SELECTING A SURFACE PREPARATION TREATMENT ON A MEDIUM ENTROPY Ti-Zr-Ta-Ag ALLOY

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Abstract. *All metallic alloys undergo some surface pretreatment before coating deposition. This preparation step influences the surface roughness and can also change the surface chemical composition, therefore influencing the coating adhesion and the physicochemical characteristics of the coated alloy. Choosing an appropriate surface pretreatment can maximize the coated alloys performances. In this work, we aimed to comparatively analyze the surface of the Ti-Zr-Ta-Ag alloy before and after two different surface pretreatments. The surface composition and morphology were investigated using atomic force microscopy, scanning electron microscopy, and energy dispersive spectroscopy, while surface energy and mechanical properties were investigated using contact angle measurement and Vickers hardness test.*

Keywords: surface preparation, titanium alloy, acid etching, alkaline treatment

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1. Introduction

In the context of enhanced negative effects associated with traditionally metallic alloys implants due to the increased aggressivity of bacteria [1,2] and to the allergenic and toxic potential of metals [3–5], new strategies are under investigation to improve the performance of metallic biomaterials. In the last decades such strategies have been especially focused on surface modifications and chemical composition changes [6,7].

It is to mention that such negative aspects, with impact on safe use and people health are controlled by the European Commission (EC) [8–10], which is continuously introducing new directives and regulations in the frame of new carcinogenic, mutagenic or toxic to reproduction substances (CMR) [10]. An example is the substitution of biomaterials according to the Regulation 2017/745 of the European Parliament in two transition periods, the first one starting in 2017 and the second one in 2021. The manufacturers need to find until 2025 alternatives to substitute the well-known CoCr implants that have carcinogenic

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and mutagenic effects with Ti and Ti alloys without toxicological risks and allergenic potential [11,12].

Such strategies are being oriented especially in two directions. One approach is the development of new alloys with superior mechanical and stability properties, introducing elements that are able to change the structure and properties for improved corrosion resistance and antibacterial behavior [13]. The other approach is to employ new surface treatments that will improve the overall performance of the material [14,15].

Recently, a new Ti-20Zr-5Ta-2Ag alloy [16,17] was proposed, elaborated and microstructurally characterized. This alloy is a medium entropy alloy (MEA). It has a bi-phase $\alpha + \beta$, acicular, homogeneous microstructure that was evidenced in scanning electron microscopy (SEM). Its native passive film, responsible for a very good stability, consists of the protective TiO_2, ZrO_2, and Ta_2O_5 oxides, Ti and Ta suboxides, and metallic Ag able to increase antibacterial effect. Being a newly elaborated alloy, investigation of the coated and uncoated Ti-20Zr-5Ta-2Ag alloy are of utmost importance.

Various surface pretreatments can be employed to modify the physicochemical characteristics of the naturally formed layer so that the bonds between the deposited coating and the substrate to be stronger and to obtain a better adhesion [18–21]. Acid treatments can increase the roughness and therefore the surface area [22], while alkaline treatments can lead to the formation of hydrated oxide layers, improving coating adhesion [23].

The performance of the coated alloy can be greatly influenced by the employed surface pretreatment [24–27], therefore a careful investigation of this intermediate step can bring much benefits. It is the novelty of the present manuscript and is aim as well to develop and investigate the alloy surfaces treated in different ways to select the one with better characteristics.

2. Materials and methods

2.1.Materials

The substrate used was 73Ti-20Zr-5Ta-2Ag. The alloy surfaces were prepared in three different manners. The first one (V1) was only degreased in isopropanol (99.7%) for 10 minutes in an ultrasonic bath and washed with distilled water. The second modification (V2) consisted of grinding the sample with SiC abrasive paper up to a granulation of #1200, after which it was placed in HCl (36.5%) for 10 minutes and then washed with distilled water. The third modification consisted of grinding the sample with SiC abrasive paper to a final granulation of #1200, after which it was placed in NaOH 10 M for 24h and then washed with distilled water.

2.2. Surface analysis

The morphology of the samples was analyzed using a scanning electron microscope (SEM, Hitachi SU8230), while energy dispersive x-ray spectroscopy (EDX) was used to investigate the atomic distribution of the elements on the sample surfaces and the surface roughness was evaluated using an atomic force microscope (AFM, Molecular Vista, Vista One).

2.3. Wettability and microhardness analysis

The contact angle was measured with a contact angle meter (KSV Instruments CAM100), using the falling drop method. Three measurements were made per sample, using droplets of approximately 2 μL. The microhardness was tested using a Vickers hardness tester (Wilson, Tukon 1102).

