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THE INFLUENCE OF VOLTAGE AND ANODE JACKETS ON THE MICROSTRUCTURE, MICROROUGHNESS AND MICROHARDNESS OF COBALT COATINGS DEPOSITED ON Ti-6Al-4V USING BRUSH PLATING

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ABSTRACT

This paper presents preliminary results about the influence of the technological parameters – voltage and anode jackets on the microstructure, microroughness, and microhardness of cobalt coatings deposited on titanium alloy Ti-6Al-4V using brush plating. SEM and EDS analysis were used to study the structure and morphology of the obtained coatings. It was found that the cover material of the anode affects the microroughness of the coatings in the range from Ra = 0.028 μm to Ra = 0.039 μm. Changing the voltage from 8V to 12V was found to affect the microhardness of the coatings between 495 HV and 600 HV. Visual control and bend tests were performed to verify the adhesion strength of the brush-plated cobalt coatings.

INTRODUCTION

Titanium and its alloys provide a unique set of properties, including high specific strength, low density, and a wide working temperature range [1-3]. Because of their high corrosion resistance rates, titanium and its alloys are particularly suitable for the production of various parts and assemblies working in contact with a variety of aggressive environments [4-12]. Therefore, they are preferred as structural materials for modern load-bearing structures, particularly for high-tech systems and specialized equipment products for the aerospace industry. The α + β titanium alloy Ti-6Al-4V is the most popular titanium alloy. Originally, it was developed for aircraft structural applications in the 1950s. Being lightweight and yet strong, this alloy is used to save weight in highly loaded structures, such as jet. engines, gas turbines, and airframe components. While the demand for Ti-6Al-4V is still dominated by the aerospace industry, other industrial fields such as marine, automobile, energy, chemical, and biomedical ones have found its wide acceptance during the last 30 years [1, 2, 11-14]. Among its remarkable properties as high specific strength, low density, and high fracture toughness, Ti-6Al-4V alloy has high corrosion resistance to most aggressive environments, both acid, and alkaline. However, this alloy is known to demonstrate poor tribological properties at low operating temperatures or in the presence of abrasive media, in the sections working under conditions of sliding contact. For example, in the field of sliding bearings or mechanical seals, tearing and wear occur rapidly, which is unacceptable. For improving the mechanical, and tribological properties of this metal, various surface treatment methods are applied, which also have a significant impact on its corrosion resistance. [3, 4, 15-18].

To maintain the desirable properties of Ti-6Al-4V in the contact region on the surface, various coating methods and techniques for localized deposition have been reviewed. It has been found that during the last couple decades, the development and application of the selective plating method are constantly growing [4, 11, 12, 19]. This high-tech, electrochemical, low-temperature process provides good control over the coating, both on localized areas and entire details. Applying this method, the coating thickness can be precise within 1 μm by controlling particular process parameters, such as voltage, time, etc. The mechanical properties, microroughness, and microhardness of the surface layer can be tailored to specific requirements without any additional expensive surface treatment [3, 4, 14-18].

The main technological parameters of the selective brush plating process are average current density, voltage range, anode-to-cathode speed, etc., but the most discussed parameter is voltage. Voltage control is very important as it regulates the current supply in the process.

In many different industries, such as aircraft construction, general mechanical engineering, etc., various types of hard sponge (White TuffWrap, Gray TuffWrap, and Red TuffWrap) are used as abrasive materials for the preparation of various parts for operations prior to the selective plating. During selective brush plating, these materials are used as anode jackets. Their function is to act as an insulator between the anode and the cathode and to

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ensure smooth deposits. These jackets have different relative denting abrasivity that can influence the quality and properties of the deposit. The results discussed in the various scientific references regarding the influence of anode jackets on the structural and mechanical properties of the coatings are often divergent or missing [4, 11, 21].

Despite the known fact that electrodeposited alloys often have slightly different characteristics than metallurgical ones, cobalt retains its basic thermal and corrosion resistance as well as its durability and strength at high temperatures. These cobalt coatings have been found to demonstrate very good tribological behavior at high loads. In addition, these coatings exhibit magnetic behavior, offering new opportunities for application [11, 19-21].

