



COMPARATIVE CORROSION BEHAVIOUR OF TITANIUM ALLOYS (TI-15MO AND TI-6AL-4V) FOR DENTAL IMPLANTS APPLICATIONS: A REVIEW

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ABSTRACT

Nowadays there is an increasing need of biocompatible materials due to the toxicity of the metals used. Focusing in dental implants, there are several problems concerning the corrosion of implants, for example, the high concentration of fluoride ions, which make an acid medium. Considering that titanium has excellent biocompatibility and some resistance to corrosion, one way to enhance this property is alloying Ti with other metals. The most used alloy is Ti-6Al-4V, in spite of its toxicity. Hence, there is a need to make new alloys which are resistant to corrosion and less toxic. One that stands out is Ti-15Mo. The objective of this review is to compare these two alloys in terms of corrosion behaviour and possible treatments to improve their corrosion resistance.

Keywords: Titanium Alloys, Corrosion, Dental Implants, Osseointegration, Surface Treatments

COMPARAÇÃO DE COMPORTAMENTOS DE CORROSÃO DE LIGAS DE TITÂNIO (TI-15MO E TI-6AL-4V) PARA APLICAÇÕES EM IMPLANTES DENTÁRIOS: REVISÃO

RESUMO

Atualmente existe uma necessidade crescente de materiais biocompatíveis devido à toxicidade dos metais usados. Nos implantes dentários existem vários problemas relacionados com a corrosão dos implantes, como a elevada concentração de íons fluoreto, tornando o meio ácido. Considerando que o titânio tem uma excelente biocompatibilidade e alguma resistência à corrosão, uma forma de melhorar esta propriedade é formando ligas de Ti com outros metais. A liga Ti-6Al-4V é a mais usada, apesar da sua toxicidade. Consequentemente, há necessidade de fazer novas ligas que sejam resistentes à corrosão mas menos tóxicas. Uma que se destaca é a Ti-15Mo. O objetivo desta revisão é comparar estas duas ligas em termos do comportamento à corrosão e possíveis tratamentos para melhorar a resistência à corrosão.

Palavras-chave: Ligas de Titânio, Corrosão, Implantes Dentários, Osseointegração, Tratamentos de Superfície

1. INTRODUCTION

Currently there is a growing concern in developing implants due to aesthetical and medical reasons [1]. In Table 1, some properties of implants are listed, the most relevant are biocompatibility, low toxicity and high resistance to corrosion since the medium they are exposed to is extremely aggressive [2]. Aesthetically there is a greater demand in dental implants, which face several problems concerning corrosion due to certain aspects, such as temperature and pH. Titanium and its alloys are used in these applications since they are biocompatible in human beings, have extremely good bioactivity and present resistance to corrosion. In spite of this, it is needed to increase their resistance and, in some cases, lower their toxicity.

Titanium can crystallize in three different forms such as alpha, alpha + beta and beta. At 1155.65 K, Ti is in phase alpha (hexagonal packed, hcp) and above this temperature it crystallizes in phase beta (body centred, bcc) [3, 4]. Although alpha titanium alloys are resistant to corrosion, they have limited low temperature strength. Hence, beta phase is more attractive since it has high strength, low elasticity modulus, good corrosion resistance and presents excellent biocompatibility [1, 3, 5]. Also, alpha + beta alloys can possess high corrosion resistance depending on the amount of alpha and beta phases.

There are two methods to stabilize a phase, using high temperatures or alloying new elements. To obtain the alpha phase, elements like aluminium, oxygen, nitrogen and carbon are used. For beta phase, it is used molybdenum, vanadium, niobium, tantalum, iron, tungsten, chromium, silicon, cobalt, nickel, manganese and hydrogen. Elements like zirconium are neutral, since they won't preferentially stabilize a phase. In Figure 1, there is an illustration of how the phases are stabilized, considering temperature and the amount of beta stabilizers. Implants can undergo several kinds of corrosion, from uniform to stress corrosion. However, galvanic corrosion and pitting are the most common types in titanium implants [1, 6-18].

Table 1 - Implant properties. Adapted from [2]

Implant Characteristics		
Mechanical Properties	Manufacturing	Compatibility
Toughness Hardness	Capability of material to get safe and efficient sterilization	Changes in mechanical/physical/chemical properties
Strength and Fatigue strength	Superior techniques to obtain excellent surface finish or texture	Degradation leads to harmful effects
Wear resistance	Quality of raw materials	Tissue reactions
Ductility Elasticity	Consistency and conformity to all requirements	
Time dependent deformation	Fabrication methods	Local damaging changes
Yield stress	Cost of product	

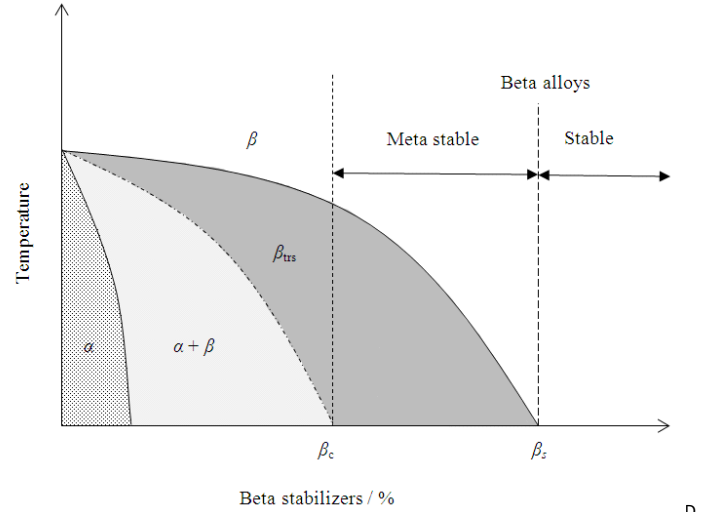


Fig. 1 - General illustration of a phase diagram for titanium alloys. β_c corresponds to the minimum amount of β stabilizer to have a metastable β phase and β_s refers to the minimum amount of β stabilizer for obtaining β stable alloys, adapted from [1, 19].

Even if an implant does possess great corrosion resistance, it can fail due to low osseointegration, which is a direct structural and functional connection between the bone and the surface of an implant [20, 21]. This means that an implant cannot just have great resistance to corrosion but also good osseointegration since this is correlated with the corrosion process [8]. To enhance this aspect there are several methods to improve the surface roughness of the implant for better osseointegration, and therefore better corrosion resistance [22].