3. Results and discussion

3.1. Surface analysis

Firstly, the alloy surface without any treatment was mapped using EDX on a large scale to check the homogenous distribution of the elements in the sample. The results obtained can be seen in Figure 1.

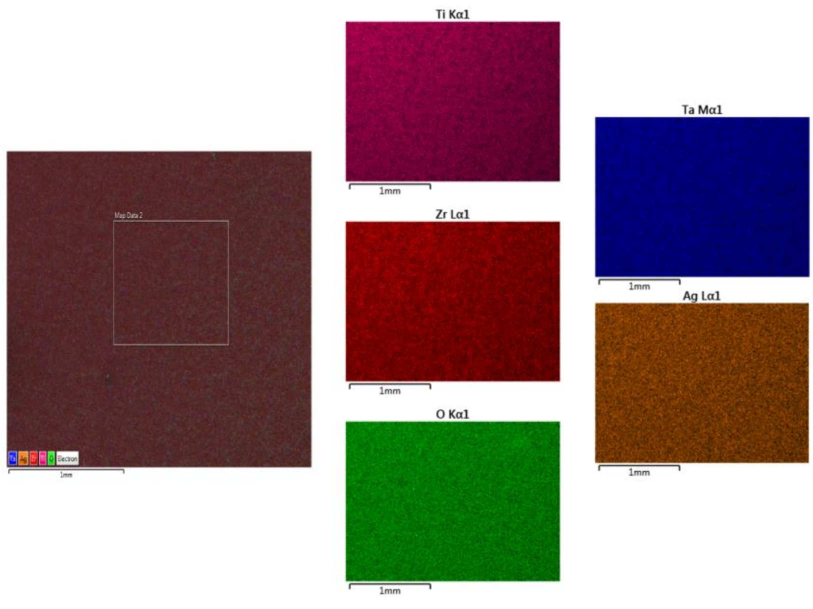

Fig. 1. Surface mapping of alloy V1 by EDX

It is observed that the individual elements are uniformly spread, while in the overlayed image it can be seen that Ti has the bigger contribution, followed by Zr, O, Ta and Ag, as expected, due to the alloy composition and to the natural oxide layer formed on the surface.

In Figure 2 is shown the morphology of the three samples, one without treatment (V1) and the other two, etched in acid (V2) and kept in alkaline solution (V3).

