EVALUATION OF SURFACE PROPERTIES FOR DIFFERENT ANODIZED TITANIUM ORTHOPEDIC SCREWS

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For therapeutic purposes, the coloring of a material for implant manufacturing is required to distinguish its components and form. In this manuscript, an experimental study was aimed at the connection between the color of the anodization and the surface properties of some commercial osteosynthesis screws. The purpose was to investigate whether or not the color difference implies different surface properties in the case of osteosynthesis screws, and what other influence can have, apart from the easier differentiation of osteosynthesis screws according to diameter. These aspects are of great importance in orthopedic clinic.

Keywords: titanium and titanium alloys, anodization, colored implants screws.

1. Introduction

Through natural selection and based on an amalgam of important properties, in the field of biomaterials among the materials intended for the manufacture of medical implants, titanium (Ti) and its alloys are some of the most important

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materials in this category [1]. Ti and its alloys exhibit suitable characteristics when it comes to their use in the manufacture of implants usable in various medical branches such as dentistry and orthopedics. When exposed to air, Ti and its alloys naturally form on the surface a film of titanium oxide (TiO_2), which presents a very good chemical stability, resulting in these favorable properties such as satisfactory corrosion resistance, and adequate biocompatibility [2, 3]. However, the native oxide film that forms on the Ti alloys surface, respectively TiO_2, has a bioinert character which can lead to unsatisfactory osseointegration. It is typically necessary to modify the surface of titanium and its alloys to increase their bioactivity [1-5].

Over time, multiple techniques for improving the surface of Ti-based implants have been tested, like deposition of hydroxyapatite layers, acid etching or sandblasting, but these techniques have presented some disadvantages [6]. Either controlling the structure that has developed on the implant's surface is challenging, or there is the possibility of some chemical waste remaining on the surface of the implant that can induce toxicity on tissues or cells [7-11]. Therefore, in order to develop other properties of Ti and its alloys, they are often anodized due to their predisposition to wear in clear wear conditions [12-14].

In the 1950s, research into titanium anodic oxidation started [15]. A simple, effective, and flexible method for creating oxide coatings with very precise nanostructures is anodic oxidation. A result of their direct in-situ development on metal surfaces, anodic oxidized films often exhibit good interfacial adhesion. TiO_2 coatings with controllable nanostructures have recently been produced on Ti surfaces by anodic oxidation and these coatings have shown to have significant bioactivity. The anodized TiO_2 coatings therefore have enormous potential as clinical implant materials [16].

An electrochemical method, anodic oxidation is used to modify titanium-based substrates by forming TiO_2 ceramic layers ranging in thickness from hundreds of nanometers to hundreds of micrometers [17]. Also, the TiO_2 ceramic layer formed can have distinctive properties. To obtain these properties, it is needed to adjust the electrochemical parameters during the electrolytic oxidation process, namely, the composition and concentration of the electrolytes in the solution, the applied voltage, the current density, but also the implant surface characteristics and composition [17-19]. As previously mentioned, the TiO_2 layer's thickness generally increases as the applied voltage increases. But more than that, in addition to different layer thicknesses, different morphologies can also be obtained which, in addition to voltage, also depend on the composition of the electrolyte in which the electrodes are inserted [20, 21]. These factors that have been mentioned (applied voltage, type of electrolyte, time, etc.) in addition to the appearance of the morphology and the layer thickness, influence the color of the oxide layer to the same extent [17].

U.R. Evans carried out the earliest research on the development of interference colors onto metals [22]. The colors given off by metal corrosion and the accompanying thin oxide layers on the metal's surface captured his interest. Was discovered that the noticed color can be an indication of a representation showing the thickness of the transparent oxide coating that was responsible for the phenomenon, which was instantly attributed to interference [17, 22].

In addition, transparent films on metals produce interference colors as follows: part of the incident white light is reflected on the surface of the film, while the other part of the remaining light is refracted inside the film. The light components amplified by moving out the oxide in phase (constructive interference) and the components diminished or cancelled by moving out of phase are the ones that determine the color [23, 24]. By locating the interference maxima and minima that characterize the surface reflectance spectrum, these correlations can be utilized to anodize a surface to produce the desired color or to generate an indirect assessment of the thickness of an anodic film. [22, 25-27].

Several authors have remarked that Ti takes on a colorful hue after anodizing [24, 27-29]. The research on this aspect included several options, in the sense that indeed color can come from interference, but there is also the possibility that it comes from a stoichiometric effect.