2. DISCUSSION

Ti is the metal of choice for several kinds of implants (commercially pure - c.p. - Ti and unalloyed Ti being the most used [23-25]) since it has half the density of copper (Ti - 4.5 g·mL⁻¹, Cu - 8.94 g·mL⁻¹), which makes it a very light metal, and possesses high resistance to corrosion when compared to other metals used [26]. This comes from the fact that Ti forms a spontaneous TiO₂ passive film due to the presence of oxygen in the air. As can be seen in Figure 2, this is the thermodynamically most stable form at the range of neutral pH (saliva's pH) [27]. It is also possible to see that this passive layer is maintained over a wide range of pH and potentials (-0.95 to 1.85 V). However, its elastic modulus, tensile and yield strengths are low, as can be seen in Table 2, making it hard to use in stress situations [23, 28, 29]. To overcome this problem, titanium alloys are developed.

Table 2 - Mechanical properties of unalloyed Ti and c.p. Ti.

Material	Mechanical Properties				Reference
	Tensile Strength (Mpa)	Yield strength (MPa)	Elastic Modulus (Gpa)	Elongation (%)	
Ti (unalloyed)	785	692	105	-	[3]
Ti (grade 1)	240	170	103	24	[29]
Ti (grade 2)	345	275	103	20	[28, 29]
Ti (grade 3)	450	380	103	18	[29]
Ti (grade 4)	550	483	104	15	[29]

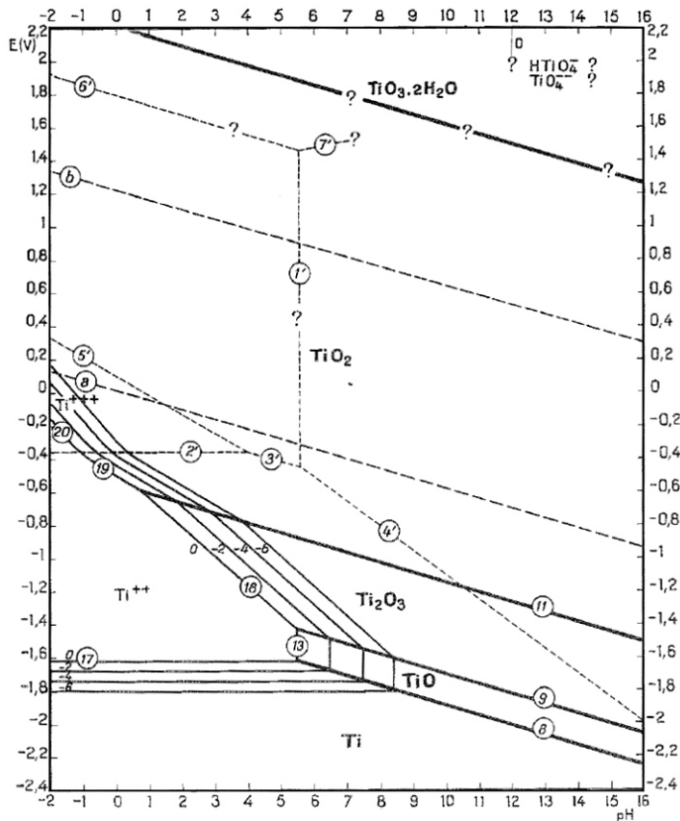


Fig. 2 - Pourbaix diagram for the system titanium-water at 25 °C and 1atm, from [30].

Nonetheless, not every alloy can be turned into an implant, according to the metallic element that is in its composition, due to the toxicity of some metals *in vivo*, as it is shown in Figure 3 [31]. In spite of this, the mainly used alloy is Ti-6Al-4V since it presents greater elastic modulus and yield strength than Ti. As a non-toxic alternative, new alloys like Ti-15Mo have emerged. The objective of this review is to compare corrosion and mechanical properties of these two alloys.

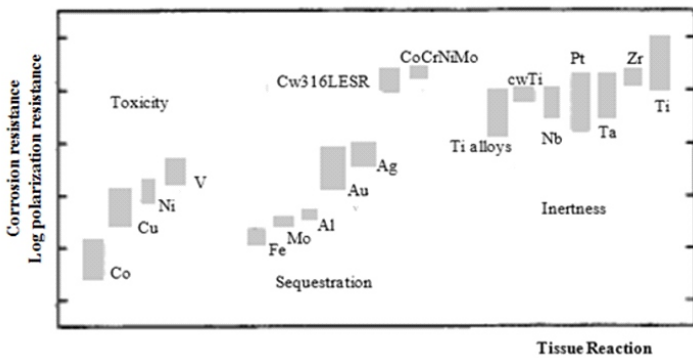


Fig. 3 - Possible tissue reactions according to corrosion resistance from different metallic elements or alloys. Adapted from [31].

• Titanium alloys

There are several methods to obtain these alloys, which can be casting, superplastic forming, melting using vacuum arc (VAR), electron beam (EB) or plasma arc hearth melting (PAM) [5, 28, 32]. According to the type of method used, the alloys can have different properties, as can be seen in Table 3. As mentioned earlier, the optimal characteristics for the implants are low elastic modulus and high tensile and yield strengths, being Ti-15Mo the best alloy to fulfill these parameters.

Table 3 - Mechanical properties of Ti-6Al-4V and Ti-15Mo according to the manufacturing process and different treatments.

Alloy	Mechanical Properties				Reference
	Tensile Strength (MPa)	Yield strength (MPa)	Elastic Modulus (GPa)	Elongation (%)	
Ti-6Al-4V	976	847	-	5	[28]
Ti-6Al-4V (as-cast)	1173	999	113	6	[33]
Ti-6Al-4V (superplastic forming)	954	729	-	10	[34]
Ti-6Al-4V (annealed)	895-930	825-869	110-114	6-10	[28]
Ti-15Mo	700	480	78	20	[35]
Ti-15Mo (as-cast)	921	745	84	25	[33]
Ti-15Mo (annealed)	874	544	78	21	[28, 36]

• Ti-6Al-4V

Ti-6Al-4V is an alpha plus beta type alloy, in which the stabilizers are aluminium (alpha) and vanadium (beta), the nominal composition is listed in Table 4. This alloy presents great mechanical properties and high resistance to corrosion [10, 37], being one of the most used materials in dentistry. In spite of this, it has a much greater elastic modulus than bone, causing stress shielding effect [5, 38]. Adding to this, the implant is not electrochemically stable, which can undergo a process of leaching, leading to an increase of vanadium and aluminium concentration in the soft tissues [39] that can cause several diseases like osteomalacia, peripheral neuropathy and Alzheimer's disease [40-42]. This fact presents a major concern in human health care, requiring other implants with no possible damage to human health. In this line of thinking, other alloys with non-toxic components like Mo are being developed.

