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Clean technologies

ECOLOGICAL ASPECTS OF ELECTRO-SPARK DEPOSITION TECHNOLOGIES FOR IMPROVEMENT OF THE METAL SURFACES QUALITY PREPARED BY 3D PRINTING. PART II. COMPOSITION, STRUCTURE, DURABILITY, AND ENVIRONMENTAL COMPLIANCE

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Abstract. Additive technologies (ATM) are one of the most promising ways to reduce environmental pollution and solve various environmental problems. However, their widespread use is limited by the presence of high roughness, unevenness, cracks, and pores in the surface layer of the products. This paper investigates the possibility of improving the surface of ATM products through low-energy electro spark deposition (ESD) with low-melting AlSi electrodes. The research work consists of two parts. In the first part, a considerable decrease in the roughness and surface defects of metal alloys based on Ti and Fe has been achieved by ESD. This section examines the impact of ESD regimes on the composition, structure, and wear resistance of coatings. The conditions for ESD have been determined and optimised, in which as a result of the targeted synthesis of new wear-resistant phases and amorphous-crystalline structures a simultaneous reduction of roughness and surface defects and increase of wear resistance of treated surfaces are realised. The environmental benefits of both technologies are presented. Their joint application makes it possible to avoid energy- and resource-intensive finishes, expand the scope of 3D printing and reduce labour costs, energy, and materials, as well as significantly reduce environmental pollution.

Keywords: Additive technologies (ATM), Selective laser melting (SLM), Electro spark deposition (ESD), wear resistance.

AIMS AND BACKGROUND

The continuous expansion of the production of metal products is associated with significant pollution of the atmosphere and the environment, resulting from

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technologies for extraction, production, and processing, as well as the increased electricity consumption and the sustainability of metal waste[1–3]. The connection between the further increase in the volume of machine-building production with the reduction of pollution and the emission of pollutants are new technologies and technological innovations[2–5]. One of the most promising approaches to solving several environmental problems is additive technologies (ATM), also known as "Additive Manufacturing Process", or 3D printing of metals[6–8]. The environmental efficiency of 3D technology consists of a significant reduction in both pollution and the cost of labour, energy, materials, machinery, tools, and equipment in the production of even the most complex metal products. While in traditional technologies the loss of material can reach 90% of the initial workpiece[6,7], and the final product is obtained by welding or assembling the individual components, in ATM the finished product is formed without industrial waste, without the need for many and different production processes and machines, from tools and technological equipment, which leads to significant savings in material, labour, and energy costs[8]. For the implementation of these methods, a direct source of energy is mainly used laser. The selective laser melting of metals (SLM) (Refs 6 and 7) is one of the most common in practice ATM technology, which allows for the production of parts and assembled units with complex geometry and shapes, with holes and cavities in the sides, that can not be created by the traditional production methods. The main disadvantage that prevents the widespread use of these advanced technologies is the high roughness and the presence of cracks and pores in the surface layer. To improve the quality of the surface, after the process of additive production, various additional treatments[9–14] are used, which are related to both costs and environmental pollution. Often finishing can take up to 3 times longer than printing the part[7,8].

In this regard, the present work aims to expand the scope of use of ATM technologies by researching and creating opportunities for environmentally friendly improvement of the quality of treated surfaces and removal of surface defects from SLM printing, using the method of electro spark deposition[15–17]. In the first part of the present work[18], a significant reduction in roughness and filling of depressions and pores was achieved by ESD with electrodes from a low-melting eutectic alloy of AlSi. This section examines the changes in the composition, structure, and wear resistance of coatings, as well as the possibilities for local synthesis of wear-resistant phases with amorphous and nanocrystalline structures to establish empirical dependencies that allow determining appropriate process parameters for ESD, which to provide both reduction of surface defects and increase of surface hardness and wear resistance.

EXPERIMENTAL

The investigations were carried out at process parameters, optimised in advance, and at impulse energy for the ESD, whereupon one can obtain uniform and dense coatings having acceptable ruggedness. The materials of the electrode, the substrate, the research equipment, and the ESD modes are described and given in the first part of the present paper[18]. Electrodes from the low-melting eutectic alloy AlSi12 were used for ESD processing. The coatings of the electrodes[19–21] used in Part I of the work reduced the surface defects and the roughness of the SLM specimens while increasing the microhardness of the treated surface[18].