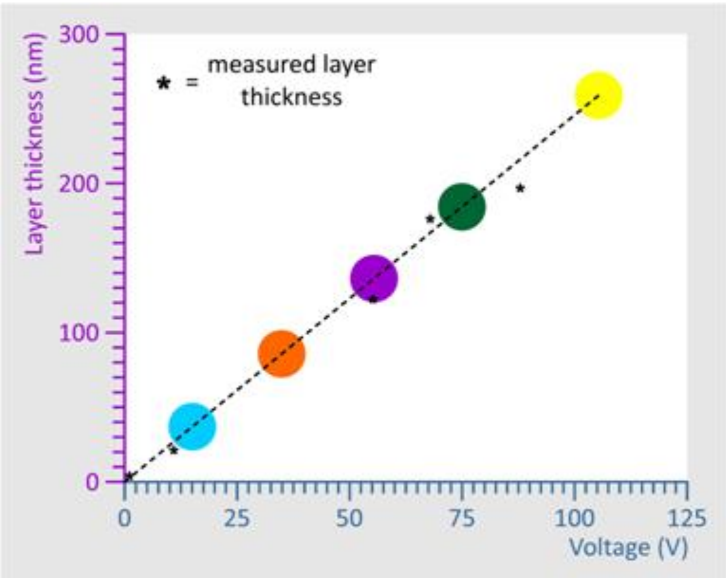


Fig. 1. Correlation between voltage and layer thickness for different colors associated to the anodized screws [33]

S. Van Gils et al. [25] performed Ti anodization obtaining different thicknesses by applying various voltages. The colors obtained were different and could be observed visually. The gray shade is expressed by the zero value, and the values obtained are much different, therefore the chromaticity is increased (from 9 to 46).

Velten et [29] comparatively analyzed the Ti oxide layers developed on cp-Ti substrates and the Ti6Al4V alloy by different methods. But for the present study, we focused only on the rough results obtained by anodic oxidation and, more precisely, what are the parameters that influenced the obtaining of different colors. In the research, the current density that was constantly applied was 5 mA/cm^2 at a final potential of 50 V, which did not result in any increase in the oxide layer. The interpretation of this phenomenon could be that throughout the formation of the oxide coating, the structure changed from amorphous to crystalline. Progressive anodization leads to the transformation of the amorphous coating from the commencement of oxidation into an increasingly crystalline one. The ionic conductivity initially required for the growth of the coating passes to the electronic conductivity which delays the increase of the oxide coating until it no longer grows at all. Thicker films can be produced before growth stops by increasing the current density up to 10 mA/cm^2. For the Ti6Al4V alloy, the application of a current density of 2 mA/cm^2 was sufficient for the entire potential up to 100 V. The alloy's vanadium and aluminum appear to prevent TiO_2 from crystallizing in the film. Following the determinations made and comparing the thickness of the TiO_2 coatings with the applied final potential, the authors concluded that, both for cp-Ti and for the Ti6Al4V alloy, the thickness of the oxide film depends linearly on the applied voltage. There is also a dependence between the color of the specimens and the thickness of the oxide film (Table 1).

Table 1

Layer thickness versus colors layers obtained after anodization.

Thickness (nm)	11-26	26-39	39-49	49-79	79-119	119-149	149-179	179-215
Color	Golden	Purple	Deep blue	Light blue	Yellow	Orange	Purple	green

The aim of our study was to analyze four commercial Ti alloy screws for orthopedic applications, with different colors, in order to determinate their surface properties and to establish a correlation between screw color and surface properties. According to literature, it is already established that the color of the anodized Ti alloy screws depends on several parameters like voltage, electrolytes, and anodization time. One limitation of our study is the fact that our analysis was made on the commercial screw, so we didn’t know the anodization parameters. The results obtained were interpreted and compared to those reported by different research groups.

2. Experimental Methods

2.1. Materials

Anodizing is a metal surface processing technique that can be used to improve their properties. This technique involves the growth of an oxide on the surface of the metal, forming a protective layer resistant to corrosion and wear. One of the outstanding features of anodizing is the ability to achieve a variety of different colors on the surface of the anodized orthopedic implant.

The materials analyzed in this study were four osteosynthesis screws, cannulated and non-cannulated, made of anodized titanium alloy (Ti6Al4V), having different colors (copper, blue, purple and green). The screws were characterized and tested from the point of view of the surface properties induced by the anodizing process.

