Improvement of the surface properties of titanium products by reactive electro-spark processing. A short review

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Abstract: This work presents a brief overview of the essence, principles and technological features of reactive electrospark processing (RESP), based on a simple, economical and ecological method – electrospark deposition (ESD), which avoids many of the disadvantages inherent in other existing methods. This treatment can optimize the physicochemical properties of the substrate surface and improve the structure, hardness and wear resistance. The application of RESP technology in surface modification of titanium alloys is considered. Research results, including those of the authors of this work, are presented, which demonstrate the possibilities of RESP for reducing roughness and surface defects and for the synthesis of new phases and ultrafine structures that are not present in the electrode and substrate. The effect of RESP technology on the wear resistance of titanium and titanium alloys is shown. The main dependences of the quality and properties of the treated surfaces on the process parameters are identified, and ways to form reaction phases, to avoid and remove surface defects and to obtain “in-situ” new intermetallic and wear-resistant compounds are presented. The possibilities and prospects for the use of RESP to improve the surface characteristics and properties of titanium and its alloys are indicated.

Keywords: TITANIUM ALLOY; ELECTRO-SPARK DEPOSITION; REACTION ELECTROSPARK PROCESSING, INTERMETALLIC COMPOUNDS, CARBIDES, NITRIDES, BORIDES, ROUGHNESS, MICROHARDNESS, WEAR RESISTANCE

1. Introduction

Titanium and titanium alloys are attractive for many industrial and household industries and the medical industry [1], but the high tendency to intensive wear, the appearance of pores and cracks, as well as the high coefficient of friction, low hardness and wear resistance significantly hinder the widespread use of these unique materials [2,3]. In order to eliminate this drawback, various methods are used to form wear-resistant coatings [4-6]. However, the use of the known and established methods [4-6] is associated with a number of difficulties resulting from their physical nature and natural technological features and limitations, such as the inability to modify complex geometric contours, or to produce coatings with greater thickness, unsatisfactory strength of the connection with the substrate, generation of adverse effects such as thermal deformation, annealing and damage of the titanium bases or complex, energy-intensive and expensive equipment, complex technologies and high production costs. The Electrospark Deposition (ESD) additive method is suitable for solving these difficulties. Due to its simplicity and flexibility, universality and low cost, ESD is increasingly used for surface modification and strengthening of titanium alloys [7-10]. The interest in ESD, its growing popularity and the ever-expanding applications of titanium surface strengthening are mainly due to the simple technology, negligible heating and no thermal deformation of the layered products, strong bond with the substrate material, very low power consumption, easy portability and the low cost of equipment, environmental compatibility and the ability to change the properties of metal surfaces in a wide range, [8-11]. ESD is mainly used to strengthen the surface layer of metal products by transfer from deposition electrodes most often from hard alloys materials based on WC, TiC and TiN [7-11]. The material eroded from the electrode is transferred to the substrate in vapor, liquid and solid (softened) phases. Due to the high erosion resistance of the carbides used and the high fragility of the hard alloy electrodes, a significant part of the transferred material is in a solid (softened) phase, which limits the course of chemical reactions. The resulting coatings usually have a thickness of 4-5 to 50-60 μm, irregularities from the transferred solid phase, defects and increased roughness compared to that of the substrate, which reduces the effect of their use [10-12]. In recent years, a significant number of studies have appeared, in which many authors use ESD to reduce roughness and increase wear resistance by synthesizing new phases and structures and giving the coating different properties suitable specific use cases. A new concept known as reactive electrospark processing (RESP) [11-17] has been introduced, where through ESD and appropriate choice of electrode materials and the spark discharge parameters, an in situ directed synthesis of new phases, that are not present in the electrode and in the substrate, including amorphous and nano structures are realized. Many authors claim that such coatings applied by ESD using RESP give different properties and improve the life of coated products by a factor of 2-5 [7-10,17-23]. At this stage, RESP is still insufficiently well studied.

In this regard, the aim of the present work is, based on the literature data and the results of previous own research, to study the nature and usefulness of reactive surface electrospark treatment, to consider the characteristics and features of the coatings and to evaluate the possibilities of their use for surface modification and improving the hardness and wear resistance of titanium alloys.

2. Process description of resd and evaluation of the possibilities of its use for titanium alloys. review and analysis on the literature.

