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Regularities of the structural-phase state formation of the electro-spark coating at the initial stage and the surface layers of the steel substrate

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The regularities of the formation of an electro-spark coating (ESC) and near-surface layers of a steel substrate were investigated by the X-ray method. The microstructure of the coating at the early stage of formation was studied by observing individual areas of the discontinuous coating. The mechanism of mass transfer of individual phase components of the alloying electrode material in the electric discharge channel is analyzed. The possibility of the reverse $\alpha\rightarrow\gamma$ (bcc→fcc) transformation in the near-surface layers of the substrate under conditions of upward carbon diffusion was demonstrated.

Keywords: electro-spark coating, structural-phase state, diffusion, reversed α–γ transformation, carbonitride.

Закономірності формування структурно-фазового стану електроіскрового покриття на початковій стадії та поверхневих шарів сталевої підкладки. *В.Є. Данильченко, В.Й. Бондар, Є.М. Дзевін, В.І. Яковлєв*
Рентгенівським методом досліджено закономірності формування електроіскрового покриття (ЕІП) та приповерхневих шарів сталевої підкладки. Проведено мікроструктурні дослідження ранньої стадії формування покриття зі спостереженням окремих утворень несуцільного покриття. Проаналізовано механізм масопереносу в каналі електророзряду окремих фазових компонентів легуючого електродного матеріалу. Показано можливість зворотного $\alpha\leftrightarrow\gamma$ (bcc↔fcc) перетворення у приповерхневих шарах підкладки за умов висхідної дифузії вуглецю.

1. Introduction

The complex of physical and mechanical properties of electro-spark coatings (ESC) on a steel substrate is determined by their chemical composition and structural-and-phase state.

The creation of the technological foundations of high-energy electro-spark treatment (EST) of metallic materials is associated with the use of fundamental regularities of structural-and-phase transformations in the process of coating formation. The further development of the coating technology and the significant improvement of their efficiency are determined by the possibility of targeted changes in the structural-phase state of the coating material and the surface layers of the substrate. The need to build a general picture of ESC structure formation requires a detailed study of the mechanism of mass transfer of alloy electrode erosion products to the metal substrate. During the formation of an ESC layer on a steel substrate, a

complex mechanism of mass transfer between the anode and cathode is realized. As a result of erosion, the anode material enters in the discharge channel and in the interelectrode gap in the form of particles that can be in the vapor, liquid droplet or solid phases. These particles bombard the substrate and participate in the formation of ESC, alloying and strengthening of its near-surface layers [1-4]. This intense influence can significantly change the distribution of chemical elements in the coating and near-surface layers of the substrate as well as change their phase composition and structural state.

The phase components of the alloy electrode material can differ significantly in the type of interatomic bond, structural state, thermal properties, and ability to interact during the formation of the coating [5-8]. As a result, the erosion of the electrode material and the subsequent mass transfer of individual phase erosion products to the substrate occur according to different patterns. These patterns cannot be fully investigated due to methodological difficulties in observing individual formations on the substrate, possible mutual diffusion of coating elements and the formation of transition zones between different components. The features of structural transformations under non-equilibrium conditions of electro-spark treatment (EST) have not been sufficiently studied. In this situation, it is difficult to establish a connection between the technological parameters of the EST and the complex of physical and mechanical characteristics of ESC, and it is still not possible to create a complete picture of the structure formation. In this regard, the main goal of the work was to study the patterns of formation of the structural-phase state of coatings and near-surface layers of the steel substrate under nonequilibrium conditions of EST.

2. Materials and Methods

Electro-spark treatment of AISI W 1 steel was carried out using an "Elytron" installation in an air atmosphere with an electric current of 0.5-2.8 A and a processing time of 1.0-5 min. To prevent sticking of the electrode to the sample, a vibration mode with a frequency of 50 Hz was used. DIN HS123_hard alloy (80% WC; 14.5% TiC; 5.5% Co) was used as an alloying electrode. Phase analysis and measurement of residual stresses were performed by the X-ray method on a "DRON-3M" diffractometer in the radiation of a cobalt or iron anode. The number of phases was determined by the intensity of diffraction reflections, taking into account the repeatability factor of proper crystallographic planes and the radiation absorption coefficients of various chemical elements. The study of the microstructure of the ESC was carried out on a "Philips" electron scanning microscope.

