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SYNTHESIS OF TERNARY COMPOUNDS (MAX-PHASES) IN LOW-VOLTAGE PULSED DISCHARGE PLASMA

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Abstract. *Systematic studies have been carried out to establish the main regularities of synthesis of ternary compounds (MAX-phases) in the plasma of low-voltage pulse discharge on metal surfaces of steel and titanium in the process of electrospark alloying with compact electrodes made of Ti, Al, graphite, titanium nitride (TiN), silicon carbide (SiC) and their powders. Tribological tests of steel and titanium samples with coatings containing MAC-phases have been conducted, which demonstrated their high wear resistance under dry friction conditions.*

Keywords: synthesis, ternary compounds, electric spark alloying, compact electrodes, wear resistance

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1. Introduction

MAX-phases are a family of ternary layered compounds with the formal stoichiometry Mn+1AXn (n = 1, 2, 3...), where M is a transition d-metal; A - p-element (e.g., Si, Ge, Al, S, Sn, etc.); X - carbon or nitrogen. The layered ternary carbides and nitrides of the d and p elements (MAX-phases) exhibit a unique combination of properties characteristic of both metals and ceramics.

These materials possess a number of noteworthy properties, including low density, high values of thermal and electrical conductivity, strength, low modulus of elasticity, excellent corrosion resistance in aggressive liquid environments, resistance to high temperature oxidation and thermal shock, and ease of machining. Furthermore, these materials demonstrate a notable melting point and substantial stability at temperatures reaching 1000°C and above [1-3].

Triple compounds, also known as MAX-phases, are of particular scientific and practical interest due to their distinct combination of properties that are characteristic of both metals and ceramics. Of the numerous MAX-phases that have

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been synthesized to date, those based on titanium (Ti_2AlC, Ti_2AlN, Ti_3AlC2, Ti_3SiC) are of particular interest in terms of the variety of their properties [4-8].

The methods employed to synthesize these materials necessitate the utilization of sophisticated and energy-intensive technological equipment [5, 6].

In light of the performance characteristics exhibited by these triple compounds, their potential application as protective coatings on the working surfaces of machine parts subjected to intense mechanical stress is a subject of particular interest. In this context, the objective of the present study is to conduct a detailed analysis of the prospects for the formation of coatings of these triple compounds on metal surfaces using the electric spark alloying (ESA) technology [11, 12].

The ESA process is based on the phenomenon of polar transfer of the electrode (anode) material onto the cathode (workpiece) surface when pulsed electric discharges occur between them. The ESA technology is simple, low energy and material consuming, and the equipment required is small, reliable and transportable.

Compact electrodes made of materials that form ternary compounds can be used as alloying materials: These include titanium (Ti), aluminum (Al), graphite (as a carbon source), and silicon carbide (SiC), as well as powders of these materials.

2. Results and discussion

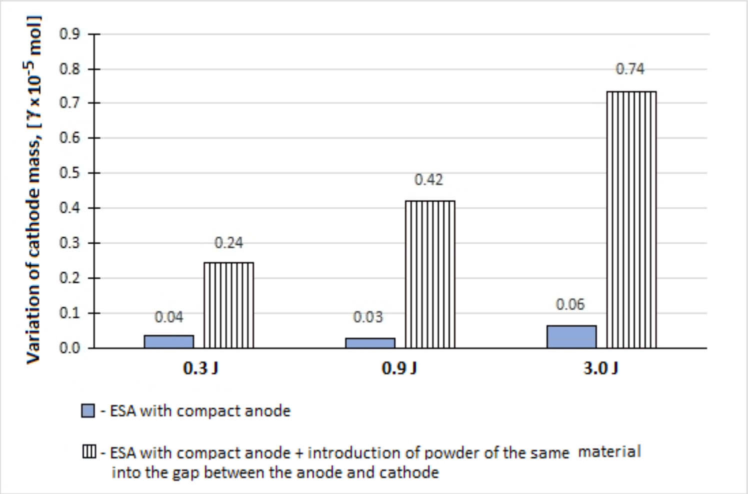
Two processing methods were utilized in order to obtain MAX-phases by ESA: with compact electrodes of the materials contained in the triple compositions and with their powders. Samples of OLC 45 structural steel and a titanium alloy of technical purity were used as a support. The electric spark alloying process was carried out at a number of industrial and experimental plants in a wide range of pulse discharge energy values (0.5-6.0 J).

An alternative processing scheme was used, in which powders of the same materials (graphite, Ti, Al, TiN, SiC) were used as alloying elements, which were introduced into the interstice between anode and cathode in the ESA process at the same energy regime. An intensification of the coating formation process on the substrate surface was observed (Figure 1, a).