Although many researchers have used ESD for the synthesis of new compounds, for the first time the concept of reactive electrospark processing and the conditions for its realization have been introduced in the works [11-14]. The main idea of RESP is to form a local liquid reaction phase on the surface of the cathode through an appropriate selection of precursor electrodes and parameters of the electric pulses, in which the components of the electrode and the substrate are actively mixed, fill the voids and the pores, and evenly distribute over the layered surface by reacting with each other to form new phases. In addition, the extremely high cooling rate of the reactive melt (105-106 °C/s [7,9,10]) allows the formation of new ultradisperse, amorphous and nano-sized wear-resistant structures. The main conditions for the formation of the reaction phase as a prerequisite for a strong chemical interaction of the electrode or electrode components with the substrate components are defined in the works [11-14]. In order for reactive phasing to occur during ESD, it is necessary to ensure the transfer of anode material in a molten (liquid) state, which has a higher chemical activity compared to traditional deposition. Appropriately selected pairs of “glass-forming precursor - crystalline substrate” are used to obtain coatings containing new phases and a metallic mixed (metallic glass and nanocrystals) structure with improved properties. Due to the eutectic’s ability to disperse (fluidity), the electrospark treatment improves the quality and within certain limits reduces the roughness of the coatings, and the strength of the connection with the base and their thickness are higher. This has been used to improve the surface quality of manufactured products through additive manufacturing [11,13-17]. The formation of a modified
Ways to implement RESP

Most often, RESP is performed using the classic ESD equipment with a vibrating or rotating electrode, or by mechanized non-contact local electrospar deposition with a rotating electrode and automatic maintenance of the inter-electrode distance (LESD). RESP processing is usually performed by successive deposition of layers of different electrodes, by multicomponent alloys, or in a defined gas environment. A new scheme is proposed in [18] - Fig. 1, in which RESP is implemented by feeding powder material directly into the processing area through a hollow electrode (a) or from the side (b), with the anode-electrode periodically contacting with the substrate (cathode). Through this scheme, the synthesis of carbide phases (TiC and WC) was realized during electrospar alloying with Ti, W and graphite electrodes, with additional supply of powders from these materials in the processing area, and also synthesis of three-component compounds - MAX-phases: Ti_{x}AlC, Ti_{x}AlN and Ti_{x}SiC_{y} by ESD with TiAlC, TiAIN and TiSiC powder compositions.

The coatings obtained by this scheme have increased density, microhardness, thickness and wear resistance compared to those obtained by classical ESD methods with hard alloy electrodes.

Another increasingly popular way to RESP is by using classical electrical discharge machining (EDM) machines [24-26]. The method is known as the electro-discharge coating (EDC) process. By using pulses with low energy, duration less than 100 µs, reverse polarity and different processing electrodes and powder, liquid and gaseous additions to the dielectric fluid, on the surface of the substrates various new compounds have been synthesized such as: W_{x}Cu, WC-Cu, TiC-Cu [24], TiN, Ti_{x}N, Ti_{x}AlN, Ti_{x}O and CuO [25] Mo, Cu, MoS_{2} [26] and many others. The above authors reported a coating thickness of up to 0.6 mm, up to a tenfold increase in microhardness and a fivefold increase in wear resistance of the coated samples. Problematic with this method, however, is the RESP of substrates with a complex spatial surface, which requires the fabrication of processing electrodes with a surface mirroring that of the substrate.

Electrodes - precursors for RESP

RESP implies numerous possibilities for the use of materials of different composition and for the synthesis of intermetallics and wear-resistant phases. Depending on the requirements for the processed surface, researchers use different precursor electrodes, which can be divided into the following main groups:

- Low-melting eutectic and near-eutectic alloys, which have a lower melting temperature than their constituent materials and are able to ensure more complete and uniform spilling and spreading of the melt on the surface of the substrate. Such are AlSi alloys [11-17, 19]. The authors report that RESP with AlSi electrodes has significant potential to improve lifetime and corrosion resistance both due to the elimination of microcracks and the formation of new intermetallic and oxide and nitride phases such as TiN, TiAlN, Al_{2}O_{3}, TiSi, TiO. The Al-based metallic glasses obtained in the coatings possess excellent mechanical properties. Various two-component - Ni-Al [9,20], Ti-Al [21,22], Ni-Ti [23], W-Cu [24,25,26] and multi-component metal alloys such as - Ti- Al-C [27], Ti-Ta-C [18], Ni-Ti-C [24], MoSi_{2}+Cu [26], Ti-Zr-C [27], ZrTi_{2}Ti_{3}NiO11Cu12.5Be22.5 [28], EP741NP [29], nichrome, Inconel [30,31], Mo-Si-B, Ti-Ni-Zr-Mo-Al-C [32]. A significant advantage of metal alloys is that they show the ability, through appropriate selection of the pulse parameters of the ESD process, to form coatings with an increased content of amorphous and nanostructured phases [7,10,18-20,28,29,33], which has a favorable effect on their wear resistance. Layers obtained by RESP in argon, helium, and vacuum always have fewer defects than similar processing in air.

