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CORROSION BEHAVIOR AND WETTING PROPERTIES OF CAST TNZT ALLOYS

KOROZIJA IN OMAKANJE LITIN NA OSNOVI Ti, Nb, Zr IN Ta

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Five experimental alloys Ti-9Nb-8Zr-xTa-2Ag (x = 0, 5, 10, 15) were obtained and analyzed in the as-cast condition. The microstructure, corrosion behavior and surface free energy on the samples polished and corroded in artificial saliva were investigated. The microstructure is comprised of a mixture of α and β phase and the proportion of β phase increases with tantalum content increase. At 10 % Ta a drastic change in the microstructure was observed that severely altered the corrosion behavior, as the corrosion rate increased significantly beyond this point. The alloys are hydrophilic and corrosion tends to increase the surface free energy of the alloy with 15 % Ta that was mostly affected by the corrosion. The tantalum content increase affects directly the microstructure and indirectly the corrosion and surface wetting properties of the experimental alloys.

Keywords: TNZT, corrosion, surface wetting

Avtorji v članku opisujejo analizo petih eksperimentalnih TNZT zlitin v litem stanju z različno kemijsko sestavo; Ti-9Nb-8Zr-xTa-2Ag (x = 0, 5, 10, 15). Določili in analizirali so mikrostrukturo, korozijsko obnašanje in prosto površinsko energijo na poliranih in na z umetno slino korodiranih vzorcih. Mikrostruktura zlitin je sestavljena iz α in β faze. Delež β faze narašča z naraščajočo vsebnostjo tantala v zlitini. Avtorji ugotavljajo, da pri 10 *w*/% Ta pride do drastične spremembe mikrostrukture, kar močno spremeni korozijsko obnašanje in zato pomembno naraste hitrost korozije. Zlitine so hidrofilne narave (se dobro omakajo s kapljevinami) in korozija ima tendenco povečevanja proste površinske energije zlitine. Tako je zlitina s 15 *w*/% Ta najbolj občutljiva na korozijo. V zaključku avtorji poudarjajo, da povečevanje vsebnosti Ta v zlitini direktno vpliva na mikrostrukturo ter s tem indirektno na korozijo in omakanje površine eksperimentalnih zlitin.

Keywords: biokompatibilne Ti-Nb-Zr-Ta zlitine (TNZT), lito stanje, korozija, omakanje površine

1 INTRODUCTION

Alloys from the titanium–niobium–zirconium–tantalum system (TNZT) are of specific interest for medical applications given their good biocompatibility, mechanical properties and their unique feature of a low and controllable elastic modulus, and, with the addition of specific alloying elements (Cu, Ag), antibacterial properties can be induced.

Titanium and its alloys show an excellent corrosion resistance in the human environment,[1,2] but their chemical composition and microstructure[3,4] are major influencing factors that need to be accounted for when new alloys are obtained.[5]

The microstructures of the alloys from the TNZT system show a mixture of α, β, α', α'' and β' (in various proportions) that depend on the chemical composition and processing route.[6] This association of phases plays a crucial role on the efficiency of the biomaterial.

Once inserted in the human body the alloys interacts with the biological aqueous media and it can be damaged, causing the release of metal ions and the adhesion and spreading of the cells around the implant is affected. The biomaterial efficiency depends on the interaction with surrounding tissues. According to the studies of Hallab et al.,[7] Schakenraad et al.[8] and Ruardy et al.[9] the surface free energy (SFE) of the material is the main factor that affects cell adhesion and proliferation. The surface free energy of a solid depends mainly on the chemical composition and texture of the surface,[10] thus a vicious circle appears where both factors can be altered when corrosion occurs and the surface characteristics are modified.

This study aims to verify whether the surface free energy of the experimental alloys is modified after the corrosion tests. The surface free energy was determined on an as-polished surface of the alloys, and then on the surface of an alloy that was corrosion tested in artificial saliva.

2 EXPERIMENTAL PART

The chemical composition of the alloys was designed using the molecular orbital calculation of electronic structures,[11] and, following a study by design of experiment, a chemical composition of Ti-9Nb-xTa-8Zr-2Ag

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Table 1: Chemical composition of the alloys (in *w*/%)

Code	Nb	Zr	Ag	Ta	Ti
A0	9.17 ± 0.33	8.13 ± 0.24	1.92 ± 0.13	Not available	Bal.
A5	8.62 ± 0.59	7.90 ± 0.42	1.91 ± 0.04	4.91 ± 0.33	Bal.
A10	9.51 ± 0.74	7.37 ± 0.45	1.85 ± 0.03	9.94 ± 0.36	Bal.
A15	9.35 ± 0.19	7.75 ± 0.23	1.79 ± 0.12	15.71 ± 0.55	Bal.
A20	9.78 ± 0.57	8.83 ± 1.33	2.51 ± 0.65	19.08 ± 1.53	Bal.