Table 4 - Ti-6Al-4V composition. Adapted from [32].

Element	Nitrogen	Carbon	Hydrogen	Iron	Oxygen	Aluminium	Vanadium	Titanium
Composition (max.)	0.050	0.100	0.013	0.300	0.200	6.750	4.500	balance

• Ti-15Mo

One of the most promising elements for alloying titanium is molybdenum, since it is one of the materials that can highly stabilize the beta phase, having superior properties when compared to c.p. Ti, Ti and Ti-6Al-4V [43, 44]. Also Mo increases the passive range of titanium alloys [44] and it is expected to be a non-toxic and non-allergic element [45]. Ho *et al.* studied several Ti-Mo alloys with different Mo concentration, demonstrating that a minimum amount of 10 % Mo is needed to stabilize the beta phase [46], which goes to previous data presented by Bania [47]. In this binary system Ti-15Mo stands out due to the combination of great corrosion resistance and mechanical properties [48, 49]. In Table 5 is listed the nominal composition of this alloy [35].

Table 5 - Ti-15Mo composition. Adapted from [35].

Element	Nitrogen	Carbon	Hydrogen	Iron	Oxygen	Molybdenum	Titanium
Composition (max.)	0.050	0.010	0.015	0.100	0.200	16.000	balance

• Corrosion, analysis and treatments

Corrosion definition according to IUPAC, is an "irreversible interface reaction of a material (metal, ceramic or polymer) with its environment, which results in consumption of the material or in dissolution into the material of a component of the environment" [50]. In Figure 4, it is shown an illustration based on all types of corrosion. Although all these types of corrosion can occur in dental implants, the most commonly reported for titanium are galvanic and pitting, as mentioned earlier.

Galvanic corrosion comes from coupling two different types of metals together. In dentistry, this mainly happens when the titanium implant interacts with a support structure made from other material with a different galvanic potential, in the presence of saliva or other body fluid. This difference in the galvanic potential leads to the corrosion process. Galvanic corrosion of an implant can lead to biological effects due to the dissolution of some components of the alloys as well as to the destruction of the bone because of the current flow resulting from the galvanic coupling of the metals [1, 6-8, 11, 17, 26].

The pitting corrosion process occurs when the potential of the film is superior to the oxide. For titanium this usually occurs in the presence of fluoride, chloride and sulphide ions which are present in different mediums, attacking the passive layer and causing it to break into pits [9-16, 18].

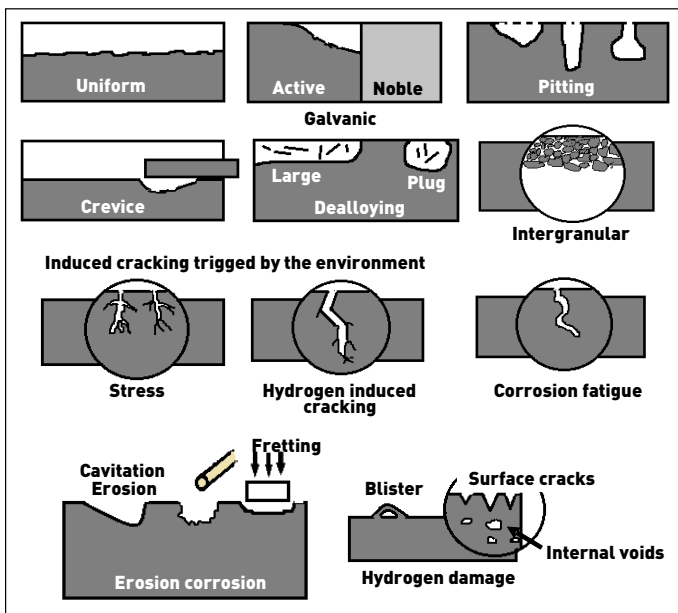


Fig. 4 - Illustration of different types of corrosion. Adapted from [51].

• Mediums

To study *in vitro* corrosion resistance, there are three types of mediums commonly used, all of them with applications in dentistry. Hank's [52] and Ringer's [44] solution with typical compositions which can be seen in Table 6 and artificial saliva that according to different concentrations of the components can be grouped in three types, as shown in Table 7 [53]. Besides these specific mediums, it is possible to work in an acidic one containing a great amount of fluoride ions which will lead to the formation of fluoronic acid [54]. The objective of using this kind of medium is to have the most aggressive one. When the concentration of fluoronic acid is superior to 30 ppm, the TiO₂ passive film changes and loses its mechanical properties, this being one of the reasons why alloying some elements with titanium is important [55-57]. One of the problems when analysing data from several research groups, is that each one

uses different concentrations in the presented mediums or other mediums, making it hard to compare all the results and reach to a definite conclusion [5, 10, 24, 33, 37, 44, 52, 53, 55-60].

Table 6 - Typical composition of Hank's [52] and Ringer's [44] solution.

Compounds	Solutions (g·L ⁻¹)	
	Hank	Ringer
Sodium chloride	8.0	6.80
Potassium chloride	0.40	0.40
Sodium bicarbonate	0.35	2.20
Sodium phosphate monobasic monohydrate	0.25	0.14
Di-sodium hydrogen phosphate dehydrate	0.06	-
Calcium chloride	-	0.20
Calcium chloride dehydrate	0.19	-
Magnesium chloride	0.19	-
Magnesium sulphate heptahydrate	0.06	0.20
Glucose	1.00	1.00
pH	6.9	7.8

Table 7 - Composition of several types of artificial saliva. Adapted from [53].