The microstructure and microhardness (HV) of the coatings were studied by using a metallographic microscopes "Neophot 22" and "Zwick 4350" hardness tester, according to ISO 6506-1: 2014.

The phase identification, the distribution of elements in the surface layer, and microstructural analysis of the coatings were performed by an X-ray diffractometer Bruker D8 Advance in "Cu Kά" radiation, and by a Scanning electron microscopy (SEM) "EVO MA 10 Carl Zeiss".

The comparative friction tests were performed with a tribotester type "Thumb-on-disk" under dry surface friction with hard-fixed abrasive particles in plane contact at the following conditions: load 4 and 10 N; sliding speed 0.239 m/s; type of abrasive surface – Corundum No 1200. The mass wear was obtained as a difference between the initial mass of the sample m_0 and its mass m_i after a certain number of friction cycles: $m = m_0 - m_i$, mg. The mass of the samples before and after a given friction path was measured with an electronic balance WPS 180/C/2 to the nearest 0.1 mg.

The following wear characteristics were calculated:

– Wear intensity – the amount of wear per unit of friction work: mg/m (1)

– Wear resistance – the reciprocal value of the wear intensity: $I = 1/i = S/m$, m/mg (2)

RESULTS AND DISCUSSION

Microstructure of coatings. Figure 1 illustrates the morphology of the coatings using the AlSi12 electrode on steel (*a*) and on titanium (*b*) substrate.

The resulting coatings have a low degree of porosity and do not mix with the substrate. Coatings are observed to have a thickness of 12–15 μm, compactly attached to the substrate. It can be clearly distinguished that there are brighter spots of interphase diffusion layers of thickness of several microns, whose presence is determined by the interaction between the reactive mixture and the substrate. It is visible that the cavities are filled up by the melt as well as the surface pores, as well as the comparatively smooth and even surface of the coatings. The primary extrusions left from the SLM treatment are burned out and molten as a result of the spark-plasma discharges.

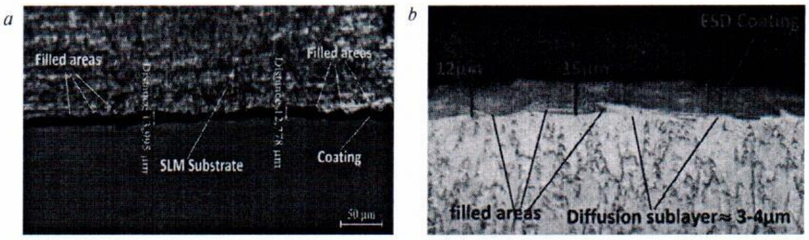

Fig. 1. Cross-section microphotographs of the LESD and ESD coatings with AlSi12 electrodes on SLM surfaces with energy $E = 0.04$ J: LESD on 1-2709 steel – *a* and ESD on Ti-GR2 – *b*

Phase composition of coatings. From the data, obtained by the XRD analysis it is established that in the case of local melting in the process of spark discharges there were occurring interactions of the materials of the electrode and the substrate and the elements of the environment, and the formation of new intermetallic and wear-resistant phases (Fig. 2).

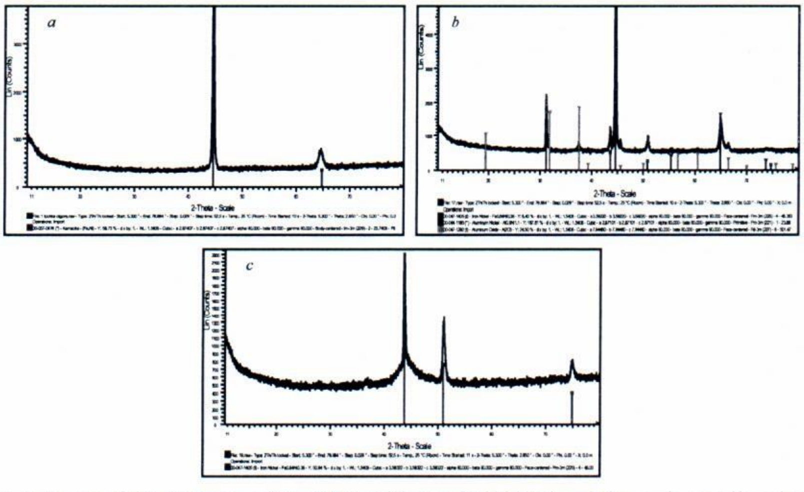

Fig. 2. Patterns of XRD spectra of the ESD coatings of AlSi12 electrodes on invar alloy: invar FeNi36 after SLM – *a*; ESD coating at $E = 0.03$ J – *b*, and LESD coating at $E = 0.03$ J – *c*