(where x = 0, 5, 10, 15 and 20) was chosen, to study the influence of tantalum addition on the corrosion and surface free energy of the alloy.

The alloys were obtained by vacuum arc remelting using an ABD MRF900 from bulk titanium (99.95 % pure), niobium (99.95 % pure), zirconium (99.95 % pure), tantalum (99.95 % pure) and silver (99.97 % pure) as cylindrical ingots 10 mm in diameter and 150 mm in length.

The alloys were first studied by scanning electron microscopy (SEM) using an ESEM Quattro S and an Everhart–Thornley detector (ETD) and an acceleration voltage of 30 kV. The microscope is equipped with an EDS UltraDry60M detector for energy-dispersive spectroscopy analysis. The surface free energy was determined using a contact-angle tensiometer KRUESS DSA30 using three liquids (water, diiodo-methane and ethylene glycol) and the corrosion tests were conducted using a Gamry Potentiostat/Galvanostat/ZRA model 600 in artificial saliva (0.84 g/L NaCl + 0.15 g/L $CaCl_2$ + 1.2 g/L KCl + 0.05 g/L $MgCl_2$ + 0.34 g/L K_2PO_4).

The surface free energy of the alloys was determined first on the as-polished surfaces (0.2 μm emulsion) and on the surfaces resulting after the corrosion tests.

3 RESULTS

The chemical composition determined by energy-dispersive x-ray spectroscopy for the 5 alloys is presented in **Table 1**. The sample coding is represented by an uppercase "A" followed by numbers that represent the target tantalum content, in weight percent.

The resulting chemical composition is in close agreement with the projected one. The microstructure of the alloys can be observed in **Figure 1** revealing a gradual transition from a Widmanstätten microstructure for a typical $\alpha + \beta$ alloy (**Figures 1a** to **1c**) towards a structure comprised of predominant β phase with α lamellae (**Figures 1d** and **1e**).

The corrosion tests were performed on samples that were previously immersed for 168 h in artificial saliva, and the Tafel curves are depicted in **Figure 2**.

The aspects of the Tafel curves presented above show that mild corrosion occurred (most likely pitting corrosion) by slight fluctuations in the positive region of the potential, followed by repassivation, reflected by the slope change.[12] This behavior can be observed on all samples, except A15.

