

POSSIBILITIES FOR IMPROVING SURFACE DEFECTS OF 3D PRINTED TITANIUM PRODUCTS THROUGH REACTIVE ELECTRO-SPARK PROCESSING

A. Nikolov², G. Kostadinov^{1*}, T. Penyashki¹

¹ISSAPP “N.Pushkarov”, Agricultural Academy, Sofia, Bulgaria

²Technical University of Sofia, Bulgaria

Abstract

There are two main reasons why researchers are looking for solutions to improve the surface characteristics of products produced by 3D printing (most often by SLM, DMLS technologies): low hardness and the low tribological characteristics of titanium alloys, which limit their application in friction assemblies in many industrial branches; high roughness and defects such as irregularities, micropores, and cracks on the surface of 3D titanium products, which require complex labor-intensive and energy-intensive finishing operations.

In the present work, an analysis of literary sources was carried out on ways to improve the surface characteristics and properties of titanium surfaces produced by selective laser melting (SLM). The technological characteristics of the electrospark deposition method as the lightest, most accessible and inexpensive way to improve the surface qualities of 3D products are indicated. The authors' results are presented, where reactive electrospark treatment based on the ESD method has been used based on the ESD method. A simultaneous multidirectional effect is achieved, which is expressed in: up to a fivefold reduction in the roughness of 3D titanium surfaces; filling of the surface pores, cavities and voids; a double increase of microhardness of the modified surfaces; ecological replacement of finishing treatments and economy of labor, equipment, consumables, and energy.

Appropriate process and electrical parameters and materials are indicated to realize the above effects.

Keywords: 3D printing, selective laser melting (SLM), Direct metal laser sintering DMLS, electrospark deposition (ESD), titanium alloys, roughness, microhardness

1. INTRODUCTION

The combination of high strength and corrosion resistance and low relative weight (Gorynin, Chechulin 1990) of titanium and its alloys make them desirable materials for many industrial applications. However, the wide application of these attractive materials is severely limited by their low surface hardness, low wear resistance, and poor machinability (Dong 2010).

The additive technologies - ATM or 3D printing of metals provide wide opportunities to replace casting processes and mechanical processing, avoid the problems of poor machinability of the titanium and to produce increasingly complex parts, assemblies and assembled units with high accuracy (Freedman 2012, Laplume, Petersen & Pearce 2016). A major advantage of additive processes is the possibility of direct production of assemblies and parts and replacing the need for machines and tooling, expensive and time-consuming technological processes with a single process and on a single machine. While with traditional technologies, losses of expensive titanium materials can reach 90% of the initial blank, with 3D printing the finished product is formed without unnecessary production waste, resulting in significant savings in materials, labor and energy.

However, the wide spread of 3D printing of titanium products is also limited due to the high surface roughness and the presence of surface irregularities, pores, protrusions, cracks and traces of the layer-by-layer construction of the products, which significantly worsens their manufacturability and operational characteristics (Freedman 2012, Laplume, Petersen & Pearce 2016).

The surface of the samples produced by the most common forms of 3D printing, Selective Laser Melting (SLM) and Direct Metal Laser Sintering (DMLS), most often have values of the Ra parameter between 12 and 30 μm for SLM and 8-15 μm for DMLS technology - Fig.1.

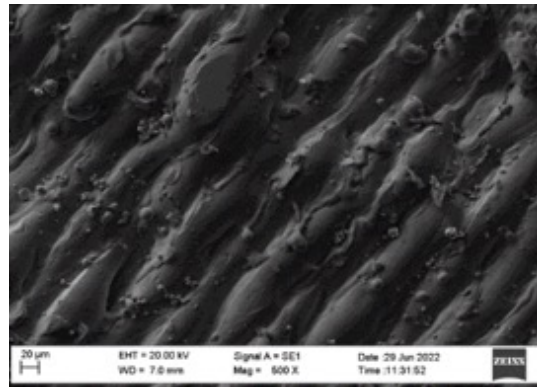


Fig. 1. Scanning electron microscope (SEM) image of a 3D printed titanium alloy surface.

The presence of asperities, pores and unfused fused spherical powder particles creates the need for additional full or local processing, without which many surfaces would be unusable or would have a much shorter life as a result of their higher wear.

To improve the surface characteristics of the current stage, various methods and additional treatments are applied, such as: selection of appropriate manufacturing modes (Shipley et al. 2018); repeated passage of a laser beam (Yasa, & Kruth 2011); sandblasting and blasting; mechanical processing by (chipping, grinding, polishing, isostatic hot pressing, etc.); electrochemical, electroerosion and thermal treatments; creating a new layer on the 3D surface, etc. (Garbacz et al. 2012, Labudovic et al. 1997, Penyashki et al. 2021). Most of these methods require the application of specific processes and associated machinery, technology, fixtures, tools and consumables, resulting in increased processing time and costs. Often, post-processing can take up to 3 times longer than the 3D printing itself (Freedman 2012). The use of coatings to improve surface characteristics and wear resistance (Penyashki et al. 2021, Labudovic, D. Blečić, Z. Blečić 1997, Yankov, Nikolova et al. 2018, Mullin, Verkhoturov & Vlasenko 2006) shows that there are still unsolved problems and consequences due to various limitations such as high cost and complexity of processes, complex and expensive equipment, environmental pollution, unfavorable structural changes and thermal deformations of the substrate, incompatibility of mechanical properties, poor interface connection, etc., which are unfavorable for their application. These problems have not yet found their solution, and there is still no sufficiently effective way to reduce surface roughness and porosity, which has limited the application of additive technologies.

Most of the limitations and problems mentioned above can be overcome by a simple, economical, ecological, easy, affordable and waste-free technology - electrospark deposition – ESD (Mullin, Verkhoturov & Vlasenko 2006, Zhang Zhengchuan et al. 2021, Mikhailov et al. 2013, Penyashki, Kamburov, Kostadinov et al. 2022). ESD implies opportunities both for the reduction of roughness and defects in the surface layer of ATM products, and for higher wear resistance of the treated surfaces compared to that achieved by other finishing processes (Kostadinov et al. 2021, Penyashki et al. 2022, Kostadinov et al. 2022).