3. Results and discussion

The X-ray structural study of ESC showed that the phase composition of the coating material differed significantly from the composition of the alloying DIN HS123 electrode. The diffraction pattern of the coating contained reflections from the lattice of carbides W_2C and Fe_3W_3C, as well as TiC-based compounds with an fcc lattice. In addition, reflections from bcc α-phase and fcc austenitic γ-phase, which belonged to the steel substrate, were recorded.

Microstructural studies at the initial stage of ESC formation showed unevenness of its thickness and significant discontinuity. The discontinuity of the coating was up to 20% of the entire area. This made it possible to trace the formation of various phases of the coating when individual (primary) formations did not contact or interact with neighboring formations. On a significant part of the substrate area, the applied coating was not observed (Fig. 1, a). The corresponding X-ray spectrum from this area contained intense lines of iron from the steel substrate (Fig. 1, b).

The coating was formed by the deposition of both liquid droplets (Fig. 1, b) and solid phase particles (Fig. 1, c) on the substrate. Formation 2 was the result of crystallization of a drop of liquid substance with noticeable splashing. At the same time, branches in the form of thin whiskers, tapering away from the center of the drop, extended from the main drops. The cooling rate of the whisker material was significantly higher than the cooling rate of the main droplet material due to their smaller mass. As a result, high residual stresses formed in the whiskers, which, when relaxed, led to the formation of cracks. The stresses in the deposited particles propagate to the substrate material, causing cracks to also occur in areas of the substrate that were not coated. It is obvious that the conditions of condensation of the whisker material have become close to the conditions of jet forming of liquid metal used in the production of highly dispersed and amorphous ribbons.