The XRD patterns of the coatings differ in intensity and the width of the characteristic lines of the iron and the intermetallic phases. The widening of the characteristic lines, which is most strongly expressed in the case of LESD (Fig. 2*c*), is an indicator of the presence of sold solutions and amorphous-crystalline structures on the surface of the coating. The phases registered in the coatings are: (Fe, Ni), $NiAl_3$, Al_2O_3, AlFe, $Al_{0.9}Ni_{1.1}$, $AlFe_{0.23}Ni_{0.77}$, $Fe_{0.7}Ni_{0.3}$, AlO.

Figure 3 shows XRD patterns of ESD coatings upon Ti-GR2. At ESD on Ti-GR2, one can register in the coatings: α-Ti, $TiN_{0.3}$, Ti_5Si_3, $TiAl_3$, TiAl, TiO_2, Al_2O_3, $AlSi_3Ti_2$, $Al_{2.5}Ti_{1.5}$, Al. As it was in the case of Fig. 1, the lines of the characteristic peaks are shifted and become wider, which is most clearly visible again in the case of LESD having impulse energy of 0.03–0.04 J.

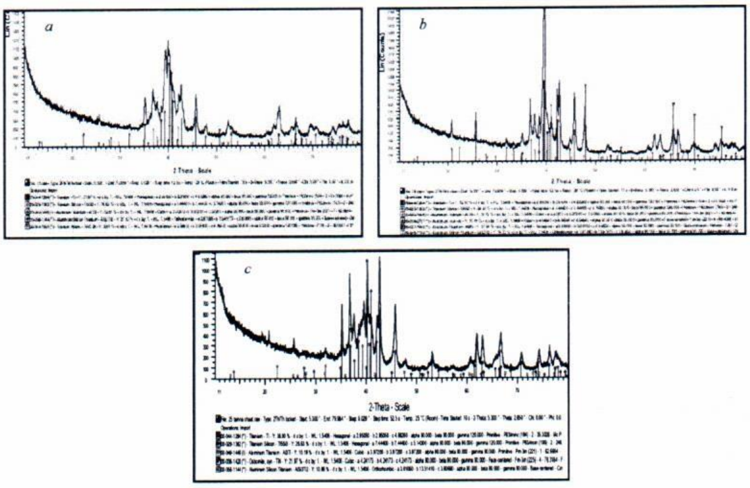

Fig. 3. Patterns of XRD spectra of the ESD coatings of AlSi12 electrodes on Ti-GR2 alloy: AlSi12/Ti-GR2 – $E = 0.03$ J – *a*; AlSi12/Ti-GR2, $E = 0.07$ J – *b*, and AlSi12/Ti-GR2, after LESD, $E = 0.04$ J – *c*

The XRD spectra of the coatings on SLM steel 1.2709 are similar. The main registered phases are (Fe, Ni), $NiAl_3$, AlFe, AlNi, FeSi, Al_5Fe_2, and $Al_{3.2}Fe$. In small quantities (having low intensities and a small number of peaks) one can observe FeSi, $Fe_{0.9}Si_{0.05}$, $FeNi_3$, $AlFe_{0.23}Ni_{0.77}$, $Al_{2.67}O_4$, AlO, Al_2O_3 and traces of AlN, Si_3N_4. The registered Al_2O_3, as well as the traces of AlN and SiN, show that during the transfer process the aluminum and the silicon have reacted with oxygen and nitrogen in the air, forming highly stable and wear-resistant compounds. The average size of the crystallites, calculated by Scherer's formula, varies from 12 up to 80 nm for the various phases, which shows that the obtained new phases in the electro-spark coatings possess nano-crystalline structure.

The presence of newly registered phases implies higher micro-hardness, stronger bonding with the substrate, and, respectively, higher wear-resistance. The increase in the impulse energy leads to an increase in the degree of dispersion and the degree of alloying of the substrate with some elements from the anode and the environment, as well as an increase in the quantity of the newly obtained intermetallic phases.