The method has a number of advantages (Penyashki et al. 2022, Kostadinov et al. 2022, Mukanov, Kudryashov & Petrzhik 2021, Mukanov, Petrzhik et al. 2019), the main of which are: universal, maximally simple and accessible technology and ease of deposition under normal atmospheric conditions, strong metallurgical connection of the coating with the titanium substrate; low thermal impact and absence of heating and deformation of the layered product, possibility of local processing of any surface, even of the most complex shape, simple, cheap and portable equipment, high efficiency with low material and energy costs. ESD coating changes the treated surface both in terms of geometry

and topography, as well as in terms of its composition, structure and properties, which are controlled by changing the electrical and physical parameters of the regime and the composition of the electrode materials. This allows obtaining fundamentally new materials and structures, including nanostructural effects, which cannot be obtained under conventional metallurgical conditions.

The technological characteristics and advantages of this process indicate that ESD may be the easiest possible way to improve the surface properties of ATM (SLM and DMLS) titanium alloys. The traditional task of ESD is to strengthen the surface layers of metallic materials by transferring high-hardness phases contained in the deposition electrode. With such mass transfer, the formed coatings usually have an increased roughness. The reduction of the roughness can be realized by reactive electrospark processing (RESP) (Kostadinov, Penyashki et al. 2021, Kostadinov et al. 2022, Mukanov, Kudryashov & Petrzhihik 2021, Mukanov, Petrzhihik et al. 2019). The main idea of RESP [18-20] is the formation of a liquid reaction phase, in which the components of the electrode and the substrate are actively mixed and spread evenly over the layered surface, ending with the synthesis of new phases and structures and rapid solidification of the reactive melt.

In this regard, the aim of the work is, on the basis of previous and current results of the authors, to carry out a systematic analysis of the conditions for smoothing surface irregularities, filling the voids and parallel local synthesis of new phases and structures with increased hardness through RESP with appropriate energy and science-based selection of deposition electrodes.

2. MATERIALS AND METHODS

2.1. ESD equipment

The formation of the liquid reactive phase is carried out by creating conditions for rapid local melting of the precursor electrode and the cathode spot. This is possible due to the strong chemical interaction of low-melting (almost eutectic) electrodes with the substrate components. The schematic diagram of this process is shown in Fig. 2.

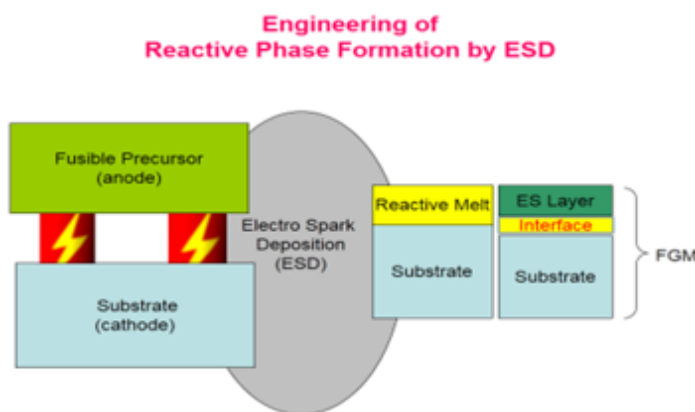


Fig. 2. Scheme of the formation of reactive phase

Two ESD schemes were used – semi- automated non-contact local electrospark deposition with a rotating electrode (LESD) and manual deposition with a vibrating electrode (ESD). The apparatus by which the coatings were applied are shown in Fig. 3. In order to obtain a lower roughness of the deposited coatings, modes with low pulse energy $E=0.01-0.05$ J and low pulse duration $T_i=5-20\mu s$ are used at LESD, and at ESD with a vibrating electrode - pulse energy $0.01-0.07$ J and pulse duration $T_i \approx 100 \mu s$. In addition to the lower roughness of the coatings with these modes, conditions are created for smaller sizes of the cathode spot and of the erosion craters on the surface of the substrate and,

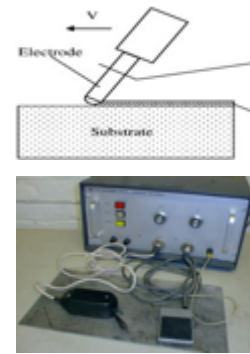
accordingly, an extremely high cooling rate of the mixed melt and obtaining coatings with an increased amount of amorphous phases.

2.2. Substrate

Model plates of titanium alloys Ti6Al4V (GR5) and technical titanium GR2 (AISI UNS R R56200 and R50400) with square and rectangular shapes with different initial roughness were used. The plates were obtained directly by SLM and DMLS and by electrodischarge cutting (EDM).



a) Machine Elfa 541 for contactless LED



b) Device for manual discharge deposition with vibrating electrode

Fig. 3. Used equipment for RESP

2.3. Electrode materials

Layering electrodes of low-melting Al-Si alloys with 9 and 12%-Si were used, from which compact samples with fine metal-glass structures were made using a specially developed technology by high-speed cooling of the melt (Mukanov, Kudryashov & Petrzhik 2021, Mukanov, Petrzhik et al 2019). The use of aluminum and Al-Si electrodes is recommended to increase the corrosion resistance, wear resistance and heat resistance of aluminum, copper, steel and titanium alloys (Mihailov et al 2023, Cadney et al 2009).

Additionally, hard alloy electrodes TiB₂-TiAl with nano-additives of ZrO and NbC obtained by high-temperature self-propagating synthesis (Levashov et al. 2006) were also used, as well as based on WC-TiB₂-B₄C with a low-melting near-eutectic brazing multi-metallic mass of (Co-Ni-Cr-B-Si-Fe-C) and designation KW10B10T10 (KW), and with multi-metallic solder mass (Ni-Cr-B-Si-Fe-C) and designation NWW10B10T10 (NW) developed by powder metallurgy methods (Kostadinov et al. 2022, Penyashki et al. 2022). The low melting point of NiCrBSi alloys, as well as the fluxing effect of Si and B, allow these materials to be lightly melted by RESP, reacting with the substrate elements and the environment to form a "spilled" melt and new phases. The many components allow the emergence of new advantages due to the synthesis of new phases in the process of coating formation. Table 1 shows the composition and designations of the used electrodes.