Sample 1 – copper anodized screw *Sample 2 – blue anodized screw*

Sample 3 – purple anodized screw *Sample 4 – green anodized screw*

Fig. 2. Macro images of the investigated osteosynthesis screws.

2.2. Determination of morphology and elemental composition

Energy dispersive X-ray spectroscopy (EDS) and scanning electron microscopy (SEM) can be used to properly evaluate the sample surfaces of the. These determinations are often used for analysis of investigated samples from several points of view (investigation of material defects, manufacturing errors, surface analysis and others). Surface morphology and elemental composition of anodized samples surfaces were analyzed using a Scanning Electron Microscope equipped with an X-Ray Energy Dispersive Spectrometer (SEM-EDS, Phenom ProX, PhenomWorld, Eindhoven, Netherlands).

2.3. Roughness investigations

Surface roughness represents the set of micro-irregularities of a surface, obtained because of the manufacturing process applied and which do not constitute a deviation from the shape. Roughness with high values can be an undesirable characteristic because it causes increased friction and wear, but it can also be beneficial because it allows adhesion of the surrounding tissue to the biomaterial. The determination of the surface roughness was carried out by the profilometry method, the Form Talysurf® i-Series PRO Range device was used from Taylor Hobson (Leicester, United Kingdom). It is composed of a transducer with a standard stylus (fixed on the column of the measuring stand) for measuring flat surfaces with a diamond tip with a radius of 2 µm and an angle of 60° (the pressing force being less than 1 mN). The software used is Metrology 4.0 Software. The column of the measuring stand moves in the Z direction.

2.4. Contact angle measurements

Contact angle measurements were carried out using a KRUSS DSA 30 (Hamburg, Germany) optical tensiometer using three liquids: water, diiodomethane and ethylene glycol. Given the complex geometry of the test samples, slanted droplets were manually deposited using micrometer syringes for each fluid. For the calculation of the surface free energy, the characteristics of the liquids presented in table 2 were used in the Owens - Wendt - Rabel & Kaelble (OWKR) method [34].

Table 2

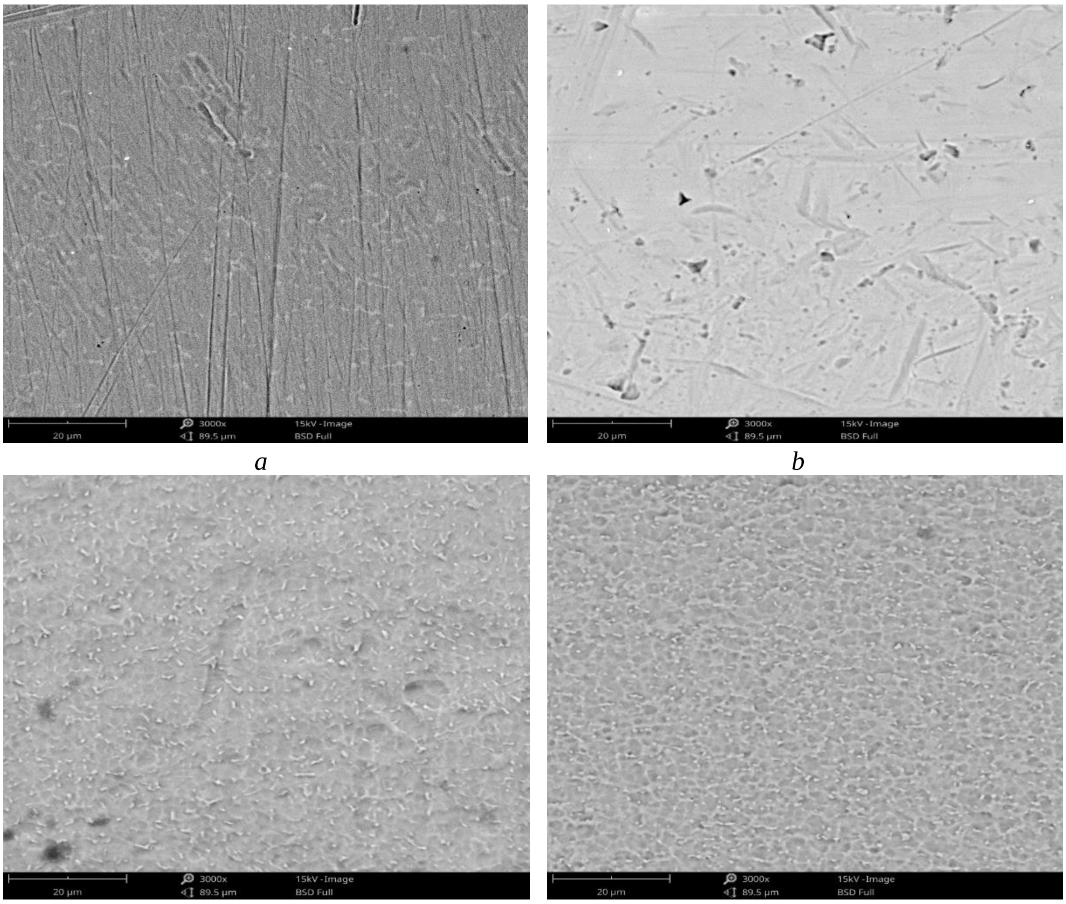
Characteristics of liquids used in the calculation of surface free energy