Some new phrases are also appearing, while the old phases, obtained at higher energy are being transformed. Therefore, by applying a suitable set of impulse parameters, it becomes possible to achieve a purposeful synthesis of some definite phases. The composition of the coatings differs significantly from the composition of the initial electrode materials. This is due to the specificity of the effect of the ESD process on electrode materials: ultra-high heating and cooling rates, contact of the surfaces with each other and with environmental elements under conditions of high temperatures and pressures, and high speed of the diffusion processes.

The detailed analysis of the diffraction patterns allows us to conclude that in cases of the reaction electro-spark treatment of impulse energy up to 0.07 J more than 10 new intermetallic phases have been synthesised, including two oxide phases and one nitride phase of the aluminum from the electrode, as well as some tri-component phases.

One of the possible ways to increase the efficiency of ESD and the wear resistance of electro spark coatings is the creation of nanocrystalline and amorphous structures in them[22–29]. The registered widening of the diffraction peaks of Al, Ti, and Fe reflects the formation of solid solutions and new compounds in the so-obtained mixture, as well as a decrease in the size of the structure, reaching the amorphous phase. Since in the wider angular zones there exist also characteristic peaks, which indicate the presence of crystallites, one can conclude that the coatings have a crystalline-amorphous structure, obtained by mixing the two materials in the newly prepared intermetallic phases. This conclusion is following the data, summarised from the optical microscopy and the electron microscopy[18]. The amorphous metal alloys based on Al possess high mechanical properties, high strength, and good plasticity[24–29], which is also favourable for the mechanical properties and the resource of the coatings[24,25,29].

Coatings tribo tests results – wear of coatings. Figures 4 and 5 illustrate the change in the degree of wear and the wear resistance of superficially modified invar and 1.2709 steel depending on the friction path length.

The testing of friction showed that the degree of wear of the coated surfaces is up to 2 times lower in comparison to the non-coated surfaces. There is a similar change in the wear resistance of the coatings (Fig. 5). The lowest wear degree is manifested by the samples, coated at energy $E = 0.04$ J having three pathways of the depositing electrode. The higher values of the parameters of the roughness of the coatings, deposited at energy 0.07 J, obviously influence unfavourably the wear degree.

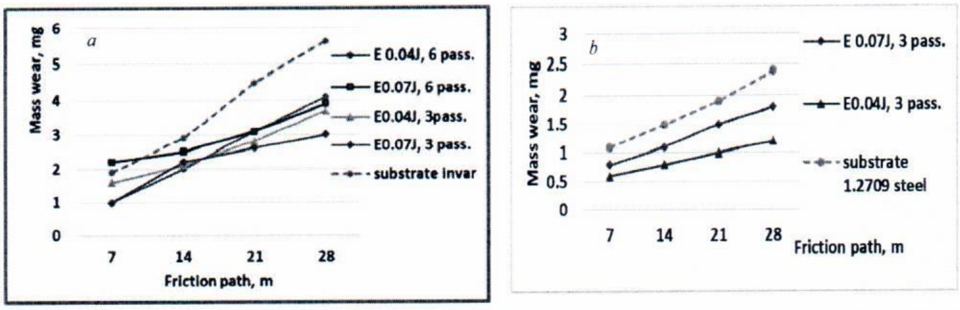

Fig. 4. Wear of coated surfaces versus sliding distance: wear of coating AlSi12 on invar – *a* and wear of coating AlSi12 on 1.2709 steel – *b*

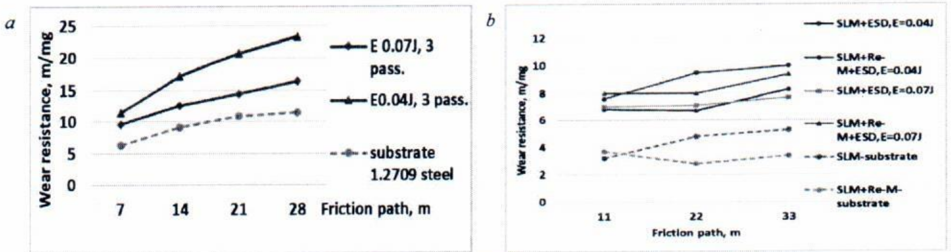

Fig. 5. Wear resistance versus sliding distance –AlSi12/steel – ((SLM+Re-M = SLM + re-melting): coatings AlSi12 on 1.2709 steel after SLM, $P = 4$ N – a, and coatings AlSi12 after SLM, $P = 10$ N – *b*

The surface layer at ESD changes the friction conditions in two main directions:

1. The change of the microgeometry of the surface;
2. Change the composition and structure of the surface – a layer with high hardness and wear resistance is created.