Type of electrode	Chemical composition
TiB ₂ -TiAl	74%Ti + 12%C + 14%Al [14,19,20]
NWW10T10B10 (NW)	50%WC + 10%TiB ₂ + 10%B ₄ C + (Ni-Cr-B-Si-C)
KW10T10B10 (KW)	50%WC + 10%TiB ₂ + 10%B ₄ C + (Co-Cr-Ni-B-Si-C)
AlSi9 and AlSi12	9 and 12%Si + Al

Table 1. Composition of used for ESD hardalloyed electrodes

2.4. Types of research

The effect of RESP at low pulse energy (0.01 - 0.07J) on the roughness, thickness, composition, structure, mechanism and wear characteristics of modified 3D (SLM and DMLS) titanium surfaces was investigated by profilometric and metallographic analyses, optical microscopy, electron microscopy (SEM, EDS and TEM), X-ray diffraction (XRD), and "scratch" test. A comparative analysis of the obtained coatings was carried out, identifying the differences in the degree of filling of the recesses and pores, the morphology, the structural-phase composition, the properties of the modified 3D surfaces with the investigated electrodes at different regimes for RESP.

3. RESULTS AND DISCUSSION

3.1. Topography and morphology of modified titanium surfaces

Analysis of literature data (Mukanov, Kudryashov & Petrzhik 2021, Mukanov, Petrzhik et al. 2019, Mihailov et al. 2023) and experimental data obtained by the authors (Kostadinov et al. 2021, Penyashki, Kamburov, Kostadinov et al. 2022, Kostadinov et al. 2022, Penyashki, Kostadinov, Dimitrova et al. 2022, Penyashki, Kostadinov, Kalitchin & Kandeveva 2022) show that by means of RESP at low pulse energy on titanium 3D surfaces it is possible to obtain coatings with reduced roughness and reduction of the initial erosion of titanium substrates. Table 2 shows the range of changes in the roughness, thickness and microhardness of the coatings applied by non-contact and vibration electrospark deposition on Ti6Al4V titanium alloy.

Electrode	Contactless LESD (E= 0.01÷0.04 J)			Vibrationally ESD (E=0.02÷0.07 J)		
	Ra, μm	δ , μm	HV, GPa	Ra, μm	δ , μm	HV, GPa
AlSi12	1.3 -3.2	4.5– 14	7-10	1.8-3.5	6-18	7-10
NW10B10T10	1.6-3.5	5.5-18	8-13	2.5-4.2	8-35	8-13,4
KW10B10T10	1.5-3.5	4.5-16	8-14	2.5-4.5	8-30	8-14,2
Substrate Ti6Al4V	4-5	-	3,7	-	-	-

Table 2. Range of variation of roughness, thickness and microhardness of coatings applied by LESD and ESD on titanium alloy Ti6Al4V obtained by EDM

Table 3 shows the roughness parameters Ra, Rz, Rq, Rt the thickness of the modified layer δ and the microhardness HV at RESP of 3D Ti-GR2 surfaces received with different pulse energy and AlSi12 electrode.

Substrate	Process parameters	Ra, μm	Rz, μm	Rq, μm	Rt, μm	δ , μm	HV, GPa
Ti, GR2	Substrate-After SLM	10.4	29.4	12.6	29.7	-	3.43
Ti, GR2	ESD- E=0.03J	4,27	12.1	4.23	12.9	10	7.88
Ti, GR2	ESD-E=0.07J	4.92	14.18	4.85	14.85	16	8.84
Ti, GR2	LESD-C=0.7 μF , Ti=12 μs , I=16A, E=0.02J	2.49	6.47	2.3	6.54	7	7.66
Ti, GR2	LESD-C=1 μF , Ti=12 μs , I=19A, E=0.03J	3.12	8.54	3.22	8.62	10	8.54

Ti, GR2	LESD-C=4.4μF, Ti=20μs, I=24A, E=0.04J	3.47	10.1	3.6	10.2	14	8.43
----------------	--	------	------	-----	------	----	------

Table 3. Surface characteristics of coatings on SLM substrates after ESD with AlSi12 electrode

Table 4 shows the parameters of roughness Ra, Rz, Rq, Rt, the thickness of the modified layer δ and the microhardness HV at RESP of 3D surfaces of Ti-GR5 after LESD with different pulse energy and electrodes NW, KW and AlSi9. Figures 4-8 show images of various 3D surfaces before and after RESP, from which the improvement after RESP can be observed. Fig. 9 graphically shows the variation of the roughness parameters of RESP modified by ESD and LESD surfaces as a function of the pulse energy and the material of the processing electrodes. Fig. 10 shows microsections of RESP surfaces processed by LESD with an AlSi12 electrode at different pulse energies.

№	Type of the electrode	Ra, μm	Rz, μm	Rq, μm	Rt, μm	δ , μm	HV, GPa
0	substrate Ti6Al4V	8.92	23.38	8.83	24.6	-	3.75
1	NW, E=0.02 J	3.47	9.8	3.29	10.48	10.75	9.85
2	NW, E=0.04 J	4.81	13.59	4.91	14.22	18.53	13.34
5	KW, E=0.02 J	3.4	9.55	3.36	10.74	9.67	11.87
6	KW, E=0.04 J	4.33	13.12	4.49	16.63	14.66	13.22
7	AlSi9, E=0.02J	2.29	6.47	2.3	6.54	6.7	8.03
7	AlSi9, E=0.03 J	2.46	6.9	2.48	6.97	8.6	7.86
8	AlSi9, E=0.04 J	3.38	11.17	4.02	11.38	9.55	9.43

Table 4. Roughness, thickness δ and microhardness HV of coatings on SLM Ti6Al4V substrates after LESD [18]