Liquid	Dispersive component (mN/m)	Polar component (mN/m)	Surface tension (mN/m)
Water	21.8 [36]	51.0 [36]	72.8 [36]
Diiodomethane	44.1 [36]	6.7 [36]	50.8 [36]
Ethylene glycol	32.8 [37]	16.0 [37]	32.8 [37]

3. Results

3.1. Morphological characterization and elemental composition

The surface morphologies of the anodized samples are presented in Fig. 3. The SEM studies were performed on as received surface aiming to observe the topography of the surface for the investigated samples. At first glance there are considerable differences in the topography that can be related to the thickness of the anodized layer. Thus, for the copper color screw (with layer thickness up to maximum 25µm) in Fig. 3.a deep and superficial grooves with a common orientation can be observed, we assume to occur following a stage of surface preparation prior to anodization. With increasing layer thickness on the surface fewer surface defects are apparent (Fig. 3.b for the blue color screw with a layer thickness between 25-50µm), while at higher thicknesses (purple color, 75-100µm, Fig. 3.c and green color, 100-125µm, Fig. 3.d) the surface topography is comprised only by the one specific for the anodized layer - clusters of nanotubes.



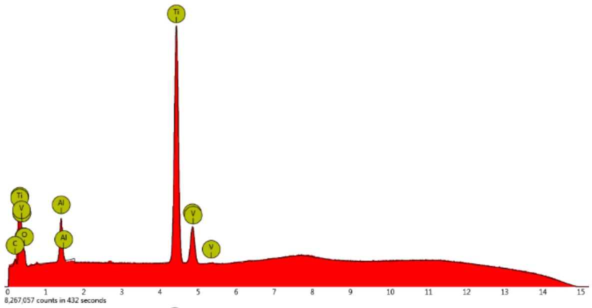
a b c d

Fig. 3. Scanning electron micrographs of the analyzed samples: a) copper anodized screw, b) blue anodized screw, c) purple anodized screw and d) green anodized screw

In general, when the anodization process is longer, it has a more homogeneous path, thus transforming the surface morphology into a more complex one [35]. In conclusion, the anodizing time is considered one of the most important parameters that can influence the type of surface morphology, but also the thickness of the obtained layer [29, 32, 35].

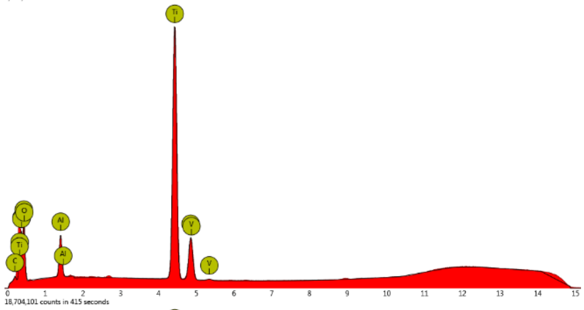
The chemical composition of the surface was determined by energy dispersive spectroscopy with the quantification of titanium, aluminum and vanadium as these elements are the constitutive ones for the alloy. The presence of oxygen was accounted also, as the formed layer is titanium dioxide, but the quantification of this element is inaccurate.

The EDS spectra are depicted in Fig. 4 with along the estimates regarding the chemical composition.