Compounds	Artificial saliva (g·L ⁻¹)		
	Sativeze	Xialine 1	Xialine 2
Sodium fluoride	0.0044	-	-
Sodium carboxymethylcellulose	10	-	-
Sodium chloride	0.87	0.85	0.85
Magnesium chloride	0.06	0.05	0.05
Calcium chloride	0.17	0.13	0.13
Potassium chloride	0.62	1.2	1.2
Di-potassium hydrogen orthophosphate	0.80	0.13	0.13
Potassium di-hydrogen orthophosphate	0.30	-	-
Sorbitol	29.95	-	-
Methyl p-hydroxybenzoate	0.35	0.35	1.00
Xanthan gum	-	0.92	0.18
pH	neutral		

• Osseointegration

Besides good corrosion resistance, there is a need to have good osseointegration properties [61]. If this does not happen, even having good resistance to corrosion, the implant will fail [22]. Some of the factors that affect this process are listed in Table 8, being the surface roughness, composition and design of the implant of the most importance [62, 63]. After the implantation process is done, it can have two kinds of response, one that leads to osseointegration and other to implant rejection. This happens due to the development of a capsule formed by fibrous soft tissue that does not allow the necessary biomechanical fixation [22]. Another reason to the rejection comes from corrosion, which affects some of the implant properties like tensile strength, fatigue life and the surrounding tissues [64, 65]. For osseointegration on titanium implants, it is needed that interactions between the bone and the implant surface are quick and suitable [22]. Several studies have shown that surface roughness in the range of 1 to 10 μm improves the contact between the bone and the implant surface [66, 67]. Also

titanium with smoother surfaces does not have a great contact with bone when compared with rougher ones [68]. Although surface roughness is one of the most important factors for the success of an implant there are still no standards for measuring this properties [69]. To improve osseointegration and corrosion resistance there are several possible treatments of implant surfaces, which can be divided in two major groups, coatings listed in Table 9 and surface roughness in Table 10. Some of the desirable coatings to enhance implant success are calcium dihydrogen phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) in form of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HA), since it has high biocompatibility and resistance [70-72]. Also used as possible coatings are perovskite (CaTiO_3), which presents greater osseointegration than titanium, with an optimal thickness of 50 μm without any degeneration and necrosis of the surrounding tissue [73]; and titanium dioxide (TiO_2), which increases the bone-to-implant contact, biomechanical fixation and survival rate [22, 66, 74, 75]. Adding to these possible treatments, surface-modified layer formation and immobilization of functional molecules and biomolecules can also be used [76]. Micro-arc oxidation, allows to form several types of coatings according to the composition of the substrate and electrolyte. Vapour deposition grants higher hardness, low friction coefficient and chemical inertness of the films.

Table 8 - Factors that affect osseointegration. Adapted from [62].

Osseointegration
Biomaterials
Implant design
Implant composition
Biomechanical factors
Surface characteristics
Surgical technique
Health and bone quality

Table 9 - Surface treatments based on several types of coating.

Treatment	Results	References
Micro-arc oxidation	Oxide/HA layers are formed with different thicknesses and porous oxide films.	[56, 60, 77]
Thermal spraying	Ti, HA, calcium silicate, Al_2O_3 , ZrO_2 and TiO_2 coatings with different ranges of thickness.	[3, 9, 55]
Vapour deposition	Hard nitrite layers (nitrogen implantation).	[3, 78]
Coating Laser cladding	TiN/Ti ₃ Al composite coatings.	[79]
Sol-gel	Calcium phosphate, TiO_2 , ZrO_2 and silica thin films.	[3, 80]
Electrophoretic deposition	Pure phases of hydroxyapatite films with uniform and wide range thicknesses, having strong adhesion properties.	[22, 64, 70, 81]
Biomimetic precipitation	Possible brushite coatings which are transformed into apatite, octacalcium phosphate or bone-like carbonate apatite deposits.	[22, 76, 82]

Electrophoretic deposition, allows a uniform and wide range of thickness, ability to coat complex shapes, ease of chemical composition control, strong adhesion and composes pure phases layers, although it is necessary to deposit a secondary one at high temperature. Through biomimetic precipitation, it is possible to control the layer thickness and heterogeneous nucleation of like-

bone crystal growth in the implant surface at control pH and temperature. In ion implantation, depending on the concentration of N^+ implanted on the surface, the layer can have different characteristics (uniform with good adherence or non-uniform).

When a surface is treated by thermal oxidation there is a decrease on the releasing ions, due to a change in the structure from anatase into rutile [83], and greater blood compatibility [3]. Also a formation of an oxide film occurs after cooling down and the treated material shows high corrosion resistance [84]. Shot-blasting improves fatigue life and surface hardness, but induces a residual stress layer in the treated material due to local plastic deformation. Laser beam irradiation gives irregular-shaped cavities and large depressions in the surface structure, contributing to a raise in interaction bone-implant. Also acid-etching increases this interaction [68]. It is said by Guéhenneq *et al.* that the process of osseointegration is still not well understood, making it imperative to develop more *in vitro* and *in vivo* studies [22]. Adding to this fact, although it is possible to use a large number of techniques, only plasma spraying is used in clinical practice, since others may contaminate the surface [85]. Although all these techniques can improve corrosion and/or osseointegration, the successes and long durability of the implant, will depend also on several factors such as prosthetic biomechanical and patient hygiene [22].

Table 10 - Surface treatments to improve the surface roughness of the implant.

Treatment	Results	References
Ion implantation	Ion implantation of N^+ consists of thin TiN particles distributed in a deformed matrix of α -Ti.	[3, 86]
Acid-etching	Micro pits (diameter from 0.5 to 2 μm).	[22, 85]
Shot-blasting	According to the type of shot-blasted particles, there are changes in the surface roughness and chemical composition.	[11, 66]
Roughness Anodic oxidation	Increasing of the oxide layer, transforming it from amorphous to microcrystalline.	[3, 22, 71, 81, 82]
Thermal oxidation	Formation of an oxide layer leads to changes in the microstructure.	[5, 69]
Laser beam irradiation	Formation of irregular cavities.	[11, 44, 85]

• Corrosion and Analysis

Since the corrosion process is strongly related to the structure/morphology of the materials there are several techniques that can be used for this type of analysis, such as optical microscopy (OM) and scanning electron microscopy (SEM), also possible with field emission (FE-SEM) for microstructure and/or macrostructure analysis [11, 22, 23, 33, 58, 71, 87, 88]. X-ray diffraction (XRD) can be used to evaluate the phase present in the sample [5, 33, 78, 89]. Electrochemical techniques that can be used to assess the corrosion response, such as potentiodynamic polarization, electrochemical impedance spectroscopy, chronoamperometric, cyclic voltammetry and several others [9, 11, 44, 60, 90, 91-93].