- Pure metal electrodes – one or more pure metals are used to create coatings for different purposes. The successive application of different metals allows obtaining multi-layer and multi-component coatings with synthesized intermetallic phases, with increased thickness and strength of the connection with the base [8-12,21,25,26,29-31,34]. Most of the authors report increased hardness of metal coatings up to 3-4 times higher than that of titanium substrates. By combining metal with a subsequent coating of graphite, many of the above authors have synthesized various metal carbides such as TiC, WC, TaC, Cr_{2}C_{3}, ZrC. Processing in an air environment allows the synthesis of oxides and nitrides, and with RESP in a nitrogen environment, metal nitrides and carbonitrides with a hardness up to 5-6 times higher than that of the substrate are obtained. The most commonly used metals are Al, Ni, Cr, Co, Mo, W, Zr, Ti, Ta, V, Cu [7-10,18,21,33], graphite [7-10,18,24,25,34], in which new phases such as TiAl, TiAlN, TiNi, Al_{2}O_{3}, TiO_{2}, TaO, TiC, TiN, WC, TiCN can be synthesized by selecting suitable process parameters in the composition of the coatings. It has been established that when using pure metal and alloy electrodes and a protective atmosphere, the thickness of the coatings is higher than that obtained with carbide, boride and nitride electrodes. In this case, the thickness of the layers reaches up to 0.01–0.15 mm, and from plastic and lower-melting materials, the covering layer can reach up to 0.5 mm.

- Hard alloy electrodes – high hardness compounds are used (classical hard alloys mainly based on carbides, borides and nitrides of W, Ti, Cr, Zr with brazing metals and alloys (Ni-Cr-B-Si, Ni-Cr-Mo, Ni-Mo, Ni-Cu, TiAl), including nanostructured ones [7-10,15-18,27,35-42,45]. Ceramics provide additional hardness to coatings, while brazing metals and alloys provide toughness, strong bond to the substrate, resistance to corrosion and chemicals. The coatings applied with hard alloy materials show higher hardness than the coatings applied with metals and alloys, but their thickness is lower. Surface defects are more, their coefficient of friction is higher. In order to reduce the brittleness of the refractory compound and to increase the performance of electrospark processing, many authors recommend increasing the metallic binder, since in this case the wear-resistant particle is surrounded by a low-melting component that provides good adhesion to the titanium surface.

- Carbide Compositions with "nano" components and additives based on WC, TiC, TiB_{2}, Cr_{2}C_{3} with a soldering mass of TiAl, Ni, Cr, Mo and with additives of nano-sized powders of ZrO_{2}, NbC, etc. obtained by self-propagating high-temperature synthesis (SHS) [27, 37,40,42] have been used to increase the wear and heat resistance of electrospark coatings. Nanomodified SHS-electrode materials ensured the creation of new strengthening multifunctional protective layers on the treated surfaces with nanocrystalline and amorphous phases, with higher physical, mechanical and tribotechnical properties.

- Multicomponent hard alloy materials from micro powders based on WC+TiB_{2}+B_{4}C with a soldering mass of NiCrCoB,Si,Fe,C with different ratios between the individual components and designations NW and KW respectively [15-17,38,44,45]. When using the multicomponent electrodes, both new intermetallic...
compounds and within a certain range of pulse discharge parameters were obtained, as well as more than 10 new wear-resistant phases, including ternary ones of the AlSi$_{3}$Ti$_{2}$ type. By changing the processing parameters and the composition of the electrodes, the synthesis process can be controlled. The use of a shielding atmosphere of Ar [7-11,13,14,18,19,27,33,36] helps to reduce the amount of oxides, reduce defects and increase the layer thickness. When N shielding gas is used [25,31,41], in addition to the improvements mentioned above, additional nitrides and carbonitrides are obtained, which help to increase both the wear resistance and the chemical resistance of the coated surface. The use of multi-component hard alloy electrodes makes it possible to synthesize ternary compounds and MAX-phases of the type Ti$_2$AlC, Ti$_3$AlC$_2$, Cr$_3$AlC and Ti$_3$SiC$_2$, TiAlC, TiAlN, TiSiC, which exhibit a unique combination of properties that are characteristic of both metals and and for ceramics [18,37,43]. Through RESD, the authors [44,45] obtained the ternary compound (Ti$_4$N$_3$B$_2$)$_{0.8}$, which belongs to the dispersion hardened composite materials (DHCM) with high hardness and shows higher wear resistance than titanium nitrides and borides.