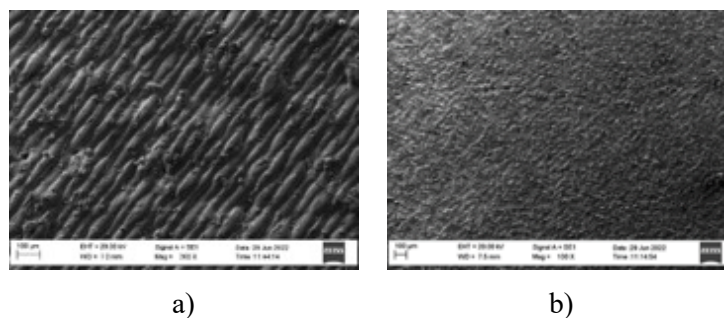


Fig. 4. SEM images of the initial surface of Ti6Al4V substrates produced by DMLS processes

a) $Ra \approx 10 \mu m$; b) RESP by ESD with KW electrode, $E=0.03J$, $Ra \approx 4 \mu m$.

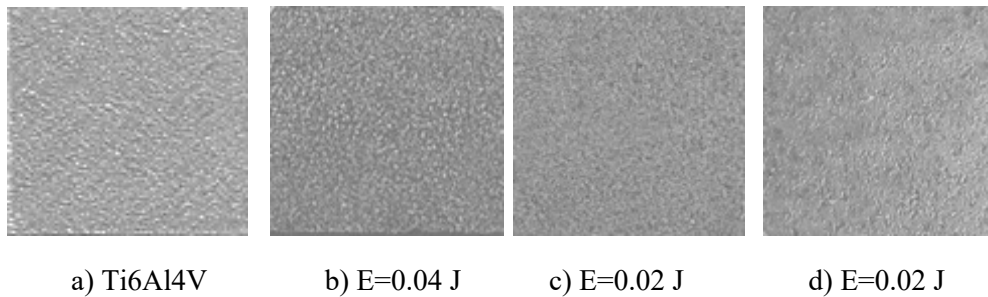


Fig. 5. View of model plates from Ti6Al4V before and after RESP by LESD: a) substrate, R_a initial $\approx 8 \mu\text{m}$; b) LESD with NW electrode, coating $R_a \approx 4.8 \mu\text{m}$; c) with NW - $R_a \approx 3 \mu\text{m}$; d) with AlSi9 - $R_a \approx 2.5 \mu\text{m}$ [23]

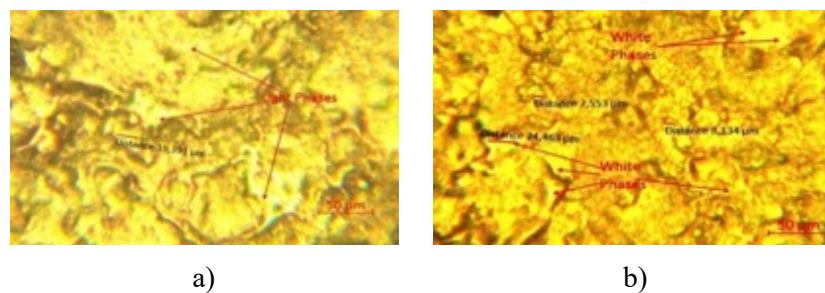


Fig. 6. Optical images of RESP surfaces with AlSi12-(a) and NW-b) electrodes on Ti6Al4V alloy produced by DMLS process.

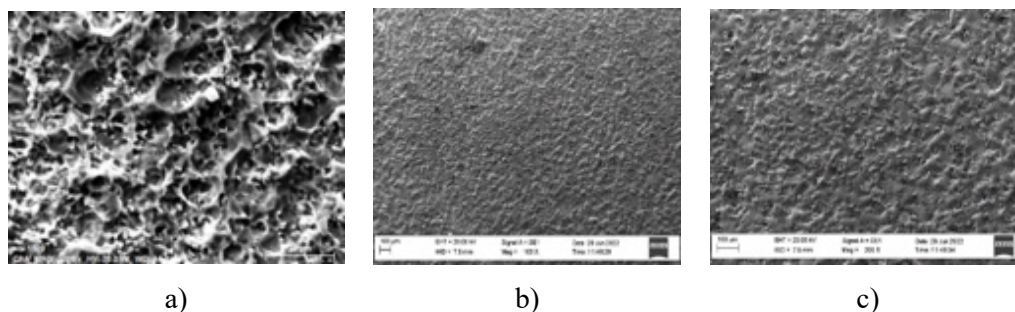


Fig. 7. SEM images; a) Ti-GR2 – after EDM- $R_a = 4.8 \mu\text{m}$; b) RESP (ESD) with electrode AlSi12, $E = 0.03 \text{ J}$ – $R_a = 2.5 \mu\text{m}$, $R_z = 14.12$, $R_q = 3.17$, $R_t = 19.74 \mu\text{m}$; (c) RESP (ESD) with electrode NWW10B10T10, $E = 0.05 \text{ J}$ - $R_a \approx 3.5 \mu\text{m}$;

Studies of the roughness parameters and topography of the coatings applied on substrates obtained directly from SLM and DMLS with roughness $R_a \approx 9 \div 15 \mu\text{m}$ and from EDM with $R_a \approx 4 \div 5 \mu\text{m}$ showed that after RESP with LESD and ESD, the roughness can be reduced to values respectively $R_a = 2.5 \div 6 \mu\text{m}$ and $R_a = 2 \div 3.5 \mu\text{m}$.

It can be seen that the surface of the coatings is formed mainly by melt. The liquid phase is present in the form of splashes and smoothed areas of the surface, formed as a result of the coalescence of individual drops. The presence of microscopic irregularities at various locations on the surface of the coatings was observed through SEM analyses. The zones with a glass-like amorphous structure are clearly visible Fig. 6 and Fig. 7b and 8b. It is established (Fig. 9 and 10 and Tables 2-4) that with an increase in the pulse energy, the roughness parameters and the thickness of the modified layers also increase.