Kumar *et al.* obtained microstructures for c.p. Ti, Ti-6Al-4V and Ti-15Mo through OM as can be seen in Figure 5. It is possible to distinguish alpha, alpha plus beta and beta phases. C.p. Ti presents a feather-like microstructure which is typical in an alpha phase (Figure 5a), Ti-6Al-4V has elongated alpha-grains (light) and intergranular beta-grains (Figure 5b), and in Ti-15Mo it is possible to see a homogeneous phase composed mainly by beta-grains

(Figure 5c) [59]. In previous studies, also done by Kumar *et al.*, it was possible to observe that the microstructure for Ti-15Mo remains unchanged [37].

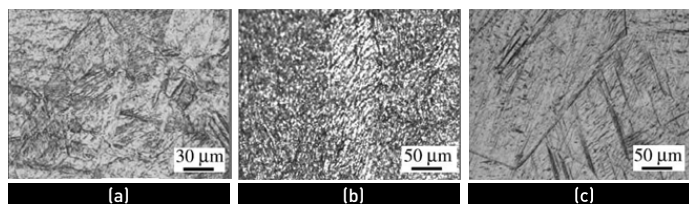


Fig. 5 - Microstructure for (a) c.p. Ti; (b) Ti-6Al-4V and (c) Ti-15Mo, obtained by OM. Adapted from [59].

Studies done by Ho *et al.* have reported the same structural type as can be seen in Figure 6, obtained by Auger electron spectroscopy (AES) [33], consistent with previous studies [46]. In earlier reports, Chen *et al.* have studied the binary alloy Ti-Mo with different concentrations of Mo, showing the same microstructure, in Figure 7, as seen in all these studies [94]. It is possible to see that there are some differences in the microstructure obtained by Kumar and other researchers, which are probably due to the method used to prepare the alloy. Kumar does not specify how the alloys were made, while other researchers use the same preparation techniques: arc-melting vacuum-pressure casting. As can be seen in Figures 6 and 7 the microstructures are in excellent agreement. Studies done by Oliveira *et al.* using (SEM) performed on the surface of Ti-15Mo, revealed that there are no defects, and a mapping of Mo and Ti showed that the surface has a homogeneous distribution of these elements, as can be seen in Figure 8.

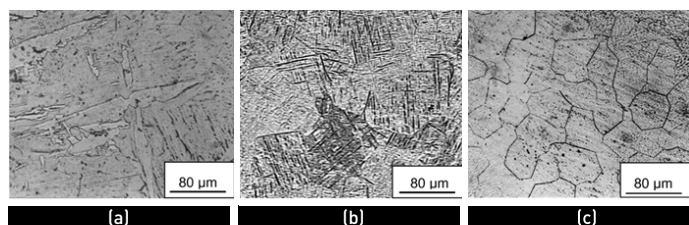


Fig. 6 - Microstructure for (a) c.p. Ti; (b) Ti-6Al-4V and (c) Ti-15Mo, obtained by AES. Adapted from [33].

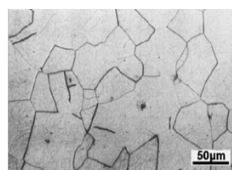


Fig. 7 - Microstructure Ti-15Mo, obtained by OM. Adapted from [94].

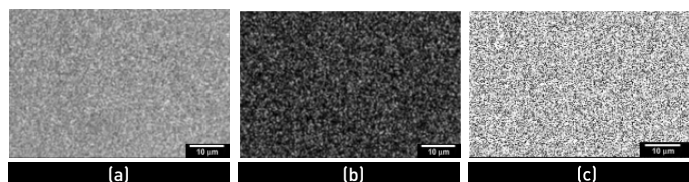


Fig. 8 - SEM images of (a) Ti-15Mo; (b) Mo (white points) mapping, and (c) Ti (white points) mapping. Adapted from [88].

Kumar *et al.* tested the corrosion resistance in Ti-15Mo in 0.15M NaCl solution with different concentrations of fluoride ions. To do so potentiodynamic polarization, electrochemical impedance spectroscopy and chronoamperometric studies were made. Results from potentiodynamic polarization show that, with the

increasing concentration of fluoride ions, the passive film becomes less insulating and less protective, due to a drop in the stability of the oxide layer. Results from electrochemical impedance spectroscopy supported the data obtained through potentiodynamic polarization, since there was a decrease in R_{ct} , an increase in C_{dl} showing the negative influence in the corrosion behaviour, which is a fact that is reported by several researchers [12, 55, 95-98]. The amount of release of Mo ions is very small, having a non-likely toxic effect, since the area exposed to the fluoride ions is limited [37]. Kumar *et al.* have also done a comparative study on the corrosion behaviour of c.p. Ti, Ti-6Al-4V and Ti-15Mo in a solution of NaCl with several concentrations of fluoride ions. All the materials showed the capability of making a passive film in the presence of fluoride ions. The behaviour of this film strongly depends on the concentration of fluoride in the solution. Chronoamperometric studies showed an increase in the steady state current density with the concentration of NaF, leading to the dissolution of the oxide film that protects the substrate, as well as the material itself, which goes accordingly to results earlier reported [37]. Also Figure 9 supports these results as it is possible to see that from the corrosion process, there was a change in the microstructure of all the materials in the alloys due to the dissolution and precipitation of the alloying elements in the material surface. In all the mediums the steady state current density was higher for Ti-6Al-4V and Ti-15Mo than it was for c.p. Ti, except for 0.15 M NaCl with 0.5 M NaF where Ti-6Al-4V had the lowest value. Oliveira *et al.*, have done several studies through the years. One of the earliest reports was the study of Ti-Mo microstructure and electrochemical behaviour, with several concentrations of Mo in Ringer solution. The passive layer demonstrated a high corrosion resistance, suggesting that it is not affected by the presence of fluoride ions. Also potentiodynamic polarization showed that the alloy presents a noble corrosion potential and a lower current density than pure Ti. Cyclic voltammetry was made at different scan rates to study the corrosion resistance for the alloys. At low sweep rates, the alloys showed high resistance to pitting corrosion [4].