**Characteristic features at RESD coatings on titanium surfaces**

RESP processing on titanium surfaces produces a new type of uniform coatings formed primarily by a liquid phase with an amorphous-crystalline structure and new phases formed. The coatings have reduced roughness, reduced defects to a minimum, increased density and uniformity, increased microhardness and wear resistance. The REST layer is not simply an accumulation of electrode material on the substrate, but a product generated by fusion reactions between the electrode and the substrate in the microdischarge zone. Coatings consist of various compounds, each with their own unique properties that directly affect their microstructure and properties, thereby improving the life and performance of titanium products.

Table 1 shows the composition and designations of some electrodes used in the authors’ previous studies [15-17,38,44,45].

<table>
<thead>
<tr>
<th>Type of electrode</th>
<th>Chemical composition</th>
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<tbody>
<tr>
<td>NWWTi10T10B10</td>
<td>50%WC+10%TiB$_2$+10%B$_4$C+(Ni-Cr-B-Si-C)-bal.</td>
</tr>
<tr>
<td>KWWTi10B10</td>
<td>55%WC+20%TiB$_2$+10%B$_4$C+(Ni-Cr-B-Si-C)-bal.</td>
</tr>
<tr>
<td>TiN</td>
<td>TiN+(Ni+Cr+1.2%Cu-B-Al$_2$O$_3$-C)</td>
</tr>
<tr>
<td>KNT16</td>
<td>TiCN+19.5%Ni+6.5%Mo</td>
</tr>
<tr>
<td>TiB$<em>2$-TiAl$</em>{nano}$</td>
<td>93%(74%Ti+12%TiB$<em>2$+14%Al) + 7%$</em>{max}$(NbC+ZrO$_2$)</td>
</tr>
<tr>
<td>AlSi9</td>
<td>9%Si+Al</td>
</tr>
<tr>
<td>AlSi12</td>
<td>12%Si+Al</td>
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Fig. 2, 3, 4 show images of the general appearance and surface, respectively, of invar - after rough mechanical processing, of Ti-GR2 after laser 3D printing and of Ti-GR5 after volumetric electroerosion processing (EDM), as well as RESP surfaces obtained with different electrodes.

![Invar coating](image1.jpg)  
*a) Invar, Ra initial = 6.66 µm, b) AlSi12, E=0.07J, Coating Ra = 4.32 µm*

**Fig. 2. General appearance of Invar surface before and after coating with AlSi12 electrode [38]**

![RESP coating](image2.jpg)  
*a) Ti-GR2 – after EDM, Ra=4.3 µm, b) Ti-GR2 – after RESD with TiB$_2$-TiAl$_{nano}$ at E=0.03 J, Ra=3.6 µm, c) AlSi12/Ti-GR2 – after after RESD at E=0.03 J, Ra=2.5 µm*

**Fig. 3. General appearance of the SEM topography of coatings applied by vibration ESD on Ti6Al4V and invar alloys at different magnification [44]**

![ALSi12/Ti-GR2](image3.jpg)  
*a) AlSi12/Ti-GR2 at E=0.03 J, Ra=2.5 µm*

**Fig. 4. SEM microphotographies of coatings from AlSi12 applied by ESD on GR2 substrate [17]**
It is clearly seen that the surfaces treated with RESP are significantly smoother and uniform. The coatings erase traces of the previous treatment of the substrate, reducing the initial roughness. SEM images of the microstructures obtained on the deposited surfaces show the formation of a melt coating.

Fig. 6 shows the variation of the roughness of the coatings as a function of the pulse energy. As can be seen, RESP has achieved a significant reduction of the surface roughness of the substrates and erasing the traces of the previous treatments. The minimum achieved roughness after RESP is $R_a \approx 2.5 \mu m$ at pulse energy $E = 0.02 J$ and initial roughness of the substrate $R_a \approx 4 - 6 \mu m$. When using AlSi electrodes, the roughness of the surfaces obtained by 3D printing is reduced to 3-4 times – Fig. 6.

The roughness and thickness of the coatings from the used electrodes (Table 1) can be changed within $Ra = 2.5 - 4.3 \mu m$, $\delta = 6 - 30 \mu m$ by changing the parameters and energy of the pulses. The microhardness of the resulting coatings is in the range of 7.5-13 GPa. Similar results were obtained by other authors. In the work [13], during RESP on 3D titanium surfaces with a roughness $R_a \approx 15 \mu m$, a minimum roughness of $R_a \approx 2 \mu m$ was achieved. Fig. 7 [13, 17] shows microsections of RESP coatings from AlSi12 electrode. The dense coatings, interface and melt-filled micropores are clearly visible. The interaction of the reactive melt and the substrate resulted in the formation of a transition interface layer and a surface functional layer.