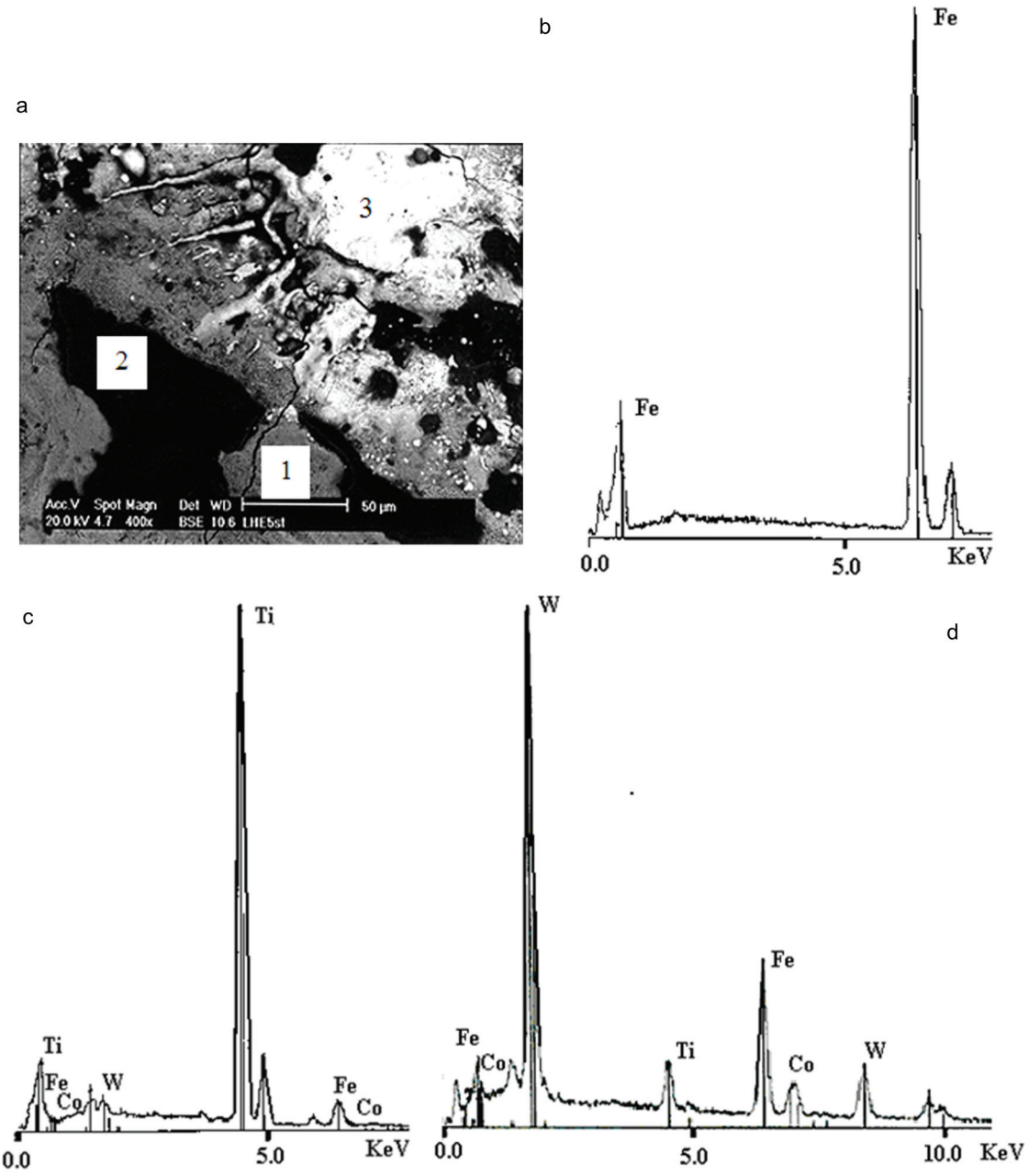

Fig. 1. Microstructure of ESC on an initial stage of forming (a), X-ray spectra (b, c, d) of a regions marked on (a) as 1, 2, 3 respectively

In the fraction formed during solid-phase mass transfer an increased content of titanium was recorded in the spectrum (Fig. 1, c). This fraction based on the TiC compound had an irregular angular shape with blurred edges due to partial melting. The solid-phase mechanism of mass transfer of a TiC-based compound was associated with the possibility of its brittle fracture caused by a significant proportion of covalent bonds [9]. The fraction containing tungsten (Fig. 1, d) was formed as a result of erosion of the alloy electrode and subsequent mass transfer in the liquid phase. The ESC fraction, which is a product of liquid droplet erosion from the electrode, had a pronounced cellular system of grain boundaries. At the same time, separate open and discontinuous boundaries were observed (Fig. 2).

During low-temperature (LT) processing of titanium alloys in air, as well as during other high-energy processing methods, intensive absorption of carbon, nitrogen and oxygen from the atmosphere by titanium may occur with the formation of chemical compounds or solid

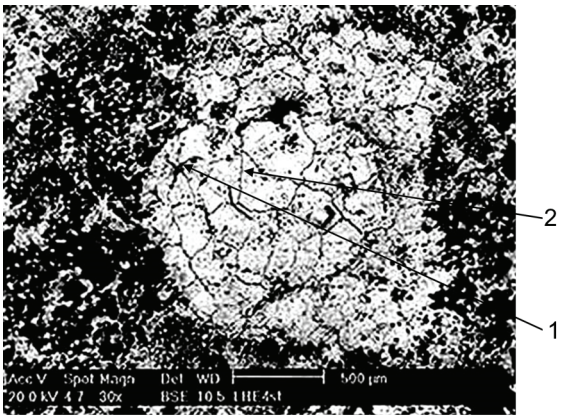

Fig. 2. Microstructure of the products of liquid-drop erosion (separate 1 and discontinuous 2 boundaries)

solutions. Fig. 3 shows the linear dependence of the fcc lattice parameter of titanium carbide, nitride and oxide on the radius of non-metal atoms [153]. A comparison of the energy of formation of these compounds showed that as a result of LT processing, the formation of TiN and TiO compounds is energetically more favorable compared to the formation of TiC. The experimental values of the lattice parameter of fcc TiC, obtained in this work as a result of LT processing of the Ti6Al4V, were between the values of the parameter for TiC and TiN. From this it is clear that the formation of TiN and TiO compounds as a result of pulsed LT processing noticeably reduced the integral lattice parameter of the synthesized solid solution. Thus, during high-energy processing of titanium carbide, a complex compound can be formed that includes isomorphic fcc components, and its chemical composition can be conditionally defined as TiCN, and under certain conditions, as TiCNO.