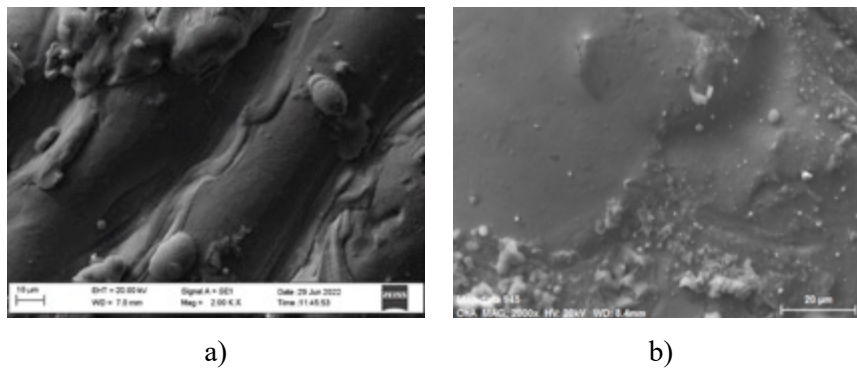


Fig. 8. SEM topography of a SLM titanium (Ti6Al4V) surface (a), and b) after RESP by ESD with electrode TiB₂-TiAl at E=0.04 J

Lowest values of roughness parameters and most complete erasure of traces and defects from SLM processing show surfaces modified with AlSi electrodes at pulse energy E=0.02-0.04J. Moreover, the surfaces treated with the AlSi9 electrode have similar roughness and thickness to those treated with the AlSi12 electrode.

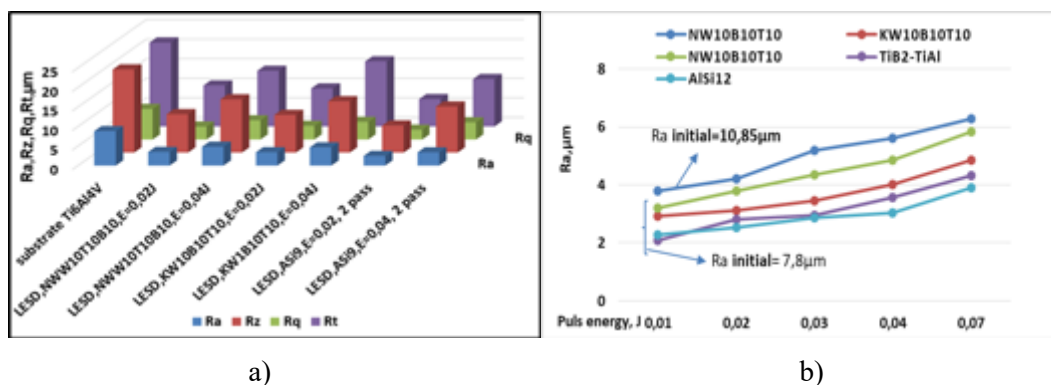


Fig. 9. Roughness parameters Ra, Rz, Rq, Rt of LESD coatings on DLMS Ti6Al4V

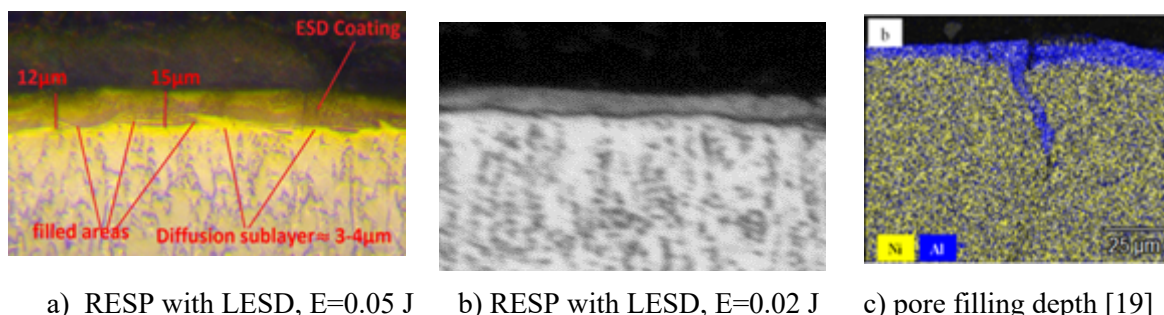


Fig. 10. Cross-sections and removed surface defects of AlSi12 coatings on DMLS Ti6Al4V alloy

The summary of observations of optical and electron microscopy and data from measurements of roughness parameters shows that for surfaces prepared by 3D (SLM and DMLS) with initial roughness $Ra > 7-8 \mu m$, RESP with the investigated electrodes allows smoothing and erasing surface irregularities and traces of previous processing, filling pores and voids and obtaining modified surfaces with improved uniformity and lower roughness. A 2-5 times reduction of the initial roughness and filling of the initial

cracks and micropores to a depth of 35–40 μm was achieved. The obtained results show that the coatings in most cases do not need additional processing.

The thickness and roughness of the modified surfaces can be controlled by the pulse energy and mode parameters for RESP in the range $\delta=5\text{--}35\text{ }\mu\text{m}$, $R_a=1.5\div 6\text{ }\mu\text{m}$ and microhardness $HV=7\div 14\text{ GPa}$, respectively. The data in Tables 2–4 show that the microhardness of ESD and LESD surfaces exceeds 2 to 4 times the hardness of the underlying titanium substrates. The lowest microhardness values are observed when using AlSi electrodes (7–10 GPa). The microhardness of the surfaces deposited with the TiB₂–TiAl electrodes, NW and KW for the different processing modes varies between 9 – 14.5 GPa. The microhardness distribution for all coatings visualizes significant deviations, different from the relatively uniform distribution of the base titanium alloys Ti6Al4V and Ti-GR2.