Due to the spreading ability (flowability) characteristic of eutectics, REST with low-melting electrodes improves the quality of the surface, reduces its roughness, allows the filling of surface cavities, and pores to a depth of 30-40 $\mu m$.

The effects of capacitance, pulse duration, and deposition time on layer thickness were also investigated, and the results showed that at relatively low capacitance and short pulses of about 20 $\mu s$, a crack-free layer of about 20-30 $\mu m$ thickness could be obtained. Most studies reported microhardness of coatings of various electrode materials in the range of 7–12 GPa. However, some authors [7,18,24,25] reported individual measured values of 16–40 GPa.

Fig. 8 shows a diffractogram of NW electrode coatings. The composition of the coatings differs significantly from the composition of the starting electrode materials. During ESD, chemical exothermic reactions occur between the components of the electrode material, the interelectrode gap, and the substrate with the formation of numerous new high-hardness phases and intermetallics that improve the properties of the substrate.

The short duration of the pulse in the RESP process causes faster supercooling and solidification of the mixed melt formed, which leads to the formation of larger amounts of amorphous-nanocrystalline structures, reduced roughness and increased density and uniformity. The amount of the amorphous phase varies between 9...15%. The analysis of the literature shows that the variation with the modes and processing electrodes allows to realize a synthesis with a predominant content of different new phases in the surface layer, required for different applications. The presence of newly
registered phases implies a higher microhardness, a stronger connection with the base and, accordingly, a higher wear resistance.

**Durability of RESP coatings**

Almost all authors report a significant increase in wear resistance after RESP, some of them reporting 5 or more times higher wear resistance [18, 24, 25]. Most of the authors also reported an increased corrosion resistance of the coated surfaces [7-10, 18, 22, 24, 26, 26, 34, 39, 46]. Some coatings are reported to reduce the coefficient of friction from 0.5-0.6 to 0.26. Based on the literature sources, it is found that coatings applied with pulses of low energy - up to 0.5 J and a duration of 5-100 µs are more suitable. Electrospark coatings on titanium obtained in these modes show a 2-5 times increase in microhardness and a 1.6-4.5 times reduction in wear at friction. Fig.9 [45] shows the wear resistance of coatings obtained by the authors.

**Fig. 9. Effect of pulse energy on wear resistance of RESP coatings on titanium Ti-GR5 [45]**

The literature data as well as the above results testify to the prospects of RESD coatings and the possibility of their application for strengthening titanium surfaces. The purposeful use of different electrodes and regimes in RESP allows different processes to be implemented in the surface layer depending on the operational conditions and the purpose of the product and to change the strength, corrosion and tribotechnical properties of the materials within wide limits.

**3. Conclusions**

Compared to classical ESD with hard alloy electrodes, RESP provides a new type of uniform coatings formed mainly by a liquid phase with an amorphous-crystalline structure and new phases formed, with improved adhesion to the titanium substrate. The coatings have reduced roughness and defects, increased microhardness, wear resistance and anti-corrosion characteristics. With increased strength of the bond with the substrate.

RESP provides ample opportunities through an appropriate choice of the modes and processing electrodes to realize a synthesis with a predominant content of various new wear-resistant phases in the surface layer (including triple MAX phases), the obtaining of which by the known existing technologies is difficult, unprofitable, or impossible. In this way, titanium surfaces can be given different properties required for different applications. The shorter duration of the pulses used in the RESP process causes faster supercooling and solidification of the mixed melt formed, resulting in the formation of larger amounts of amorphous and nanocrystalline structures and increased density and uniformity.

The simplicity of RESP and ESD, with a properly selected set of process parameters and a the wide selection of suitable precursor metals and alloys, has a significant potential and gives an excellent opportunity to significantly improve the mechanical and tribological characteristics of titanium surfaces.

RESP gives opportunities to reduce the time and costs of finishing operations after 3D printing, or after rough and semi-fine mechanical, or EDM processing by replacing them with an easy, simple, cheap and economical process - ESD. Through RESP, a triple effect is obtained - filling the irregularities, cavities, micropores and pits of the substrate, reducing the roughness and increasing the microhardness and wear resistance of the titanium surfaces.

There is a wide scope for further development and improvement of RESP technologies. The variety of possible practical cases requires the study of the changes in the roughness and properties of the coatings depending on the parameters of the ESD regimes. In these cases, conducting preliminary experiments allows not only to study the influence of process parameters on roughness, but also to influence the object of study, to actively participate in the study, and to manage and optimize the process.

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