAO coating from the surface alloy.
2. Experimental

The electron-beam machine (EBM) RITM-SP (Microsplaev OOO, Institute of High Current Electronics) was used in experiments on formation of Al-Steel surface alloy [6, 7]. This EBM was equipped by LEHCEB and magnetron sputtering systems providing thin film deposition and LEHCEB surface melting in a single vacuum cycle. The parameters of LEHCEB were as follows: energy of electrons up to 30 kV, pulse duration from 2 to 4 µs, electron current up to 25 kA and electron beam diameter up to 100 mm.

The samples were carbon steel (0.14-0.22% C; 0.15-0.3% Si; 0.4-0.65% Mn; 0.3%Ni; 0.3% Cr; Fe – balance, wt.%) parallelepipeds of 15x15x2 mm size. The procedure for forming the Al-Steel surface alloy consisted of the following alternative operations: deposition of Al film onto a substrate followed by a LEHCEB irradiation. The thickness of film deposited per one operation was 0.5 or 2.5 µm. Rate of Al film deposition was 10±2 µm per hour and it was measured on glass sample by optical profilometer. After thin film deposition, a LEHCEB surface melting and mixing of the obtained "film-substrate" system in a liquid phase has been took place. The numbers of "deposition-LEHCEB mixing" cycle were 20 or 4, total thickness of deposited Al layer was ~10 µm. The modes of surface alloy formation are listed in table 1. The MAO treatment on the samples was performed by industrial facilities in slightly alkaline electrolyte. The MAO coating deposition parameters were the following: current density – 45 A/dm$^2$, anodic voltage – 350 V, pulse frequency – 50 Hz and treatment time – 10 min. Throughout the entire range of experimentation, the temperature of the electrolyte was 18–20°C.

SEM and optical microscopy were used for characterization of morphology of synthesized Al-Steel surface alloy. The phase composition was examined by XRD in a grazing incidence diffraction geometry at the incident angle $\omega=5^\circ$. The elements composition of the surface and the in-depth elements distribution were studied by EDS analysis.

| Mod  | Charge voltage, kV | LEHCEB energy density, J/cm$^2$ | Thickness of Al film deposited per cycle, µm | Number of cycles | Number of irradiation pulses |
|------|-------------------|---------------------------------|-----------------------------------------------|-----------------|------------------------------|
| 1    | 23                | 3.9                             | 0.5                                           | 20              | 4                            |
| 2    | 23                | 3.9                             | 2.5                                           | 4               | 4                            |

3. Results and discussion

Figure 1 present SEM images from the surfaces with the Al-Steel surface alloy formed at different modes. An examination of the surface morphology demonstrated that depending on formation modes the surface relief patterns are noticeably different. The average elemental composition of the surface sample with a surface alloy formed in mode 1 is 90.5±1 – Al and 9.5±1 at.% – Fe and 100 at.% Al for sample with a surface alloy formed in mode 2. The surface of sample with Al-Steel surface alloy formed at mode 1 is rather homogeneous without any visible defects like pores or microcracks. Specifically, there are defects of the pore type on the entire surface of sample, where Al-Steel surface alloy was formed at mode 2 (figure 2b).

Figure 2 shows SEM image of the cross-section and in-depth elements distribution of the Al-Steel surface alloy formed at mode 1. One can see the coating is rather homogeneous without any visible defects like pores or microcracks (figure 2a). The thickness of pronounced coating from the surface to the visible line between coating and substrate is about 9 µm. The coating thickness scattering is less than 15%. According to in-depth elements distribution (figure 2b) the surface alloy can be divided by two zones of (1) coating of thickness of ~5 µm and Al concentration of not less than 90 at.% followed by (2) transition layer of thickness of ~5 µm. The transition layer is characterized by dropping of concentration of Al from 90 to 0 at.% whereas the concentration of Fe in this layer, in contrast, is rising to 100 at.%.
Figure 1. SEM images of the samples surface with an Al-Steel alloy formed in mode 1 – (a) and 2 – (b).

Figure 2. SEM image of cross-section – (a) and in-depth elements distribution – (b) of the Al-Steel surface alloy formed at mode 1.

Figure 3. XRD patterns of samples: (a) – 10-µm-thick Al film/steel substrate; (b) and (c) – Al-Steel surface alloy formed at modes 1 and 2 respectively.

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the visible line between coating and substrate is about 9 μm. The coating thickness scattering is less than 15%. According to in-depth elements distribution (figure 2b) the surface alloy can be divided by two zones of (1) coating of thickness of ~5 μm and Al concentration of not less than 90 at.% followed by (2) transition layer of thickness of ~5 μm. The transition layer is characterized by dropping of concentration of Al from 90 to 0 at.% whereas the concentration of Fe in this layer, in contrast, is rising to 100 at.%.

Figure 4 illustrates the surface morphology of the MAO coatings for different types of samples. It can be seen that the coating is porous near surface. The SEM images indicate that the pores distribute all over the MAO coatings surface. These pores are formed due to the discharge during MAO. For the initial aluminum sample the average diameter of pores is about 10 μm and most of the pores are "closed" and are not very deep (figure 4a). MAO coatings obtained on samples with an aluminum film and a surface alloy formed in mode 2 (figure 4b,d) are similar to MAO coatings of the initial aluminum sample, but with “open” and deeper pores. Average diameter of pores for MAO coating obtained on a sample with a surface alloy formed in mode 1 is about 30 μm (figure 4c).

The porous structure near the surface is the typical structure of MAO coating and the pores can hardly be avoided. However, usually, the porous structure is only the surface structure rather than body structure [5, 8, 9].

Figure 5 shows the phase composition of samples after MAO processing. It can be seen from figure 5a that MAO coating obtained on aluminum sample consists of γ-Al2O3 and Al, where γ-Al2O3 is the main phase, and Al is most likely a substrate. Diffraction pattern of the MAO coating obtained on 10-μm-thick Al film/steel substrate sample contains intensive peaks of Al and weakly noticeable peaks of γ-Al2O3 (figure 5b). Diffraction patterns of MAO coating obtained on surface alloys formed in modes 1 and 2 are similar. They contain wide peaks of aluminum and weak, at the background level, peaks γ-Al2O3 (figure 5c). Since the peaks are very wide, MAO coating can also contain FeAl3,
FeAl and Fe$_3$Al phases. It can be assumed that the low intensity of Al$_2$O$_3$ peaks is due to the low thickness of the MAO coating due to the short processing time. It should be noted that the MAO coating may contain some amorphous phase of Al$_2$O$_3$, since the diffraction patterns have a halo in the range of small angles 2$\theta$, at that the amorphous halo is especially noticeable for the MAO coating formed on the surface alloys.

4. Conclusion
A composite coating was produced using micro arc oxidation and forming surface alloy techniques. The Al-Steel surface alloy was formed directly on steel substrate in vacuum by alternating processes of Al thin film deposition followed by a pulsed electron-beam mixing of deposited film and a top layer of the substrate with further formation of the MAO coating from the surface alloy. According to in-depth elements distribution the surface alloy can be divided by two zones of (1) coating of thickness of ~5 $\mu$m and Al concentration of not less than 90 at.% followed by (2) transition layer of thickness of ~5 $\mu$m. According to SEM studies, the obtained ceramic coatings have a typical morphology for MAO coatings. XRD studies showed that MAO coatings consist of a $\gamma$-Al$_2$O$_3$ and may contain some amorphous phase of Al$_2$O$_3$.

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