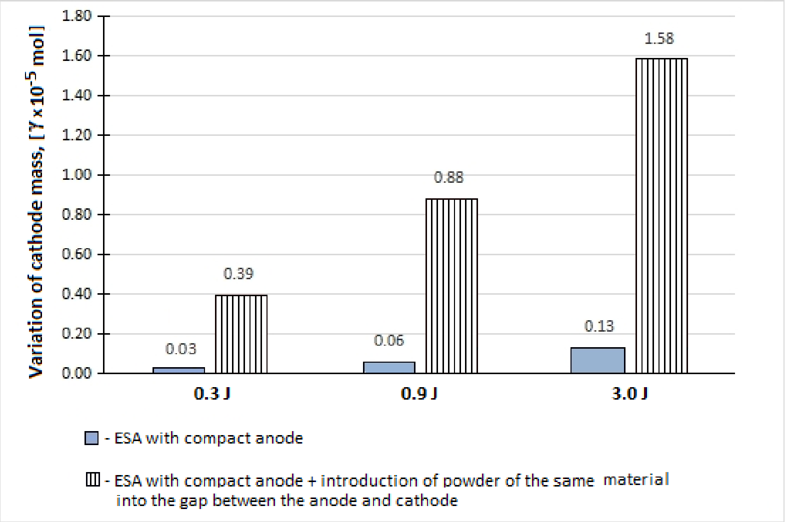
As demonstrated in Figure 1, the nature of layer formation on a substrate when utilizing powder materials remains constant, irrespective of the pulse discharge energy value. Furthermore, it was observed that the character of layer formation remains unaltered when titanium is employed as a support-cathode (see Figure 1, b).

It is noteworthy that during the course of the investigation, a stoichiometric mixture of elements was introduced into the interstice between the anode and cathode with the objective of enhancing the formation of the MAX-phase Ti_2AlC_3 in the coatings. The outcomes were then compared with those obtained when the mixture consisted of equal volumes of elements. The findings revealed that this variation had negligible impact on the quantity of the formed Ti_2AlC_3 phase.

This phenomenon can be attributed to the nature of the processes occurring in the plasma of the pulse discharge, where temperatures in the range of 10^4C and above are attained.



a. Ti + Al + C / OLC 45



b. Ti + Al + C / BT1

Fig. 1. Intensity of layer formation on OLC 45 structural steel (a) and on technical grade titanium (b) when alloyed with compact Ti, Al and graphite electrodes and the Ti + Al + graphite powder mixture is introduced into the anode-cathode gap.)

The interaction between the materials of the mixture introduced into the discharge plasma channel with those of the anode and cathode is found to be imbalanced, resulting in the formation of a layer on the support due to intense hydrodynamic mixing.

The X-ray phase analysis of the formed coatings is depicted in Figure 2. Further investigation established that the Ti_2AlC_3 phase is predominantly formed under conditions of pulsed discharge with energy values in the range of 0.8-3.0 J.

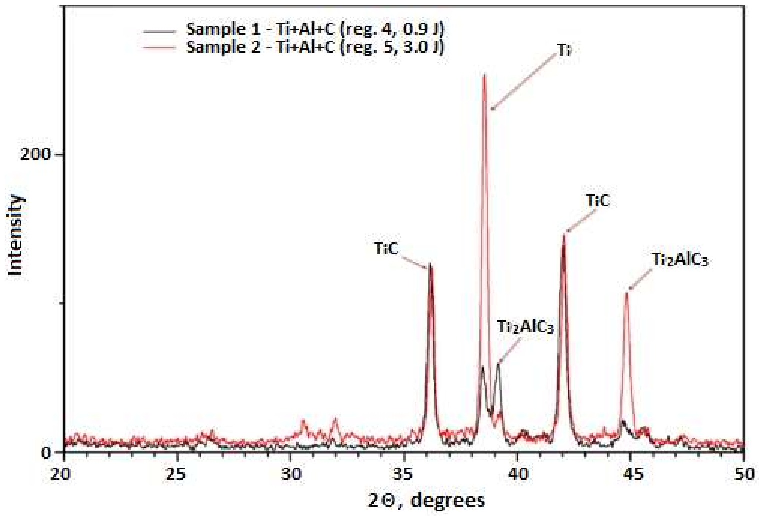


Fig. 2. X-ray diffractograms of the coating on OLC 45 steel obtained in successive processing with titanium, aluminum and graphite electrodes at pulse discharge energy equal to 3.0 J.

Concurrently, a number of other compounds are formed in the deposited layer (Table 1), which ultimately endow the coating with a wide range of properties and, most significantly, high wear resistance.

Table 1. Phase composition of the layer formed on OLC 45 (cathode) steel substrate at ESA with Ti + Al + graphite powder mixture (discharge energy value – 3.0 J).