This article presents preliminary results from a study on cobalt coatings deposited on titanium alloy Ti-6Al-4V using selective brush plating. The influence of voltage as a technological parameter and anode jackets (type of electrode cover) on the microstructure, microroughness, and microhardness is studied in this paper.

EXPERIMENTAL DETAILS

The titanium alloy specimens used for this study have dimensions of 10 mm x 10 mm x 1 mm. They were cut from a sheet of titanium alloy Ti-6Al-4V, made according to standard ISO 5832-3:2016. Before the deposition of the cobalt coatings, all samples undergo a pretreatment procedure, including mechanical polishing using 1000 emery alumina powder and electro cleaning in alkaline solution. After the specimen surface is free from contaminants, it is activated using an acid solution and a bonding layer of nickel is electroplated. The presence of nickel as a bonding layer improves the adhesive strength and acts as a hydrogen and oxidation barrier. Finally, a cobalt coating is brush-plated. The specialized equipment used for the selective electroplating process includes a DC power supply model POWER PACK 4383, with RS485-BUS interface. The power supply supports precise control on voltage (up to 20V) and current (up to 15A). Graphite plating anodes with dimensions of 40mm x 25mm x 25mm were used. The solution used for the deposition of a bonding layer consists of 5% nickel formate, 15% nickel sulphate, and 10% citric acid. The cobalt plating solution comprises 10% cobalt sulfate and 1% sulfuric acid. Important plating parameters of the cobalt electrolyte are listed in Table 3. The pH of the chemical solutions (2.5±0.2) during the plating procedures was constantly monitored to remain unchanged.

All experiments were conducted at room temperature. The temperature of the chemical solutions before electrodeposition was 20°C. The time for each experiment was 2 minutes. The controlled technological parameters of the process are voltage – (8 V, 10V, 12 V) and different anode jackets (White Tuff Wrap - WTW, Grey Tuff Wrap - GTW, and Red Tuff Wrap - RTW). The anode jackets have different relative denting abrasivity (RDA) values: WTW – 200 RDA, GTW – 320 RDA, and RTW – 400 RDA. The contact area between the anode and the part is 1.13 cm2. The influence of the selected technological parameters on the morphology and mechanical properties of the cobalt coatings were examined using cross-section analysis. The surface morphologies and the chemical composition of the coatings were examined by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) using Jeol, JSM-6060LV. The microroughness results are obtained using atomic force microscopy (AFM) and a profilometer Mitutoyo Surftest SJ-301. The microhardness of the coated specimens was measured on Vickers microhardness testing apparatus HVS-1000 with a load of 25 g held for 10 s.

RESULTS

Microstructure and elemental analysis

The microstructural analysis is very important for the detailed evaluation of the coating process. A typical SEM image of a cross-section of a coated specimen is displayed in Fig. 1. The analysis shows that the coating deposit is continuous and dense. The brush-plated cobalt layer appears to be homogeneous without a distinctive direction of growth.

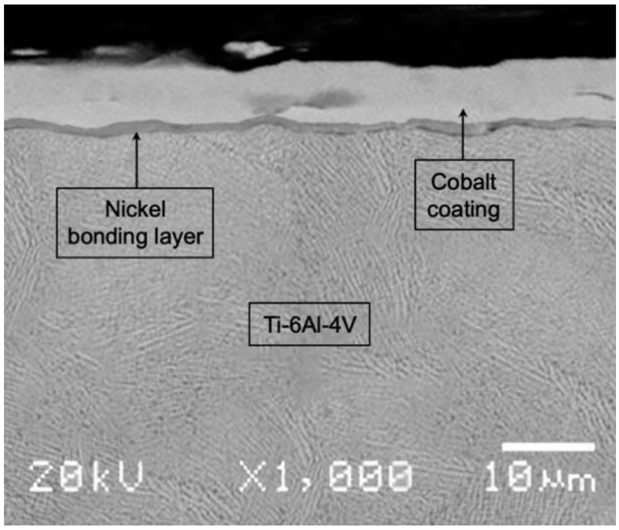
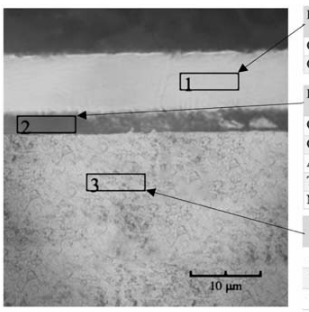