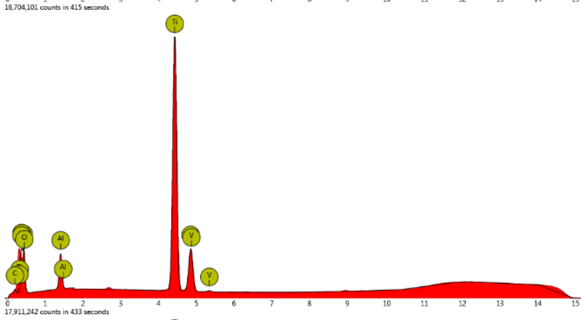
Sample 1 - copper anodized screw

Element Number	Element Symbol	Weight Conc.
22	Ti	69.76
8	O	***21.32***
13	Al	5.69
23	V	3.23



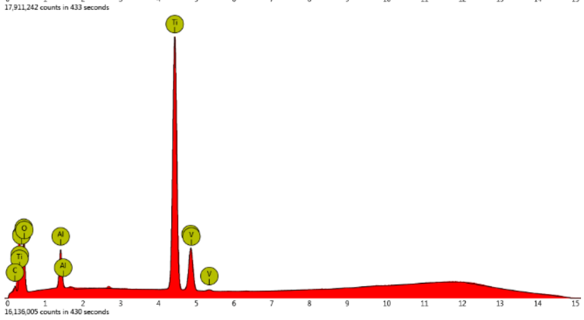
Sample 2 - blue anodized screw

Element Number	Element Symbol	Weight Conc.
22	Ti	54.18
8	O	***39.26***
13	Al	4.02
23	V	2.54



Sample 3 - purple anodized screw

Element Number	Element Symbol	Weight Conc.
22	Ti	58.75
8	O	***34.70***
13	Al	3.74
23	V	2.81



Sample 2 - green anodized screw

Element Number	Element Symbol	Weight Conc.
22	Ti	56.46
8	O	***37.00***
13	Al	3.83
23	V	2.71

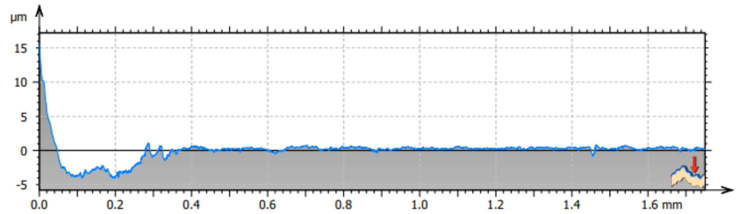
Fig. 4. Energy Dispersive X-Ray spectra and the elemental composition of the analyzed samples.

A decreasing tendency in the concentration of titanium, aluminum and vanadium can be observed as the layer thickness increases. This appears to be caused by the change of the relative position of the interaction volume of the electron beam in respect to the substrate. The tear-drop shaped interaction volume extends from 100 nm to roughly 5 µm into the surface and, as the layer thickness increases less information from the substrate is achieved. Regarding the roughly estimated oxygen concentration an increasing trend was also observed in respect to increasing layer thickness, but no direct correlation could be inferred.

3.2. Roughness investigations results

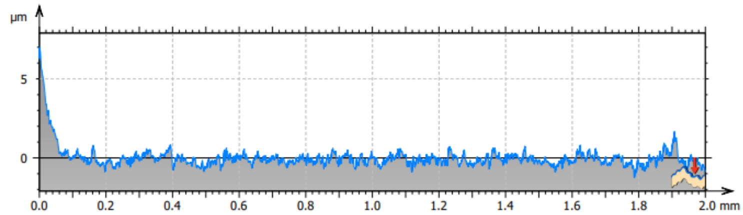
The surface roughness was studied since it is considered to be a key factor for osseointegration and it can be considered an influence factor for wetting behavior. A selection of profiles is presented in fig. 5 for the investigated samples along roughness parameters: the arithmetic mean roughness (R_a), the maximum roughness (R_z), the total height of the profile (R_t), the kurtosis (R_{ku}), skewness (R_{sk}) and root mean square roughness (R_q).