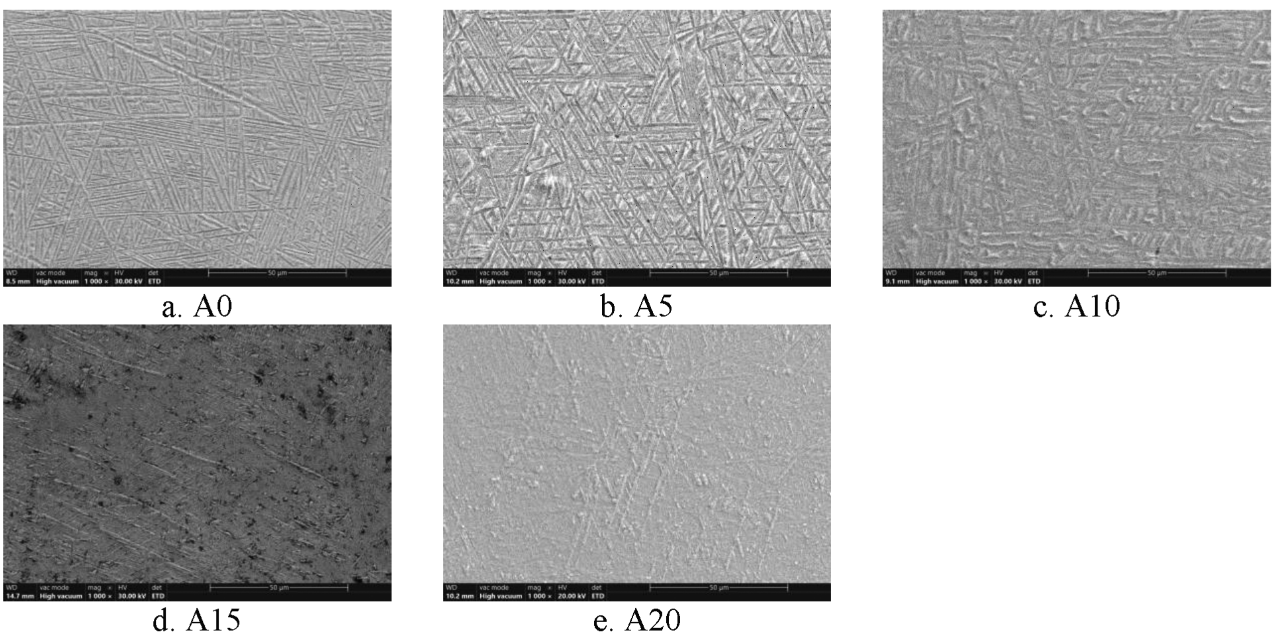

Figure 1: Scanning electron micrographs showing the microstructure of the experimental alloys

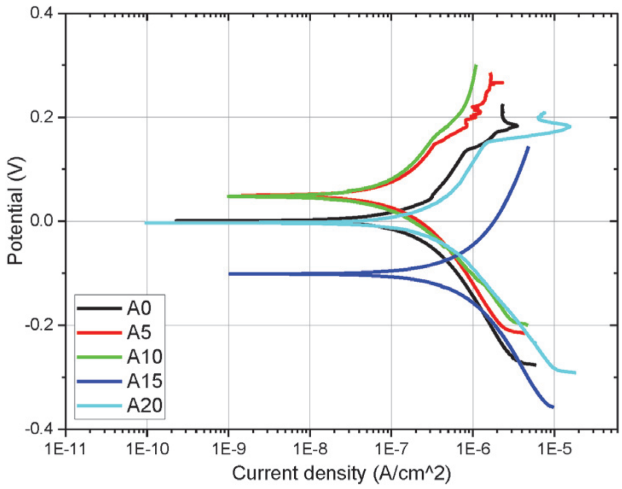

Figure 2: Tafel curves for the experimental alloys

Processing the Tafel the corrosion current, potential and rate were obtained and presented, as charts, in **Figure 3**.

From a corrosion-current perspective, a low value reflects a higher corrosion resistance, and, from the corrosion potential, a more positive value also reflects a higher corrosion resistance.[13] Given these main aspects the alloy with 10 % Ta shows the best corrosion resistance, while the one with 15 % Ta, the lowest. The corrosion rate coincides with this inference, as the highest corrosion rate appears for the alloy with 15 % Ta and the lowest at the alloy with 10 % Ta.

The study regarding the surface wetting is presented as a comparison between the samples analyzed on a polished surface, designated as "Polished" and the ones analyzed after the corrosion test in artificial saliva, designated as "Saliva". In **Figure 4** charts are presented that depict the comparison of the contact angle when water was used as a liquid (**Figure 4a**) and the values of the surface free energy were computed using the OWKR method (**Figure 4b**).

The value of the contact angle reflects a hydrophilic surface, increasing this tendency as the tantalum content is increased (the contact-angle value for water decreases). The differences between the contact-angle values for water on polished and corroded surfaces can be considered significant for the alloy with 15 % Ta and the one without.

The surface free energy does not appear to vary significantly for the alloys with (5, 10 and 20) % Ta, while for the alloys without and 15 % Ta a significant increase is observed.

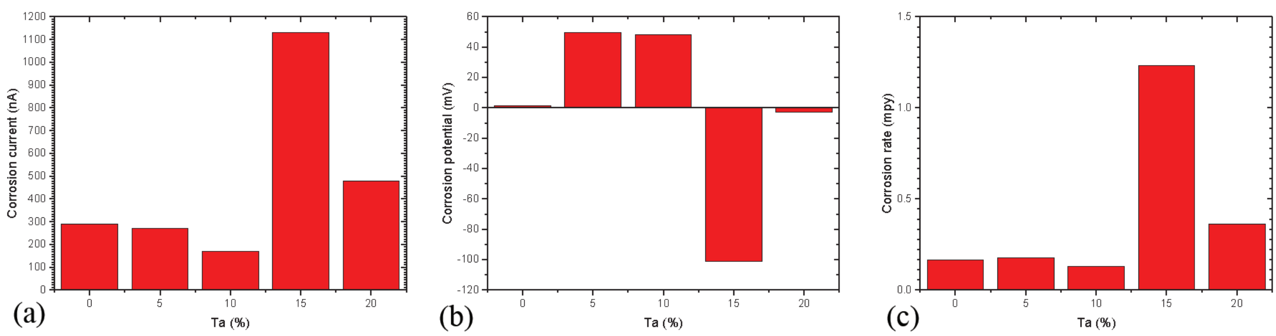

Figure 3: Comparison of corrosion results showing: a) corrosion current, b) corrosion potential and c) corrosion rate