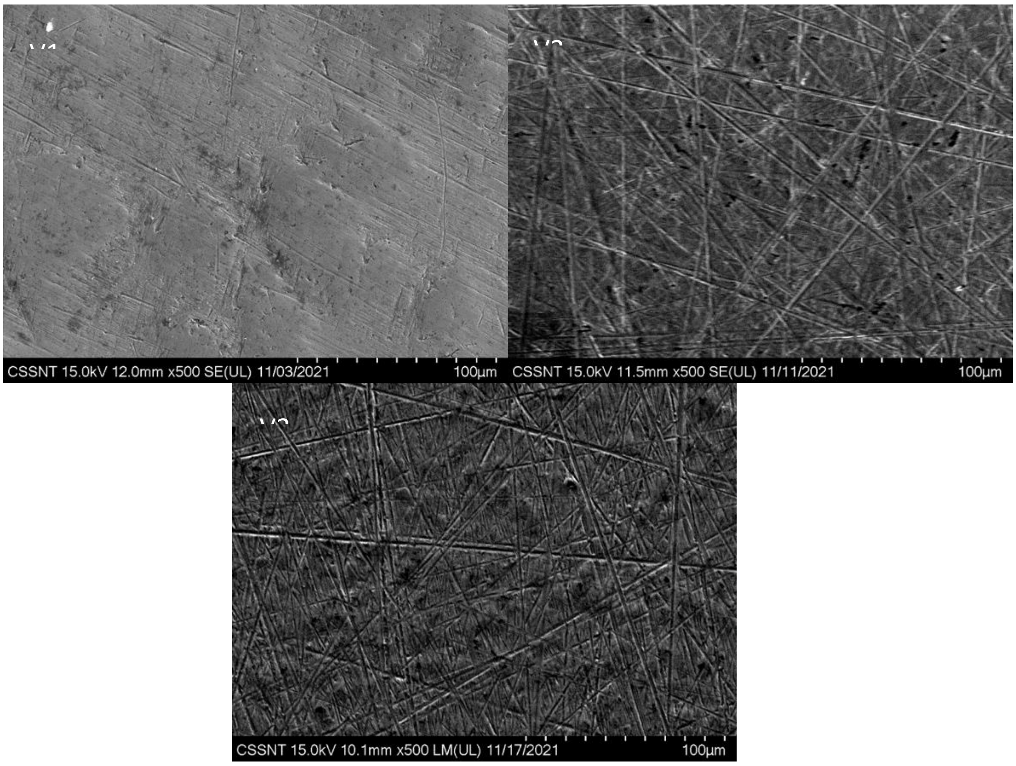

Fig 2. SEM images of the analyzed samples at x500 magnification

In the SEM images the surface of the alloy cleaned, without other pretreatment, appears smoother probably due to the oxide layer formed in time on the surface, while the other two alloys that were freshly grinded before pretreatment presents typical structures resulted from the grinding process.

The AFM measurements were performed in tapping mode, analyzing three different parts for each alloy on an area of 40 x 40 μm. The results obtained are shown in Figure 3 and Table 1.

From the obtained data it is observed that the alloy without pretreatment had the lowest Ra, followed by the one kept in acid and the one kept in sodium hydroxide, respectively. In the one without pretreatment the presence of peaks/valleys is almost equal, as seen also in the SEM image, however, it is interesting that the alloy kept in the hydroxide solution showed less extreme peaks or valley features than the one kept in acid, although the mean roughness was higher.

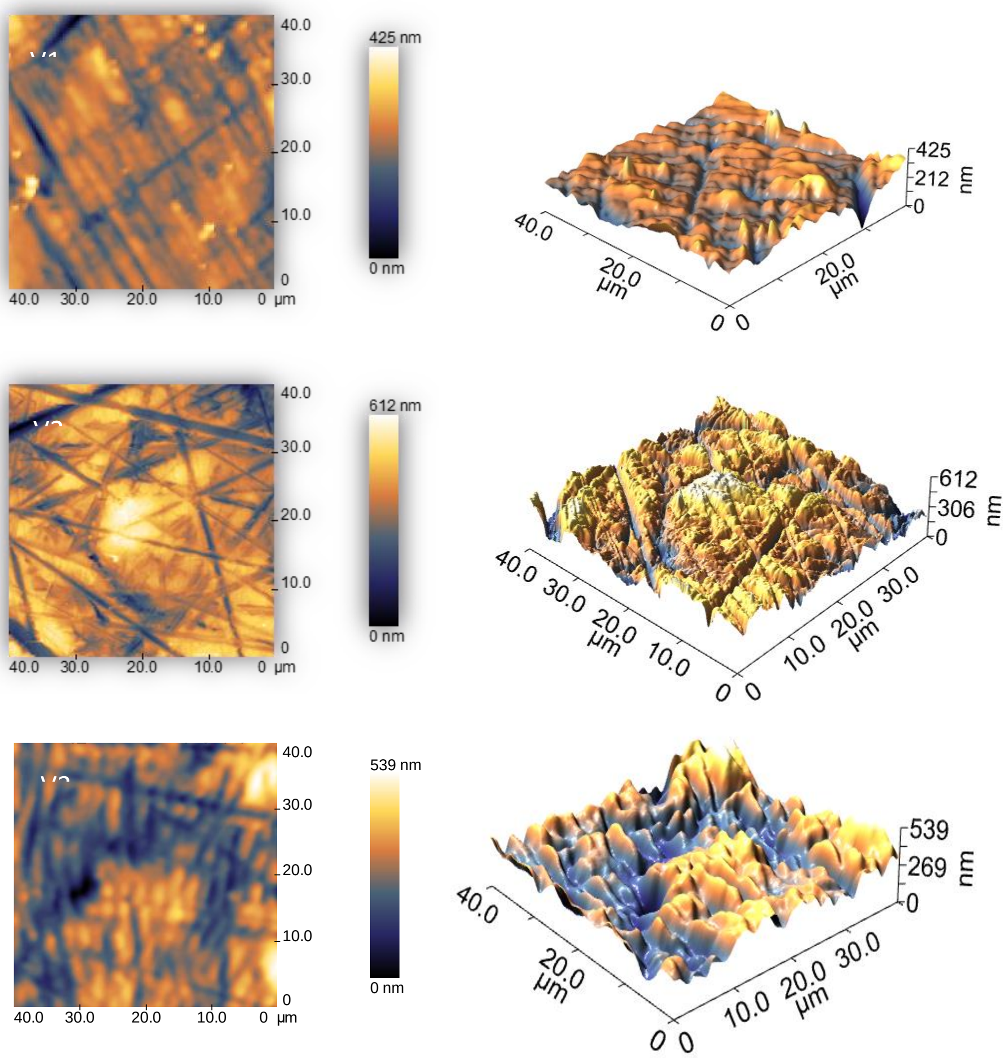

Fig. 3. Surface topographies obtained by atomic force microscopy of the three samples analyzed