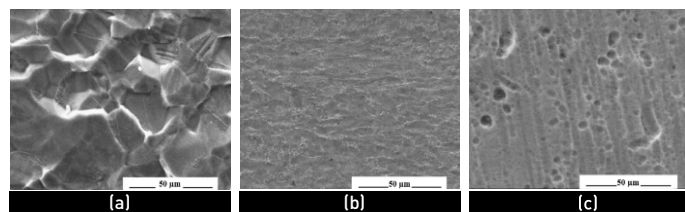


Fig. 9 - SEM images of (a) c.p. Ti; (b) Ti-6Al-4V and (c) Ti-15Mo after chronoamperometric oxidation experiments in a solution of NaCl/NaF. Adapted from [59].

More detailed studies were made by Oliveira *et al.*, in Na_2SO_4 and Ringer's solutions, showing a similar behaviour at open-circuit potential (E_{oc}), with the E_{oc} reaching a stable value, meaning that a spontaneous oxide layer is passivating the metals. Better corrosion resistance was shown in Na_2SO_4 than in Ringer's solution, due to higher E_{oc} values. Also cyclic voltammetry was made with typical profiles to support the fact that there is no pitting corrosion. This can be seen in Figure 10 where Ti-15Mo surfaces with different preparation conditions are shown. It is possible to see that there are no significant changes in the alloy surface with both solutions, in agreement with other results [99]. In other studies, done by Oliveira *et al.*, instead of changing the solution, the immersion time was changed (0, 1 and 360 h). In the first hour the E_{oc} changes quickly to higher potentials and stabilizes after 72 hours, showing

that the spontaneous passive film is being formed on the surface, as reported [4, 100]. These findings also revealed that the Ti-15Mo has the most positive values when compared to pure titanium. Also electrochemical impedance studies were done, exhibiting low impedance values for 1h immersion but increasing with the immersion time, although there is no relevant change in the impedance values after 24 h. High impedance values were also obtained, suggesting high corrosion resistance and a thin oxide passive layer, from the beginning of the studies, which goes accordingly to the analysis done by open-circuit potential.

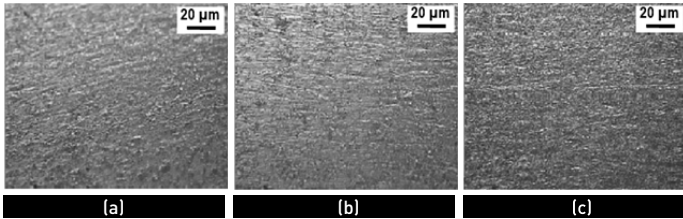


Fig. 10 - SEM images for Ti-15Mo with different preparation methods. Polished surface (a) and with anodic oxide growth in Na_2SO_4 (b) and Ringer solutions (c). Adapted from [99].

SEM analysis was done to verify changes in the surface material after the immersion time and it was possible to see that there are no significant changes in the surface, as can be seen in Figure 11, which supports the electrochemical results [100]. In recent reports done by Oliveira *et al.*, *in vivo* bone response was studied with a modified surface produced by laser beam irradiation. Initial characterization of the material was done by SEM, using as control samples machined implants (MS) and as test samples the laser-treated implants (LS). Figure 12 shows the controlled samples which present smooth surface in comparison with the laser-treated implants, which present a rougher surface. It was possible to conclude through the presented studies that the surface roughness increases the bone-implant interaction [90].

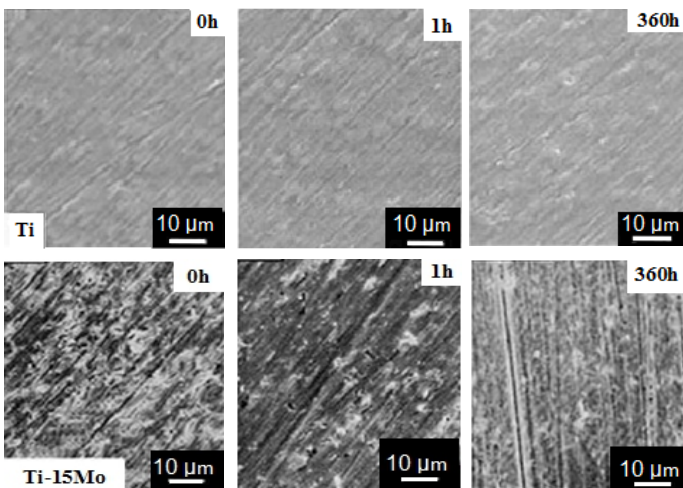


Fig. 11 - SEM images for pure Ti and Ti-15 Mo in Ringer solution after being immersed for 0, 1 and 360 h. Adapted from [100].

Barranco *et al.* have studied the influence of the surface roughness in Ti-6Al-4V by blasting the surfaces of the alloy with particles of $\text{SiO}_2/\text{ZrO}_2$ (small particles) and Al_2O_3 (larger particles) with different sizes to achieve different roughnesses. In Figure 13(a) is presented the Ti-6Al-4V surface treated with large Al_2O_3 particles and Figure 13(b) shows a magnification of the alloy treated with $\text{SiO}_2/\text{ZrO}_2$ particles. The blasting of smaller particles leads to a more homogeneous surface than larger ones, as can be seen in the

figures mention above. EDX analyses were done to study the composition of the sample blasted with $\text{SiO}_2/\text{ZrO}_2$ in different surface areas (spectra 1, 2 and 3), showing that the surface is mainly composed by Ti, Si and Zr, for spectra 1 and 2, and 3 is a free area, where the surface is mainly composed by Ti and Al, with low concentration of V as expected. In electrochemical studies done in Hank's solution after 60 minutes immersion, it was possible to verify that the increase in the surface roughness lead to an increase in the capacitance values, which means that the passive film is more exposed to pitting corrosion, due to the defects in the surface [14].