Fig. 1. SEM image of electroplated Ti-6Al-4V sample with a bonding layer of nickel and cobalt coating

Furthermore, an EDS analysis is performed for the three differentiating zones. The chemical composition of each zone is available in Fig.2. The results validate the presence of a cobalt coating, a bonding layer of nickel, as well as the Ti-6Al-4V base. The thickness of the electroplated layers is observed to be in the range of 1.2-2.5 µm for the bonding layer of nickel and 10.3-11.5 µm for the cobalt coating. The elemental concentration in the different layers remains consistent and the obtained layers do not blend, regardless of the variation of the controlled process parameters. This is due to the low-temperature nature of the process.



Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
C	Ka	1.218	0.189	0.53	wt.%
Co	Ka	296.746	4.732	99.47	wt.%

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc	Units
C	Ka	1.54	0.215	0.67	wt.%
O	Ka	3.48	0.272	5.15	wt.%
Al	Ka	18.56	0.184	1.67	wt.%
Ti	Ka	39.81	0.643	5.36	wt.%
Ni	Ka	585.94	1.776	87.14	wt.%

Elt	Line	Intensity (c/s)	Error 2-sig	Conc	Units
Al	Ka	54.75	2.650	5.33	wt.%
Ti	Ka	772.48	71.370	90.86	wt.%
V	Ka	33.71	0.824	3.81	wt.%

Fig. 2. Chemical composition of zones of cobalt coated Ti-6Al-4V specimen with a bonding layer of nickel

Moreover, an X-ray diffraction pattern of electrodeposited cobalt coating on Ti-6Al-4V substrate with a bonding layer of nickel is present in Fig. 3.

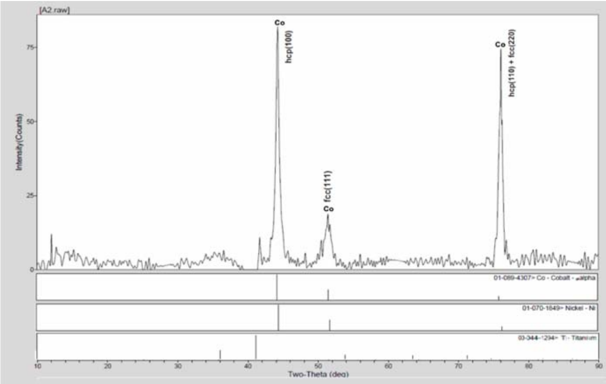


Fig. 3. X-ray diffractogram of the brush plated cobalt coating

The examined cobalt coating consists of two phases - α cobalt (hexagonal phase-hcp) and β cobalt (cubic phase-fcc). The cobalt coating has a distinct crystalline structure, which is characterized by broad basis peaks of the represented phases and with low intensity regarding the increase of the working voltage within the studied limits. The results show that, by increasing the voltage from 8 V to 12 V, the grain size is reduced and smaller cobalt crystals are formed.

Microroughness

The set of samples was used to study the influence of the initial surface roughness on the Ti-6Al-4V and final surface morphology and characteristics of the electroplated cobalt, using different technological parameters. For that reason, measurements were performed before and after the plating process. To quantify the surface roughness of the samples, the most frequently used parameter – Ra (measuring the average of a set of individual measurements of a surfaces peaks and valleys) has been adopted.

The surface characterization of the electroplated cobalt samples was carried out using atomic force microscopy and a profilometer. AFM images of the substrate and electroplated cobalt surfaces are shown in Fig. 4. By comparing the four images, it is clear that the cobalt deposits consist of many small spherical particles, depending on the type of electrode cover material. These results are corroborating to the structural characteristics of the cobalt coatings from the SEM analysis.