Table 1. Surface roughness parameters

Parameter	*V1*	*V2*	*V3*
Ra (nm)	34.03 ± 7.30	58.17 ± 9.93	72.23 ± 11.15
RMS (nm)	44.82 ± 9.48	75.06 ± 12.09	92.43 ± 13.36
Skew	-0.0576 ± 0.31	-0.4196 ± 0.29	0.2922 ± 0.29
Kurtosis	1.844 ± 0.67	2.456 ± 1.70	1.219 ± 1.73

Regarding EDX analysis the atomic percentage for the identified elements are presented in Table 2.

Table 2. Surface roughness parameters

Element	*Atomic % - V1*	*Atomic % - V2*	*Atomic % - V3*
Ti	55.07 ± 2.42	66.65 ± 1.21	35.65 ± 0.75
Zr	8.36 ± 0.52	9.99 ± 0.32	5.41 ± 0.31
Ta	0.83 ± 0.14	0.93 ± 0.09	0.51 ± 0.09
Ag	0.64 ± 0.14	0.85 ± 0.05	0.50 ± 0.06
O	35.11 ± 2.72	21.59 ± 1.41	57.70 ± 0.74
Na	-	-	0.23 ± 0.07

Viewed comparatively, it is observed the alloy kept in concentrated HCl had the lowest atomic percentage of Oxygen, which could be explained by the fact the oxide layer was dissolved [28], while the one kept in sodium hydroxide had the highest Oxygen atomic percentage and some Na presented at the surface. Most likely the hydroxide ions attacked the oxide layer presented at the surface, leading to the formation of sodium titanate and possibly sodium zirconate. A possible mechanism for the reaction of titanium oxide with sodium hydroxide is presented below [29,30]:

(1) $TiO_2 + NaOH \rightarrow HTiO_3^- + Na^+$

(2) $Ti + 3OH^- \rightarrow Ti(OH)_3^+ + 4e^-$

(3) $Ti(OH)_3^+ + e^- \rightarrow TiO_2 \cdot H_2O + 0.5H_2 \uparrow$

(4) $Ti(OH)_3^+ + OH^- \rightarrow Ti(OH)_4$

(5) $TiO_2 \cdot nH_2O + OH^- \rightarrow HTiO_3^- \cdot nH_2O$

The reaction takes place in different stages, firstly the oxide layer is partially dissolved in the hydroxide solution, after which titanium is hydrated, leading to negatively charged hydrates, that can form a titanate hydrogel layer.

3.2. Wettability and microhardness analysis

Measurements of the contact angle and of microhardness revealed that the pretreatments applied changed both the surface energy and the mechanical properties of the alloy testes. The results are presented in Table 3, showing that the alloy kept in concentrated HCl has a slightly hydrophobic surface, which could be explained by the fact that this alloy has the thinnest layer of oxides on the surface, mostly being dissolved in acid, while the alloy kept in sodium hydroxide has the lowest contact angle and the highest microhardness, which could be explained by the reaction between the sodium hydroxide and the oxide layer and by the formation of sodium titanate on the surface, titanium being the most abundant.

Table 3. Water contact angle measurements

	V1		*V2*	*V3*
Contact angle value (°)	81 ± 3.2		100 ± 1.8	56 ± 2.6
Microhardness (HV)	269 ± 7.2		272 ± 4.6	326 ± 5.1

Conclusions

Although surface pretreatments are usually employed before coating deposition on metallic alloys, the process influence is rarely investigated in more detail. It can be seen from our study how two relatively simple surface pretreatments have an influence on the surface roughness, chemical composition, contact angle and microhardness. It was observed that the alloy kept in concentrated HCl for 10 minutes presented more inordinately peaks/valley feature, having also a hydrophobic surface, while the alloy kept in 10 M NaOH for 24h formed a layer on the surface, incorporating Na, which also changed the water contact angle to more hydrophilic value and increased the microhardness. It is clear that surfaces with different physical-chemical characteristics will interact differently with a coating regarding adhesion and therefore influence the whole performance of the coated alloy. As a conclusion it is to mention as well that the present investigation it will be valuable in selecting the pretreatment of a future coating taking into account its – chemical characteristics needs.

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