Recent reports done by Krawiec *et al.* [9], studied the action of the alloying elements in Ti-6Al-4V and the action of plastic deformation on the corrosion behaviour in a solution of NaCl. In Figure 14 is presented the microstructure for the initial material after being polished, where the alpha and beta phases are present as expected, while in Figure 15 is presented the mapping for the sample for Ti, Al and V. Electrochemical studies revealed that both phases presented the same electrochemical behaviour. Although cathodic reactions mainly occur in the alpha/beta interface, the presence of aluminium oxide delays this reaction. The study of several potential ranges allows to identify the formation of grains in the passive film, behaving like a blocking electrode from -600 to 0 mV vs. Ag/AgCl, while from 0 to 700 mV vs. Ag/AgCl, no blocking effect was reported. Also the passive current density and dopants concentration showed an increase due to the dissolution of aluminium and vanadium. In addition, this alloy presented pitting corrosion at the potential of 700 mV vs. Ag/AgCl. The increase of the surface roughness and dislocation density affected the corrosion behaviour, leading to an increase of the cathodic current [9].

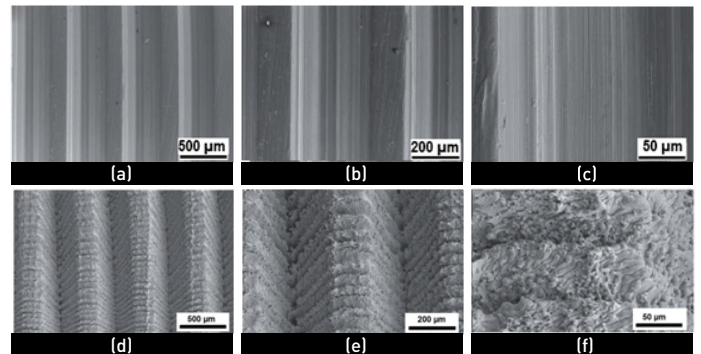


Fig. 12 - SEM images of Ti-15Mo morphology for MS - (a), (b), (c) - and for LS - (d), (e), (f). Adapted from [88].

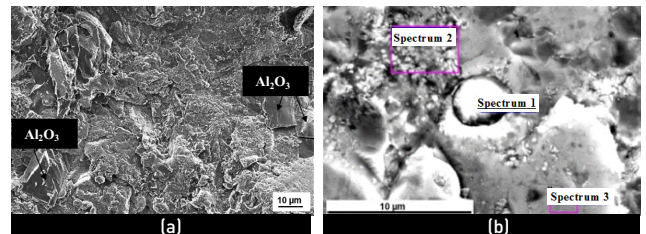


Fig. 13 - (a) SEM image for Ti-6Al-4V treated with Al_2O_3 and (b) FE-SEM images for Ti-6Al-4V treated with $\text{SiO}_2/\text{ZrO}_2$. Adapted from [14].

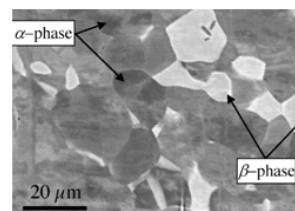


Fig. 14 - FE-SEM images of Ti-6Al-4V after treatment. Adapted from [9].

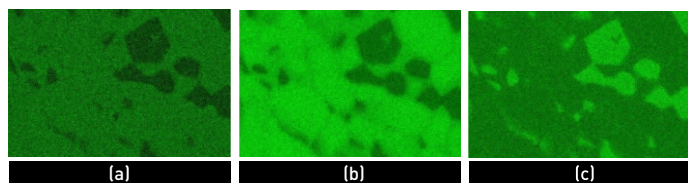


Fig. 15 - EDS mapping for (a) titanium, (b) aluminium, (c) vanadium. adapted from [9].

Fojt [101] studied other possible surface treatments for Ti-6Al-4V alloy. A nanotube structure was formed by anodic polarization and the initial alloy was coated with a diamond-like carbon (DLC) layer, as shown in Figure 16. After the manufacturing of the materials they were exposed to simulated body fluid (SBF), during 7 days. The nanostructured material revealed high adhesion to the initial sample, high resistance and capacitance for the metal/nanostructure interface, playing an important role in the corrosion behaviour, while the DLC surface is porous and homogenous which are characteristics desirable for osseointegration. Electrochemical studies revealed that the DLC layer had a decrease of the charge transfer resistance until 68 h of immersion, reaching afterwards a stable value. Impedance results showed that both surfaces have high corrosion resistance. Also both surfaces showed the deposition of calcium, phosphorus and magnesium. In the nanotubes the deposition was uniform, in opposition with the DLC surface that presents isolated points. For the osseointegration to be successful, a uniform deposition is desirable, making the nanostructure preferable for biomedical applications.

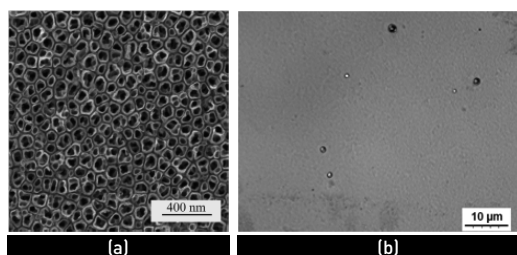


Fig. 16 - (a) SEM image of the nanotubular structure formed over Ti-6Al-4V and (b) surface of Ti-6Al-4V covered with DLC, obtained by confocal microscope. Adapted from [101].

Chen *et al.* [6], have done an *in situ* analysis of Ti-6Al-4V after being treated through solution annealing and posterior furnace cooled (SA-FC). Images of the alloy prior and post treatment are depicted in Figure 17. It is possible to see that after the treatment there were changes in the microstructure, namely the area for beta phase became larger. This phenomenon is a consequence of the fact that, at the treatment temperature, the only stable phase is beta, leading to the precipitation of the alpha phase, changing the microstructure. Posterior *in situ* monitoring of corrosion process was done by electrochemical atomic force microscopy (ECAFM), in a solution of H_2SO_4 and HCl at open circuit potential - Figure 18. It is possible to see that with the increase in immersion time the dissolution rate of the alpha phase is higher than beta phase, which suggests that vanadium is capable of resisting to corrosion. In spite of this, it was also reported that the corrosion rate in beta phase was not uniform and that the alpha/beta boundaries in the corrosion process was faster further away. These phenomena suggest a process of galvanic corrosion in the alpha/beta boundaries. In addition to this it was observed that the dissolution process is extremely slower when the post treated alloy was potentiostatically etched at -0.5 and -0.85 V vs. Pt. Nonetheless, when the material suffers the same process at -0.9 V vs. Pt, the selective dissolution of alpha phase occurs [6].