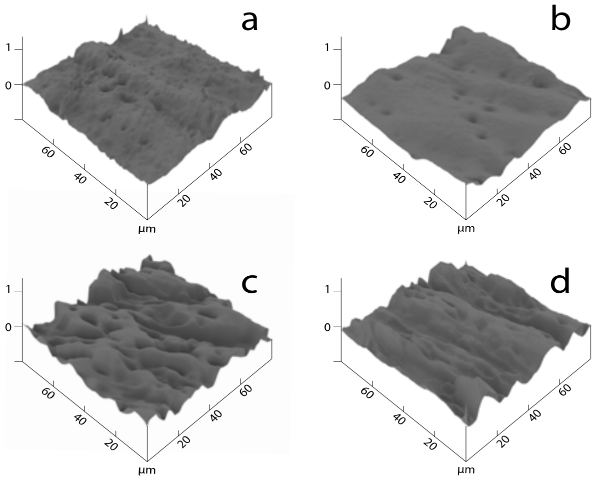


Fig. 4. Surface morphology of the samples of Ti-6Al-4V substrate, Ra = 0.036 µm (a) and after cobalt brush plating with a different type of electrode cover material: White Tuff Wrap, Ra = 0.028 µm (b); Gray Tuff Wrap, Ra=0.032 µm (c) and Red Tuff Wrap, Ra=0.039 µm (d)

The results indicate variations of the surface roughness after the cobalt is deposited. For the Ti-6Al-4V substrates, the initial average roughness of the samples is Ra = 0.036 µm. The decrease of Ra is not significant after the plating of cobalt using White and Gray Tuff Wraps as anode cover materials, as the average values are Ra=0.028 µm and Ra=0.032 µm. However, the cobalt layers deposited using Red Tuff Wrap have increased average Ra values of Ra=0.039µm (Fig. 4-d).

Despite the observed variations, there is no significant change in the microroughness on the surface of the initial substrates and the cobalt coatings. This is not surprising, as it is well-known that the cobalt coatings copy the initial surface profile completely. The voltage applied during the plating process has similar effects on the microroughness of the coatings. It is also important to note that the cobalt layer and the bonding layer have good adhesion to the titanium substrate.

The results of the surface microroughness profiles, measured with profilometer are obtained by 3 measurements for each specimen, before and after coating. The average Ra values measured correspond to those from AFM.

Microhardness

The microhardness average values of the cobalt coatings plated on Ti-6Al-4V using different voltage and electrode wraps are visible in Table 1. It is observed that the microhardness of the cobalt coatings is increasing with the voltage from 8 V to 12 V. Fig. 5 displays the microhardness profiles of the cobalt coatings. The increase of the electrode wrap abrasivity and voltage results in higher surface microhardness.

***Table 1** Average microhardness values of the cobalt coatings brush-plated on Ti-6Al-4V using different electrode wraps and voltage*

	8V	10V	12V
WTW (400 RDA)	400 HV	455 HV	470 HV
GTW (320 RDA)	430 HV	483 HV	532 HV
RTW (200 RDA)	495 HV	554 HV	600 HV

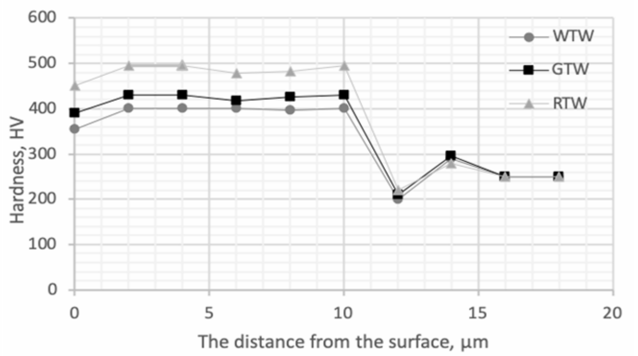


Fig. 5. Microhardness profiles of Ti-6Al-4V after brush plating of Co with an operating voltage of 8 volts.

Using WTW, the average hardness of the cobalt coatings is 470HV, whereas the brush-plated coating using RTW is 600HV (Fig. 6).