The highest degree of smoothing and erasure of surface defects, filling of pores and cavities and surfaces with the lowest roughness compared to that of the other electrodes used is reported for RESP with LESD at pulse energy 0.02–0.03 J with AlSi12 electrodes (Kostadinov et al. 2021, Mukanov, Kudryashov & Petrzhik 2021, Penyashki, Kamburov, Kostadinov et al. 2022, Kostadinov et al. 2022, Penyashki, Kostadinov, Dimitrova et al. 2022, Penyashki, Kostadinov, Kalitchin & Kandeveva 2022). At the roughness of the starting surfaces higher than $R_a>12\mu\text{m}$, however, the lower pulse energy ($E<0.03\text{ J}$) is not always sufficient for the melt from the electrode to fill the irregularities, pores and voids of the initial 3D surface and the deep traces of the previous treatment cannot be completely erased. To achieve complete erasure, it is necessary to use higher energy modes ($E>0.03\text{ J}$), but in these cases the roughness of the coatings will also be higher and the roughness of the SLM processing will be reduced to a lesser extent (up to 2–3 times lower than the initial one). It was found that, for the studied electrodes, the limit value of the energy at which uniform coatings with predominant transfer from the liquid phase are obtained is up to 0.04 J.

A comparison of the surface of the coatings obtained by the two methods shows that, in the non-contact LESD method, the coatings have smaller structural components, without visible cracks and pores, while in the vibrational ESD, individual protruding areas are observed.

Summarizing the results of the current and previous research it is possible to establish that RESP improves the quality and not only significantly (up to 4–5 times) reduces the roughness, but also up to 3–4 times increases the microhardness of the processed 3D surfaces.

3.2. Phase formation, Composition and structure of modified surfaces

At RESP with NW and KW electrodes (Fig. 11a), newly formed wear-resistant compounds and intermetallics were registered such as: TiB, WB, Ti(C,N), WC 1-x, TiC1-x, TiN0.3, Cr₃B₄, CoB, Ni₃Ti, CrNiW, Ti₃Ni, Ti₂O, W₃B₄, Cr₃B₄, BN. It is obvious that under the action of spark plasma discharges, the components of the electrode material are partially decomposed, forming new compounds. As the pulse energy increases, both the amount of carbides and borides transferred from the electrode increases, as well as the number and amount of newly formed compounds. Broadened diffraction peaks are also observed, which reflect the formation of both solid solutions and new compounds, as well as the formation of amorphous phases. Since there are also individual peaks in the wider corner areas, which give an indication of the presence of crystallites, it can be concluded that the coatings have a crystalline-amorphous structure. At RESP with AlSi electrodes (Fig. 11b) formation of TiN, TiSi₃, Al₃Ti, Ti₅Si₃, Si₃N₄, Ti₂O are registered and monitored. The recorded traces of Al₂O₃, as well as the traces of AlN and SiN, show that during the transfer process aluminum and silicon react with oxygen and nitrogen from the air, forming highly wear-resistant compounds.

The presence of the constituent elements of the registered phases is confirmed by the energy-dispersive analysis of the coatings (Fig. 12). The average crystallite size, calculated by the Scherrer formula, varies from 12 to 80 nm for the different phases, which indicates that the obtained new phases in the electrosark coatings possess an amorphous-nanocrystalline structure. According to many scientists, ESD is the easiest process to obtain amorphous and nanostructured phases (Mihailov et al. 2023, Cadney et al. 2008, Levashov et al. 2006, Levashov, Kudryashov et al. 2007). In contrast to KW and NW electrodes, in RESP by LESD with AlSi electrodes, the degree of amorphousness is higher, and with increasing pulse energy, the degree of amorphousness increases.

Amorphous metal alloys based on Al possess excellent mechanical properties, high strength and good plasticity, which is also favorable for the mechanical properties of coatings (Mihailov et al. 2023, Cadney et al. 2008, Levashov et al. 2007). Therefore, the use of AlSi electrodes provides improved properties of the surface layer due to the reduced initial roughness, the fine structure, the obtained new compounds and amorphous phases in the composition of the coatings.

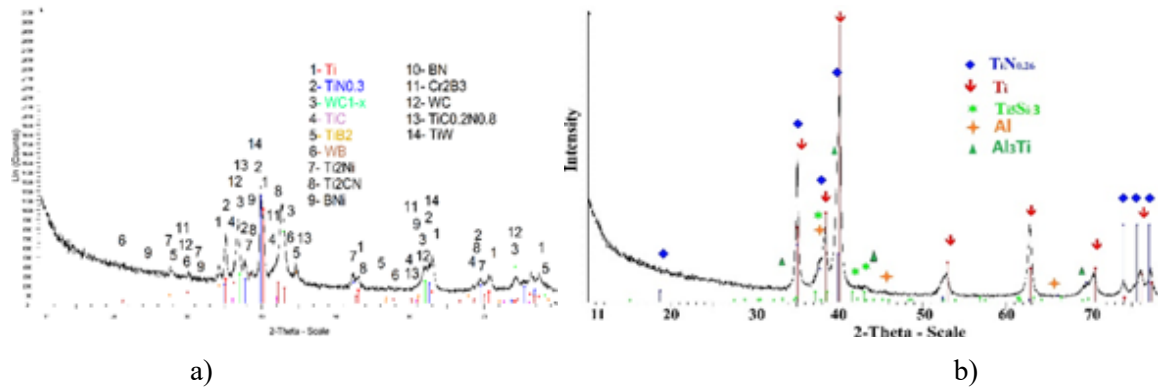
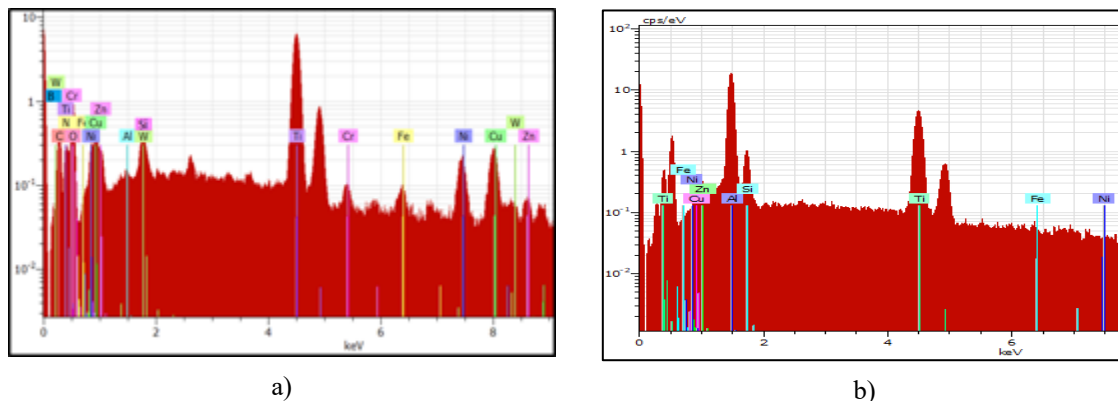