No.	*Anode material*	*Phase composition of the coating*
1.	OLC 45 without cover	a-Fe, Fe_3C
2.	Ti, Al, graphite	TiO_2, FeO, TiN, g-Fe, Fe_3C, Fe3N, $AlFe_3$,a-Fe, Ti_2AlC_3

As can be seen from the deciphering of the radiograms, a wide range of compounds were formed as a result of the interaction of the electrode and support materials with the discharge plasma in the pulse. Importantly, Fe_3N, Fe_4N and TiN phases were detected in the coatings, although neither in the support nor in the alloying materials was nitrogen present. The occurrence of these phases can be explained by the fact that when the ESA process was carried out in the atmosphere (air) and under the conditions of the development of high temperatures and pressures in the plasma of the pulse discharge, the nitrogen in the air interacts with the electrode elements forming nitrides.

Table 2. Results of crystallite size studies of the crystallites in the layer formed on the OLC 45 steel substrate (cathode) during ESA with powder mixture:

Average crystallite size	*Ti + Al + C* $E_d = 0{,}9\ J$	*Ti + Al + C* $E_d = 3{,}0\ J$	*Ti + SiC* $E_d = 0{,}9\ J$	*Ti + SiC* $E_d = 3{,}0\ J$
L, Å	58,5	58,0	50,8	60,5

The investigation yielded data (Table 2) indicating that crystalline formations in the examined materials are within the range of (50÷61) Å [13-14]. This observation suggests the potential for the formation of nanoparticles and nanophases in the coatings developed during ESA. It has been determined that the chemical composition of the coatings and their formation mechanisms significantly impact the geometrical dimensions of the crystalline phases obtained in ESA coatings.

The present study investigates the wear resistance of OLC 45 steel subjected to electric spark alloying with ternary compounds Ti + Al + C, Ti + AlN, Ti + SiC.

It is widely acknowledged that enhancing the wear resistance and reliability of the friction units is pivotal in prolonging machine life. In view of the diverse working conditions of the workpieces, it is evident that the surface layer experiences the most substantial loading. Consequently, the service life of the machine is directly influenced by the bearing capacity of the surface layers.

The coatings were deposited on OLC 45 steel samples with dimensions of 5x8x6 mm, especially on the 5x8 mm surface. OSC 8 tool steel (HV = 7800÷8000 MPa) with dimensions 2x40x90 mm was utilized as a counter-body, the surface of which was previously ground and polished.

Tribological testing of the coatings was performed at a specific load of 2 MPa under dry friction conditions. The wear measurements of prismatic samples were performed by gravimetric method using ADV-200M analytical balance. The error in the measurement of the sample mass was 0.05 mg.

The frictional force (F), resulting from the mutual displacement of the contacting surfaces, was measured using a dynamometer, the deformation of the elastic element of which was transformed into an electrical signal using a standard voltage amplifier. This electrical signal was then fed into a computer through a special device, with the frictional force being recorded 3000 times in 3 seconds after each minute of testing.

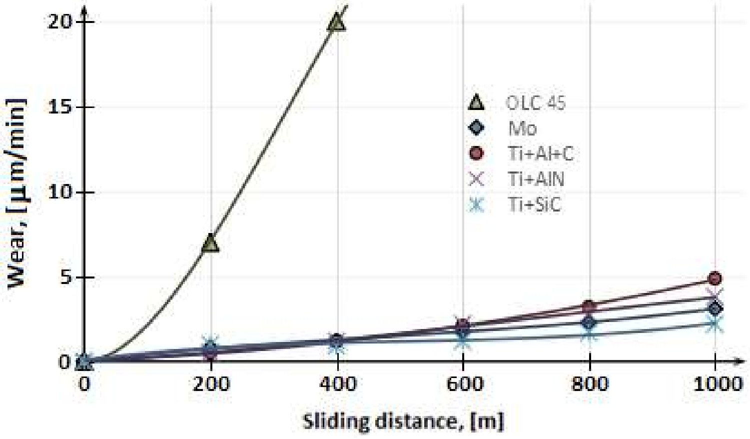


Fig. 3. Weight wear of coatings after four periods of tribological tests with a specific load of 2 MPa.

Using a special program, the frictional force values were transformed into friction coefficient values. The measured values of the friction coefficients were then subjected to statistical processing, after which the average F – capacity was determined at the conclusion of each minute of testing. As illustrated in Figure 3, the wear graph of the coatings after a sliding distance of 1000 m clearly demonstrates that the samples coated with Ti-Al-C, Ti-AlN, and Ti+SiC ternary compounds exhibited the highest wear resistance values compared to the uncoated OLC 45 steel.

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Conclusions

Conclusion (1).

The systematic investigations of the ASE process using compact electrodes of ternary Ti-Al-C, Ti-AlN and Ti-SiC compounds and their powders enabled the following findings:

- the processing regime (energy of electrical discharge) was optimized depending on the thermophysical properties of the alloying material, which ranged from 0.8 to 3.0 J;
- the specific machining time of one-unit area of the substrate (workpiece) was determined to be (1.2...2.0) min/cm^2.

Conclusion (2).

Tribological tests of coatings formed at ASE with the ternary compounds Ti-Al-C, Ti-AlN, and Ti-SiC demonstrated a substantial increase in wear resistance compared to uncoated OLC 45 steel.

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