There are two reasons for the increase in microhardness. First, because of dispersion strengthening caused by the cobalt grain particles, related to the releasing of retained hydrogen in the coating during grain growth as it was confirmed by the XRD analysis. The second reason is the higher abrasivity of the RTW, used as anode cover material, is that it removes the "soft" phases during the formation of the coating. This results in higher surface roughness, as is visible in Fig. 4-d.

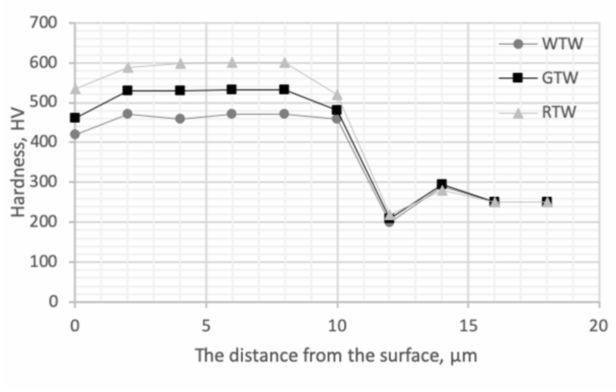


Fig. 6. Microhardness profiles of the Ti-6Al-4V after brush plating of Co with an operating voltage of 12 volts.

Visual control and bend tests

Adherent, smooth, and bright in appearance, cobalt coatings were brush plated successfully on Ti-6Al-4V substrates. It was observed, that the increasing voltage affects the color of the cobalt coating. From 8 V to 12 V, the color changes from bright silver to dull silver. Darker and more porous cobalt coatings were produced using voltage above 12 volts.

Adhesive strength testing was conducted to evaluate the adhesive bonding of the electrodeposited cobalt onto the Ti-6Al-4V substrate. The plated samples were bent through an angle of 180° repeatedly, as is required by the BS 5411-10:1977 standard. The results established that the adhesive strength of the cobalt coatings, deposited using the various technological parameters within the studied limits is very good. Additionally, there was no visual evidence the coating is separated from the base material Ti-6Al-4V after the bending tests. This concludes good adhesive strength both within the coating and at the boundary between the layers of cobalt, nickel, and the base titanium alloy Ti-6Al-4V.

In conclusion, the variation of voltage from 8 V to 12 V, as well as the different anode cover materials used in this study do not significantly affect the adhesion strength of the brush plated cobalt coating on Ti-6Al-4V.

CONCLUSIONS

The brush plating of cobalt coatings on Ti-6Al-4V substrates was successful. Visually, the coatings were characterized as adherent, smooth and bright. The EDS analysis confirmed the presence of nickel and cobalt layers. The chemical elements concentration is consistent and the layers do not blend regardless of the variation of process parameters due to the low-temperature nature of the process. The microstructural analysis exhibited homogeneous cobalt coatings. The coatings were uniform having spherical nodular morphology. The color of the brush-plated cobalt coatings on Ti-6Al-4V was silver-like.

It was found that the abrasivity of the electrode cover material affects the microroughness and microhardness properties of the coatings. This may be caused by the mechanical scrubbing using different anode wraps towards the plated details, which results in removing the softer particles, leaving primarily hard phases to form the coatings.

The results of the study conclude that the voltage has an impact on the microhardness and microroughness properties of the acquired cobalt coatings. The increase of the voltage in the studied range promotes the surface microroughness. Also, higher voltage results in improved microhardness properties of the applied coating. The variation of the voltage from 8 V to 12 V, as well as the different anode cover materials - WTW, GTW, and RTW, do not significantly affect the adhesion strength of the brush plated cobalt coating on Ti-6Al-4V.