Fig. 11. XRD patterns of modified TiGR2 SLM surfaces with sintered new phases (Penyashki et al. 2022), a) RESP with LESD and NW electrodes, $E=0.045$ J b) RESP with LESD and AlSi12 electrodes, $E=0.045$ J.



Spectrum: MOI 779

El AN Series Net unn. C norm.

	[wt.%]	[wt.%]
Al 13 K-series	153289	50.89 56.28
Ti 22 K-series	61143	34.16 37.77
Si 14 K-series	7878	3.42 3.78
Fe 26 K-series	68	0.06 0.07
Ni 28 K-series	0	0.00 0.00

Fig. 12. EDS distribution of elements after RESP: a) with NW electrode, b) with AlSi12 electrode; c) distribution of elements of RESP with AlSi12 electrode.

XRD analyzes showed that in the RESP process, chemical exothermic reactions take place between the components of the electrode material and the base with the formation of various intermetallic and wear-resistant phases in the surface layer, the presence of which implies higher microhardness, and a stronger connection with the base. Varying the modes and processing electrodes allowed for the purposeful deliberate synthesis of various new phases in the surface layer such as WB, Ti (C,N), $Ti_{1-x}Ni_x$, Ti_3Ni , $CrNiW$, Ti_3Ni , $TiSi_3$, Al_3Ti , Si_3N_4 , Al_2O_3 , AlN , SiN .

4. CONCLUSIONS

Through RESP with the use of ESD and LESD with AlSi, NW, KW and TiB₂-TiAl processing electrodes and pulse energy up to 0.07J, a liquid melt is formed on the surface of titanium alloys with different initial roughness, which changes the relief and erases the traces of the previous treatments.

The use of this technology can be achieved to 2-5 times reduction in the roughness of SLM and DMLS titanium surfaces, elimination of surface defects, filling of the initial cracks and micropores at a depth of 35-40 μm and 2-4 times increase in the microhardness.

The resulting modified layers with a certain thickness and roughness can be changed by changing the energy of the pulse and the processing electrodes, respectively within the limits: $\delta=5-35 \mu m$, $Ra=1.5-6 \mu m$ and microhardness HV 7-14 GPa.

The most complete erasure of the traces of 3D processing, the lowest roughness and the highest content of amorphous phases are received by RESP with AlSi electrodes at pulse energy 0.03-0.04J, and the highest microhardness up to 4 times higher than those of the substrate - by RESP with NW, KW and TiB₂-TiAl electrodes at pulse energy 0.03-0.04J.

The proposed possibilities, conditions and parameters of the RESP process are suitable for chemical exothermic reactions between the components of the electrode material, the interelectrode medium (N,O₂) and the substrate and are a prerequisite for the targeted synthesis of new stable compounds with high hardness, intermetallic phases and amorphous- crystal structures and at the same time to obtain surfaces with minimal roughness.

The use of RESP after SLM and DLMS allows replacing the energy- and resource-intensive and labor-intensive finishing treatments of 3D surfaces, reducing the time and costs of their implementation, reducing environmental pollution, expanding the scope of application of 3D technologies.

ACKNOWLEDGMENTS

The present work is based on researches that are funded from the Bulgarian National Science Fund of the Ministry of Education and Science under the project №KP-06-H37/19 “*Technological features and regularities of creation of new high wear resistant composite coatings on titanium alloys by electrical spark deposition process*”.

REFERENCES

1. Gorynin, IV & Chechulin, BB 1990, “Titanium in mechanical engineering” Moscow: Mashinostroenie, 400 p. in Russian.
2. Dong, H 2010, “Tribological properties of titanium-based alloys” *In Surface Engineering of Light Alloys; Woodhead Publishing Series in Metals and Surface Engineering*: Cambridge, UK, pp. 58–80.
3. Freedman, DH 2012, „Layer By Layer“, *Technology Review*, vol. 115, no. 1, pp. 50–53, Academic Search Premier.
4. Laplume, A, Petersen, B & Pearce, J 2016, “Global value chains from a 3D printing perspective”, *Journal of International Business Studies*, vol. 47, no. 5, pp. 595-609.