Sample 1 - copper anodized screw



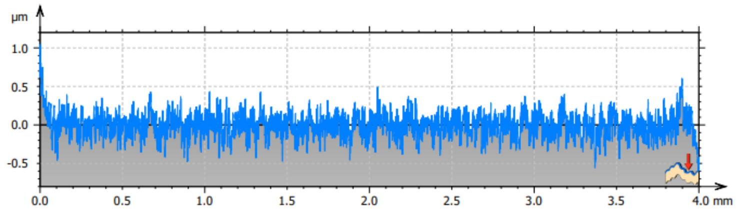
Rq	0.9846 µm
Rsk	-2.6010
Rku	8.7095
Rt	5.0385 µm
Rz	1.5591 µm
Ra	0.6044 µm

Sample 1 - blue anodized screw



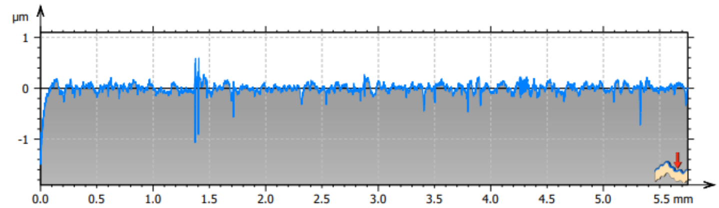
Rq	0.6937 µm
Rsk	5.3437
Rku	42.3125
Rt	8.2519 µm
Rz	2.4954 µm
Ra	0.3532 µm

Sample 1 - purple anodized screw



Rq	0.1569 µm
Rsk	0.3313
Rku	4.9449
Rt	1.6736 µm
Rz	0.8508 µm
Ra	0.1206 µm

Sample 1 - green anodized screw



Rq	0.1134 µm
Rsk	-3.8592
Rku	39.0299
Rt	2.0897 µm
Rz	0.5533 µm
Ra	0.07 µm

Fig. 5. Roughness investigations on the analyzed samples.

A comparison of these parameters is presented in Fig. 6:

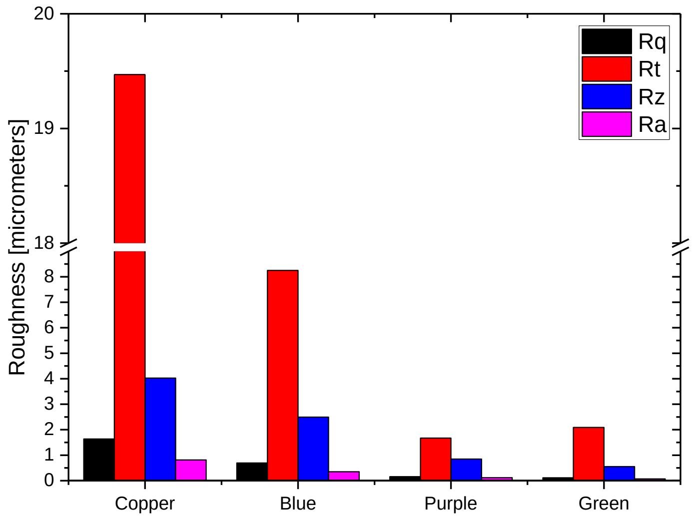


Fig. 6. Surface roughnesses of the analyzed osteosynthesis screws.

The R_a and R_q values show a decreasing trend as the layer thickness increases, suggesting that the surface becomes smoother. R_t also decreases as layer thickness increases, suggesting that the differences between highest peak and deepest value are smaller, showing that the surface is smoother, aspect confirmed also by the decreasing trend of R_z. According to R_{sk} the most symmetrical height distribution was achieved on the sample with a layer thickness of 75-100µm, aspect confirmed by the lowest value of R_{ku} that suggest the presence of low peaks and valleys. According to R_{sk} and R_{ku} values a layer thickness of 75-100µm would generate a surface with least waviness, aspects observed also by SEM investigations.

3.3. Contact angle results

The angle created when the liquid-solid and liquid-vapor interfaces collide is known as the contact angle. To determine the contact angle, sessile drops were deposited on each sample on various regions and 14 measurements were performed on each sample, for each liquid. As in the case of the results regarding the roughness of the surface of the analyzed samples, also in the case of the contact angle, a decrease of it can be observed with the increase of the layer thickness when the liquid used was water. The water contact angle was compared using the ANOVA method with $\alpha=0.05$, the test result indicating that the differences between the water contact angles are statistically significant, the thickness of the layer being an important factor on wettability. Comparative tests between mean values were performed using the Tukey and Fisher tests with $\alpha=0.05$ and it was found that statistically significant differences appear only in the case of sample 4 (green anodized screw) with a layer thickness between 180 and 210 nm (approximately) according to data from the literature [29]. A pronounced hydrophilic character is observed.