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REFERENCES

[1] Sha W., Malinov S., Titanium Alloys: Modelling of Micro-structure, Properties and Applications, Woodhead Publishing, (2009), ISBN: 978-1-84569-375-6

[2] Guleryuz H., Cimenoglu H., Surface modification of a Ti–6Al–4V alloy by thermal oxidation, Surface & Coatings Technology, 192 (2–3) (2005) 164-170

[3] Leyens C., Peters M., Titanium and Titanium Alloys: Fundamentals and Application, Wiley VCH Verlag GmbH & Co. KgaA, (2003), ISBN: 9783527305346

[4] Ayday A., Skulev H., Study of the Nickel–Tungsten and Nickel–Cobalt Coatings Plated on Ductile Iron, Acta Physica Polonica A. 129 (2016) 455-458

[5] Jones A.R., Hamann J., Lund A.C., Schuh C.A., Nano-crystalline Ni-W Alloy Coating for Engineering Applications, Plating and Surface Finishing, 97 (4) (2010) 52–60

[6] Pinc W., Yu P., O'Keefe M., Fahrenholtz W., Effect of gelatin additions on the corrosion resistance of cerium based conversion coatings spray deposited on Al 2024-T3, Surface and Coating Technology, 203 (2009) 3533-3540

[7] Sharma A.K., Gold plating on aluminium alloys for space applications, Transactions of the IMF, 67 (1) (1989) 87-88

[8] Arenas M.A., De Damborenea J.J., Growth mechanisms of cerium layers on galvanised steel, Electrochimica Acta, 48 (24) (2003) 3693-3698

[9] Pardo A., Merino M.C., Arrabal R., Viejo F., Muñoz J.A., Ce conversion and electrolysis surface treatments applied to A3xx.x alloys and A3xx.x/SiCp composites, Applied Surface Science, 253 (6) (2007) 3334-3344

[10] Tuken T., Ozylmaz A.T., Yazici B., Kardos C., Erbil M., Electrochemical synthesis of polyaniline on mild steel in acetonitrile-LiClO 4 and corrosion performance, Applied surface science, 236 (2004) 292-305

[11] Radatz D., Zhecheva A., Clouser S., Advances in selective plating on titanium alloys, Product Finishing Magazine, (2009)

[12] Mallett M.W., Surface Treatments for Titanium Alloys, NASA Technical Memorandum NASATM-X-53429, (1965)

[13] Finazzi G.A., De Oliveira E.M., Carlos I.A., Development of a sorbitol alkaline Cu–Sn plating bath and chemical, physical and morphological characterization of Cu–Sn films, Surface and Coatings Technology, 187 (2–3) (2004) 377-387

[14] Ghosh S.K., Limaye P.K., Bhattacharya S., Soni N.L., Grover A.K., Effect of Ni sublayer thickness on sliding wear characteristics of electrodeposited Ni/Cu multilayer coatings, Surface and Coatings Technology, 201 (16–17) (2007) 7441-7448

[15] Wang Y.M., Cheng S., Wei Q.M., Ma E., Nieh T.G., Hamza A., Effects of annealing and impurities on tensile properties of

electrodeposited nanocrystalline Ni, Scripta Materialia 51 (2004) 1023–1028

[16] Thuvander M., Abraham M., Cerezo A., Smith G.D.W., Thermal stability of electrodeposited nanocrystalline nickel and iron–nickel alloys, Materials science and technology, 17 (8) (2001) 961–970

[17] Gering J., Structure and Wear Resistance of Brush Plated Deposits, Master of Philosophy thesis, The University of Birmingham, Birmingham, United Kingdom, (1995)

[18] Gering J., Bell T., Farr J.P.G., R. Mountford & J. Ryan, Structure and Wear Resistance of Brush Plated Nickel, Transactions of the IMF, 73 (3) (1995) 82–84

[19] Gouldstone A., Koh H.J., Zeng K.Y., Giannakopoulos A.E., Suresh S., Discrete and continuous deformation during nanoindentation of thin filmsacta, Acta mater. 48 (2000) 2277-2295

[20] Ning Z.H., He Y.D., Rapid electroplating of Cu coatings by mechanical attrition method, Trans. Nonferrous Met. Soc., 18 (2008) 1100–1106

[21] Dong S., Yang H., Du L.Z., The research development of nano-particle composite brush electro-plating technology, Int. Heat Treat. Surf. Eng. 9 (2004) 17-19

[22] International standard ISO 5832-3, Fourth Edition, 2016-10-15 Reference source