Evaluation of energy-saving potential and ecological effectiveness as a result of the combined use of 3D technologies and consecutive ESD superficial modification. Based on the results, obtained in the present work, it can be established that the utilisation and the application of the additive technologies and the consecutively improved reaction electro-spark treatment surfaces can lead to many technological, economic, and ecological consequences. The combined use of the two methods appears to be waste-free technology, connected with the protection of natural objects and utilisation of the natural resources and continuous decrease in the negative impact upon the environment and on the human health and it offers the following energy- and resource-saving options:

– Decrease in the quantity of the used materials and the waste materials. While the traditional manufacturing processes are based on deprivation of the material and following treatments until the desired shape is achieved, accompanied by a large quantity of waste and harmful emissions, the ATM technologies are based on the addition of consecutive layers of the material to obtain the desired form enabling the production of light-weight, stronger, personalised and even preliminarily assembled elements at considerably lower material and production expenses, compared to the traditional technologies. In the case of additive production with consecutive ESD surface modification the waste product is reduced almost to zero, which leads to a considerable decrease in the production process wastes;

– Decrease in the volume of production of metal preparations, which will lead to a decrease in the expenses for heat energy and electric energy, as well as to a considerable decrease in the pollution of the environment. The superficial reaction electric spark treatment contributes to avoiding the additional expenses for labour, energy, consumables, and materials, needed for the finishing operations of articles, produced by 3D printing, connected with diminishing the roughness and the surface defects. On the other hand, the promoted levels of hardness and wear resistance after ESD in comparison with the materials used in the traditional technologies lead to an increase in the resource and energy effectiveness of the articles and, respectively, additionally decrease in the material and energy expenses and lower the pollution;

– Elimination of the necessity for instruments and equipment given the utilisation of various metal-processing machines, the accessories, and consumables for these machines, as well as diminishing the expenses for energy, consumed by these machines for the various types of pretreatment of the starting materials;

– Reducing to a minimum the need of assembling the separate parts, combined in the article and the mounting operations such as fitting of the parts, binding them by some attachment elements, welding, and sticking them together, which additionally helps for lowering the expenses for materials, labour, and energy, needed for mounting operations;

– The products used in automobile and aircraft building, produced by 3D printing give contribution to making lighter constructions and increasing the effective utilisation of the power of the engines at the lower expense for fuels and decrease in harmful emissions.

– When ATM and ESD are used together, the level of pollution is reduced due to the reduced consumption of energy, materials, machinery, and technological equipment, i.e. additive production with subsequent ESD helps to solve global problems, such as consumption of material resources, consumption of energy and environmental protection.

CONCLUSIONS

ESD enhances the hardness and wear resistance as a result of the local synthesis of wear-resistant compounds and the formation of surfaces having an amorphous-nanocrystalline structure during the chemical interaction between the melt and the substrate.

The obtained results show the interconnection between the parameters of the process and the structure and the properties of coated surface and enable the preparation of coatings having pre-set roughness, thickness, hardness, and wear resistance upon titanium and Fe-Ni surfaces.

It has been established the conditions and process parameters under which electro spark treatment of ATM surfaces using electrodes of AlSi12 enables the production of coatings having a high content of amorphous phases (metallic glass) and double increase in the wear resistance, compared to that of the uncoated surfaces. The coatings obtained at lower impulse energy – 0.04 J show higher wear resistance and they are suitable for depositing layers upon parts having high requirements to the quality of the surface, as well as concerning the wear resistance.

The conditions for electro spark treatment have been determined, under which can obtain at the same time both obliteration of the traces from the previous treatment and improvement of the characteristics of the surface and the increase in the wear resistance of the coated surfaces.

The main benefits of the combined realisation of ATM (SLM and DLMS) technologies and the reaction electro spark treatment using AlSi12 electrodes are not only technological and economical, but also ecological – they are based on a decrease in the expenses for materials, energy, and decrease in the wastes and of the harmful emissions.

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