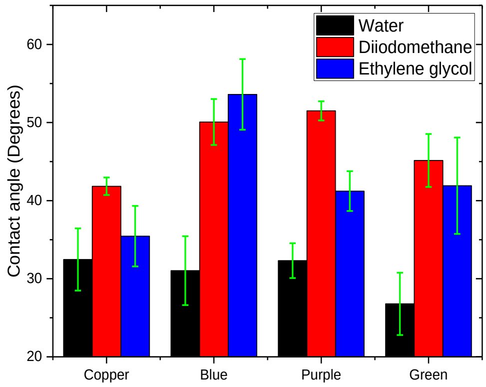


Fig. 7. Contact angle measurements of the analyzed osteosynthesis screws.

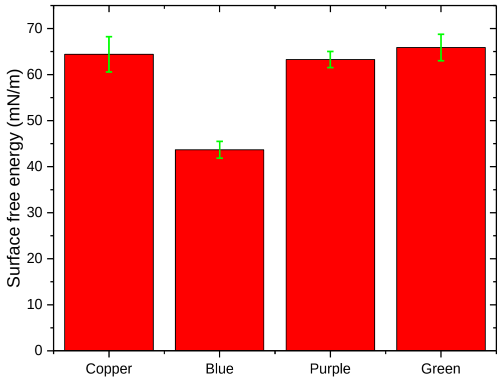


Fig. 8. Surface free energy of the analyzed osteosynthesis screws.

For diiodomethane and ethylene glycol it is observed that for samples 1 (copper anodized screw), 3 (purple anodized screw) and 4 (green anodized screw) the contact angles are higher while for sample 2 (blue anodized screw) it is the opposite, which suggests a possible change in the chemical composition at the contact surface which may be due to the electrolyte used in the process anodizing.

The surface free energy does not change significantly in value, with the exception of sample 2 (blue anodized screw) which shows a lower energy due to that anomaly between the contact angles in the case of diiodomethane and ethylene glycol generated by a change in the superficial chemical composition. Using an analysis similar to that for the contact angle (ANOVA test, Tukey and Fisher with α=0.05) it results that the values are statistically significantly different. Tukey and Fisher suggest that the surface free energy values are not statistically significant for samples 1, 3 and 4, with the exception of sample 2.

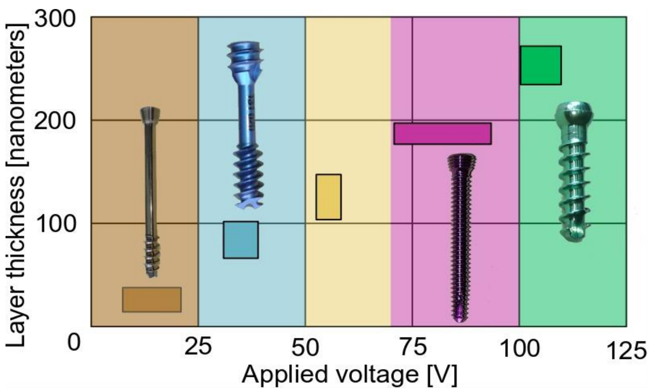


Fig. 9. Comparative diagram of the analyzed samples with the results from the literature.

Although there are differences in surface roughness and chemical composition, the surface free energy of the analyzed screws is influenced by the combined chemical composition-roughness effect, the superficial chemical composition being mainly determined by the process parameters used by the manufacturers.

4. Conclusions

The anodization of titanium alloys allows obtaining osteosynthesis screws in various colors, which facilitates their differentiation in clinical practice according to diameter and reduces the risk of wrong selection during surgical interventions. By controlling anodization parameters, different surface properties can be obtained, and these properties will influence cell adhesion, integration with bone and fracture healing process.

The anodizing process can improve the adhesion of screw-type implants with human bone, by changing the surface properties, also given the chemical properties. The colors obtained from the anodizing process may vary depending on the applied voltage. However, it should be noted that the anodizing process is complex and can be influenced by several factors, including the applied voltage, the composition of the electrolytic solution, the anodizing time, and the surface properties of the osteosynthesis screws before anodization.

The different color is not only an aesthetic or practical aspect, due to the fact that different anodization induces different surface properties of the osteosynthesis screws. Our experimental results demonstrate that the surface properties of the osteosynthesis screws are different for each type of anodization parameters.

According to this study, a layer thickness of 75-100µm would be optimal from the roughness point of view. A lower thickness would preserve preexistent surface features, while higher thicknesses generate a roughness by a preferential growth mechanism.

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