These results of the study of regularities of the initial stage of coating formation confirmed the idea of a liquid-droplet and solid-phase mechanism of mass transfer of alloy electrode erosion products to a metal substrate in the EST process [10].

In the ESC, a TiC-based compound with a crystal lattice parameter smaller than the parameter of this phase in the alloy electrode was observed. The lattice parameter decreased with the depth of the coating (Fig. 3). The decrease in the parameter from the coating surface to its depth is associated with two reasons. The first possible reason for the decrease in the lattice parameter is related to the nitriding of the TiC-based compound in the discharge channel. This is due to the thermodynamic advantage of the formation of TiN compared to TiC (the heat

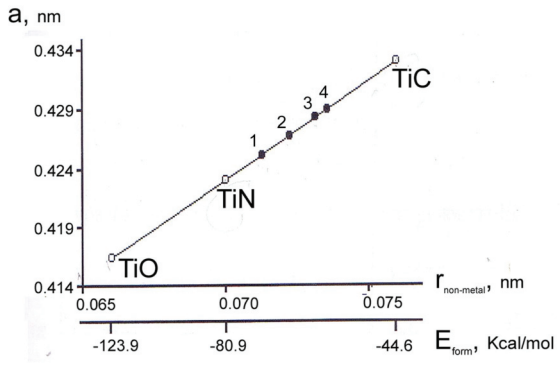

Fig. 3. The parameters of the fcc lattice of titanium compounds depending on the radius "r" of non-metal atoms; the abscissa axis shows the energy of compound formation, points 1-4 - the value of the parameter under different LT modes

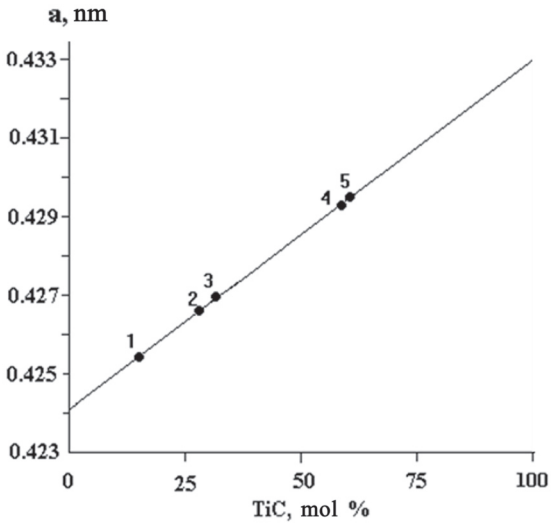

Fig. 4. Change in the crystal lattice parameter of the TiC solid phase depending on ESC manufacturing regime: 1 – 0.8 A, 2 min; 2 – 1.8 A, 2 min; 3 - 2.8 A, 2 min; 4 - 0.8 A, 5 min; 5 – 1.8 A, 5 min.

of formation of TiC and TiN at temperatures of 1115-1500°C is -44.6 and -80.9 kcal/mol, respectively) [11].

TiC and TiN compounds form a continuous series of solid solutions and the change in the crystal lattice parameter practically corresponds to Vegard's rule [11]. Fig. 4 shows the linear dependence of the lattice parameter on the TiC: TiN ratio. Based on the experimental parameters of the crystal lattice on this line, the proportion of the TiN solid solution in the TiC:TiN carbonitride can be calculated. It can be seen that the TiC:TiN ratio changes with different coating application methods. It is known from the literature that the hardness of carbonitride is also an additive quantity and is the sum of the hardness of the dual systems TiC and TiN [12].