5. Shipley, H, McDonnell, D, Culleton, M, Lupoi, R, O'Donnell, G & Trimble, D 2018, Optimisation of process parameters to address fundamental challenges during selective laser melting of Ti-6Al-4V: A review. *International Journal of Machine Tools and Manufacture*. 128.10.1016/j.ijmachtools.2018.01.003.
6. Yasa, E & Kruth, J 2011, "Application of laser re-melting on selective laser melting parts" *Adv. Prod. Eng. Manag. Q* vol.6, no.4, pp.259–270.
7. Garbacz, H, Wieceński, P, Ossowski, M, Ortore, G, Wierchoń, T, & Kurzydłowski, K.J 2007, "Surface engineering techniques used for improving the mechanical and tribological properties of the Ti6Al4V alloy", *Surface & Coating Technology*, 202, pp. 2453–2457.
8. Labudovic, M, Blečić, D & Blečić, Z 1997, "Decreasing of Friction and Wear of Ti- 6Al-4V Alloy by Surface Modification Technique" *Tribology in industry*, vol. 19, no. 4, pp. 146-151.
9. Penyashki, T, Kamburov, V, Kostadinov, G D, Nikolov A et al. 2021 "Some ways to increase the wear resistance of titanium alloys" *Journal of the Balkan Tribological Association* 27(1), pp. 1-20.
10. Grabarczyk, J., Batory, D., Kaczorowski, W., Pązik, B., Januszewicz, B., Burnat, B., Czerniak-Reczulska, M., Makówka, M. & Niedzielski, P 2020, "Comparison of Different Thermo-Chemical Treatments Methods of Ti-6Al-4V Alloy in Terms of Tribological and Corrosion Properties" *Materials*, Publisher: MDPI, vol. 13(22), 5192.
11. Yankov, E, Nikolova, M P, Dechev, D, Ivanov, N, Hikov, T, Valkov, S, Dimitrova, V, Yordanov, M. & Petrov, P 2018, "Changes in the Mechanical Properties of Ti Samples with TiN and TiN/TiO₂ Coatings Deposited by Different PVD Methods" *IOP Conference Series: Materials Science and Engineering*, 416 (1), art. no. 012062.
12. Mullin, Yu I, Verkhoturov, A D & Vlasenko, V D, 2006 "Electrospark alloying of titanium alloy surfaces" *Prospective materials*, No. 1, 79-85 in Russian.
13. Zhang Zhengchuan, Liu GuanJun, Konoplianchenko, Ie, & Tarel'nyk, V B 2021 "A review of the electro-spark deposition technology, *Home / Archives / no. 2 (44) pp. 45-53*), *Bulletin of Sumy National Agrarian University. The series: Mechanization and Automation of Production Processes*.
14. Mikhailov, V Gilevich, A, Verkhoturov, A D, Mikhaylyuk, A I, Belyakovsky, A V & Konevtsov, L 2013 "Electrospark alloying of titanium and its alloys, physical and technological aspects and the possibility of practical use". Short review, *Surface engineering and applied electrochemistry*, vol. 49, No. 5, pp. 21–44.
15. Penyashki, T G, Kamburov, V V, Kostadinov, G D, Kandeve, M K, Dimitrova, R B & Nikolov, A A 2022, "Possibilities and prospects for improving the tribological properties of titanium and its alloys by electrospark deposition" *Surface Engineering and Applied Electrochemistry*, 58(2), pp.135-146.
16. Kostadinov, G, Penyashki, T, Kamburov V, et al 2021, "Possibilities for improving the surface quality of structural steels, invar and titanium alloys through reactive electrospark treatment with electrodes of an aluminum-silicon alloys" *Journal of International Scientific Researches*, 15 pp. 105-122.
17. Penyashki, T, Kostadinov, G, Kalitchin, Zh & Kandeve, M 2022 "Ecological aspects of electrospark deposition technologies for improvement of the metal surfaces quality prepared by 3d printing" PART I. "Topography and microhardness of the coatings" *Journal of Environmental Protection and Ecology*, 23(3) pp. 1039–1048.
18. Kostadinov, G, Penyashki, T, Nikolov, A, Dimitrova, R & Kamburov, V 2022, "Geometric characteristics, composition and structure of coatings of WC-TiB₂-B₄C- Ni-CR-B-Si-C electrodes formed on 3D printing titanium and steels by contactless electrospark deposition" *Journal of International Scientific Publications: Materials, Methods & Technologies*, 16, pp. 160-171.

19. Mukanov, SK, Kudryashov, AE & Petrzhik MI 2021 “Surface Modification of Titanium VT6 Alloy Obtained by Additive Technologies Using Reactive Electrospark Treatment” *Physics and Chemistry of Material Processing*, (3), 30.
20. Mukanov SK, Petrzhik MI, Kudryashov AE & Levashov EA 2019, “Elimination of surface defects of SLM products due to a synthesis of nial intermetallic at electro-spark deposition of Al-containing precursor”, *XV International Symposium on Self-Propagating High-Temperature Synthesis* 282.
21. Mihailov, V, Kazak, N, Ivashcu, S, Ovchinnikov E et al. 2023 “Synthesis of Multicomponent Coatings by Electrospark Alloying with Powder Materials” *Coatings*, 13(3), pp. 651.
22. Cadney S, Goodall G, Kim G, Moran A, & Brochu M. 2009 “The transformation of an Al based crystalline electrode material to an amorphous deposit via the electrospark welding process” *Journal of Alloys and Compounds*, 476 pp.147-151.
23. Levashov, EA, Vakaev, PV, Zamulaeva, EI, Kudryashov, AE, Pogozhev, YuS, Shtansky, DV, Voevodin, AA & Sanz, A 2006, “Nanoparticle dispersion-strengthened coatings and electrode materials for electrospark deposition”, *Thin Solid Films*, 515 pp. 1161–1165.
24. Penyashki, TG, Kostadinov, GD, Dimitrova, RB et al. 2022 “Improving Surface Properties of Titanium Alloys by Electrospark Deposition with Low Pulse Energy”, *Surf. Engin. Appl.Electrochem*, 58, pp. 580–593.
25. Penyashki, T, Kostadinov, G, Kalitchin, Jh & Kandeve, M 2022, “Ecological aspects of electro-spark deposition technologies for improvement of the metal surfaces quality prepared by 3d printing”. PART II. “Composition, structure, durability”, *Journal of Environmental Protection and Ecology* 23 (4), pp.1483–1493.
26. Levashov, E A, Kudryashov, A E, Pogozhev, Yu S, Vakaev, P V, Zamulaeva, E I, & Sviridova, TA 2007 “Specific Features of Formation of Nanostructured Electrospark Protective Coatings on the OT4-1 Titanium Alloywith the Use of Electrode Materials of the TiC–Ti3AlC2 System Disperse-Strengthened by Nanoparticles” *Russian Journal of Non-Ferrous Metals*, 48, pp. 362–372.
27. Penyashki, T, Kostadinov G, Kandeve, M, Kamburov V & Nikolov A 2023, “Abrasive and Erosive Wear of Ti6Al4V Alloy with Electrospark Deposited Coatings of Multicomponent Hard Alloys Materials Based of WC and TiB2”, *Coatings* 13 (1),37,215.