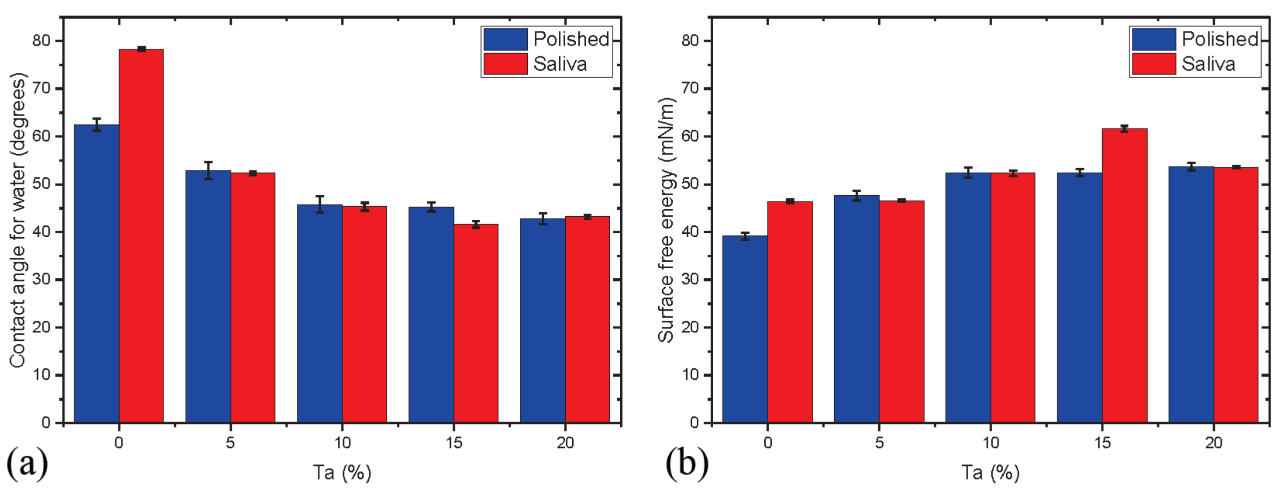

Figure 4: Comparison of: a) contact-angle values for water and b) surface free energy of the polished and corroded samples

4 DISCUSSION

The increase of the tantalum concentration modifies the α and β phase proportions, as expected, but their morphology and distribution is the main influencing factor for the corrosion and surface characteristics, especially when the material is as cast. A major change in morphology and distribution appears at 15 % Ta, when, from a basket-weave structure,[14] the microstructure changes towards a β matrix with α lamellae.[15]

The corrosion resistance of the alloys is above the one of the classical Ti-6Al-4V[16] and in close agreement with other alloys in the TNZT system.[16–21] The improved corrosion resistance, according to Gunawarman,[20] can be attributed to the formation of Nb and Ta oxides, along the Ti oxide that naturally forms. As Ta content is increased an increase in the corrosion resistance is to be expected, yet given the as-cast structure, the corrosion resistance depends mostly on the homogeneity and phase distribution.

The surface free energy on the polished and corroded samples showed significant changes for the alloy with 15 % Ta and the alloy without. This behavior most likely occurs mostly due to changes in the microstructure: as the tantalum content is increased, from a uniform $\alpha + \beta$ mixture the structure changes towards a β matrix with randomly dispersed α lamellae constituting favorable aspects for localized corrosion. As the corrosion occurs, the surface topography and chemical composition are changed, leading to an increase in the surface free energy.[22] The material is more prone to chemical interactions with the environment.

5 CONCLUSIONS

For the as-cast experimental alloys from the TNZT system it was found that a tantalum addition generates a transition from a typical basket-weave one for the $\alpha + \beta$ alloys to one comprising a β matrix with α lamellae that can be attributed to near β alloys.

The morphology and phase distribution play a crucial role in the corrosion behavior and wetting characteristics. As the microstructure shows a uniform distribution of α and β phase (up to 10% Ta in this study) the corrosion behavior is superior to the structures when β phase appears as a matrix and α as dispersed lamellae.

The surface free energy tends to increase as the tantalum content increases, while on the corroded samples the surface free energy shows significant changes on samples severely affected by corrosion.

The tantalum content appears to influence the corrosion behavior and the surface free energy in an indirect manner. The changes in microstructure (influenced by tantalum addition) appear to have a greater weight than tantalum alone.

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