Another reason for the decrease in the lattice parameter is the defectiveness of the TiC lattice in carbon. TiC_x carbide exists in a fairly wide range of homogeneous solid solutions (1>x>0.5). At the same time, the metal lattice always turns out to be complete, and the defectiveness in the carbon sublattice can vary significantly during the technological process of manufacturing and compacting titanium carbide powders as well as a result of the subsequent influence of an electric spark on the surface of both the anode and the cathode [12]. Similarly, the TiN compound can also have a defective nitrogen sublattice and, as a result, the TiN lattice parameter can be variable. There are reasons to believe that solid solutions of carbon and nitrogen in the ES-coating were formed as a result of nitrogen assimilation both in the discharge channel and as a result of bombardment of the electrode surface. Their contribution to the formation of the TiCN solid solution is obviously additive. The fact that the lattice parameter of the TiCN compound decreases with the depth of the coating suggests that the processes of dissociation of titanium carbide and its nitriding in the discharge channel are more active in the initial stages of coating formation. A sign of the presence of TiN nitride in the ESC was indicated by the appearance of a characteristic golden color of its surface in certain EST modes. Previously, it was shown that titanium carbo-nitride changed its color from yellow to gray depending on the TiC:TiN ratio [12].

Along with the change in the structural-and-phase state of the coating, significant changes in the structural state of the steel substrate were revealed during the EST process. Already at the initial stage of ESC formation, reflections of Fe_3W_3C carbide were observed. In the EST process, a thin layer of austenitic phase was also formed in the substrate. This phase differed in its crystal lattice parameters from the residual austenite of the AISI W 1 steel, which served as a substrate for the ESC. The thickness of the austenite layer did not exceed 40-60 μm. From the ratio of the integral intensity of the $(200)_\gamma$ and $(110)_\alpha$ reflections it was established that, depending on the EST mode, the content of austenite in the near-surface layer of the substrate varied from 42 to 60%. The austenite lattice parameter a_γ was in the range of 0.3580-0.3645 nm. The concentration of carbon in austenite, determined by the a_γ parameter, turned out to be equal to 1.2-1.8 wt. %. An increase in the intensity of EST led to an increase in the amount of austenitic phase and a simultaneous increase in the concentration of carbon in it.

Carbon penetrated into the near-surface layer of the substrate from the discharge channel as a product of dissociation of TiC and WC as well as from the lower layers of the steel substrate through the mechanism of upward diffusion. Diffusion of carbon induced the reverse martensitic $\alpha \rightarrow \gamma$ transformation and led to the formation of an austenitic phase, as well as to the formation of Fe_3W_3C carbide in the transition zone between the coating and the substrate. Previously, in the work [13] using the method of radioactive isotopes, a similar phenomenon was observed during laser treatment of a high-carbon Fe-Al-C alloy: upward diffusion of carbon in the austenitic phase at a distance of 750 μm. As the energy of the laser beam increased, the carbon diffusion coefficient increased significantly.

An interesting feature of the structural state of the austenitic layer was the almost complete relaxation of residual stresses in it. The austenitic layer, regardless of its thickness and carbon content, had practically no residual stress. At the same time, tensile stresses of 250 MPa were determined in the TiC-based compound, and compressive stresses of 230 MPa and 170 MPa, respectively, in the W_2C coating compound and in the α-phase of the substrate.

The complete relaxation of stresses in the austenitic phase was associated with a decrease in the specific volume of the phase during the reverse martensitic $\alpha \rightarrow \gamma$ transformation, which was realized under the condition of enrichment of the interlayer with carbon. The revealed phenomenon can be technologically useful due to the fact that such interlayer was formed directly under the ESC and relaxed the weakening tensile stresses at the boundary of the coating and the substrate.

4. Conclusions

Microstructure studies at the early stages of ESC formation using a scanning microprobe microscope revealed that TiC eroded in the solid phase with partial surface melting due to the significant proportion of covalent bonding in this compound. The coating fractions in the form of particles with irregular angular shape gave a diffraction spectrum with an intense Ti line. The mass transfer of the W_2C compound occurred through a liquid-drop mechanism.

This was evidenced by the formation of the coating component in the form of a sprayed crystallized drop, the spectrum of which contained an intense W line.

The deposition of both liquid droplets and solid particles on the substrate confirmed existing ideas about the mechanism of erosion and ESC formation, which is associated with the nature of the interatomic bond in the materials of the doping electrode.

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