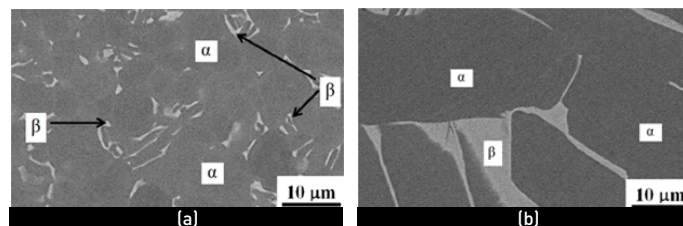


Fig. 17 - SEM images obtained for (a) Ti-6Al-4V and (b) after SA-FC treatment. Adapted from [6].

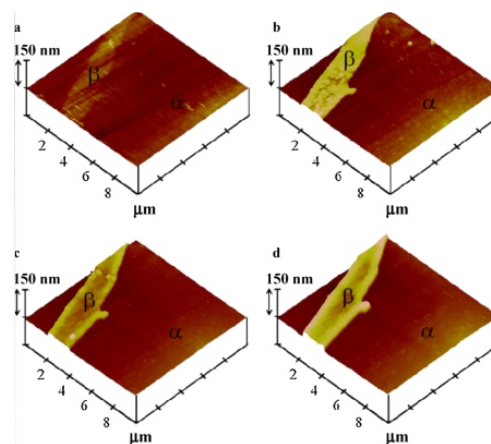


Fig. 18 - ECAFM images of the Ti-6Al-4V treated alloy (a) for 0, (b) 80, (c) 140 and (d) 200 min immersion in $0.5 \text{ mol}\cdot\text{L}^{-1} H_2SO_4$ and $1 \text{ mol}\cdot\text{L}^{-1} HCl$. Adapted from [6].

Barão *et al.* studied the influence of saliva's pH in the c.p. Ti and Ti-6Al-4V alloy corrosion behaviour. It was demonstrated that the pH has a significant influence on this process in both materials. At values of low pH, the decrease of Ti resistance to corrosion occurs due to an increase in the ion transfer between the saliva and Ti. In an acid medium it was also verified that the corrosion rate increased drastically and both c.p. Ti and Ti-6Al-4V presented the same corrosion behaviour, although Ti revealed a higher corrosion resistance than Ti-6Al-4V. The products obtained from the corrosion process may diminish the success of the implant. Also greater surface changes of Ti happened at low pH. For the potentials and solutions used, no pitting corrosion was found [102].

In reports done by Souto *et al.*, the passive films of c.p. Ti and Ti-6Al-4V were studied in a Ringer's solution at room temperature, suggesting an explanation for the reason why there is no pitting corrosion present in Ti and its alloys. It was demonstrated that the pitting process always occurs, due to transient microscopic breakdowns in the passive layer, caused by the presence of the chloride ions and the acidity increase of the solution. These breakdowns are extremely localized, forming pits, and since the process occurs beneath the passivation potential, the repassivation occurs leading to a passive layer without defects. The reason why most studies do not show this event is due to the fact that conventional corrosion analysis does not have the sensitivity to detect this phenomenon. It was also shown that Ti has a higher resistance to corrosion than its alloy [92].

Gosgogeat *et al.*, evaluated the effect of galvanic corrosion between titanium and Ti-6Al-4V implants with dental suprastructures in Fusayama-Meyer and Carter-Brugirard (AFNOR) saliva. To do so galvanic currents and potential of the galvanic couple were measured and was demonstrated that both materials present good resistance to corrosion. Although both anode and cathode have the same surface area, *in vivo* these can be different, increasing the process of galvanic corrosion and/or other types of

corrosion like pitting. Also, the electrochemical behaviour of the alloys did not change in the types of artificial saliva tested [7].

Ghoneim *et al.* [103] studied how the concentration of phosphoric acid and temperature influenced the corrosion behaviour of Ti and Ti-6Al-4V. Electrochemical results showed that Ti has higher corrosion resistance than Ti-6Al-4V, in spite of the fact that both materials presented similar electrochemical behaviour. Different behaviours were reported in function of the phosphoric acid concentration, up to 4.0 and 3.0 M for Ti and its alloy, respectively. There is a positive shift on the potential values, meaning that the passive oxide layer is being formed, accordingly to previous results [92, 102]. Above those concentrations the potential suffers a negative shift, resulting in the dissolution of the passive layer. The effect of the temperature was reflected on the formation rates of the passive layer, in which Ti always presented superior results.

More recent studies done for Ti-6Al-4V were performed by Benea *et al.*. One of those was to compare Ti-6Al-4V as cast with a nanoporous layer of TiO₂ and with a hydroxyapatite coating in a porous oxide layer. The untreated surface presents both adhesion and abrasion processes, in contrast with the treated ones which display less damage and lower friction coefficient showing that the best tribological behaviours are for the treated surfaces [71]. In posterior studies Benea *et al.*, tried to improve the connection between the Ti-6Al-4V with the hydroxyapatite (HA) coating. Initially a titanium oxide nanoporous layer was made on the material surface in a H₂SO₄ solution, which is a support material for the HA deposition. Electrochemical studies were done to compare the corrosion behaviour of the materials in which the treated surface presented a higher resistance to corrosion [58]. Studies also done with the goal of improving the tribological properties of Ti-6Al-4V were done by Dahotre *et al.* and the method applied was laser nitriding, with different laser energy densities. It was reported a high increase in corrosion resistance on the surface treated and also a decrease in the corrosive wear. The samples treated at high laser densities presented a higher cellular response than the untreated material, being metabolically active, while at lower laser densities this was not verified. However, the cell growth rate in the material treated with higher laser densities and the untreated one did not present differences [11].

3. CONCLUSION

It is evident that it is not easy to compare all of these studies to arise at a definite answer about the better material to use. From this review there are some highlights which are important to analyse. When comparing c.p. Ti and Ti-6Al-4V, c.p. Ti presents better corrosion resistance, but Ti-6Al-4V presents better mechanical proprieties than c.p. Ti, which, for the implant to be successful, is of extreme importance. However, the dissolution of the passive layer of Ti-6Al-4V, leads to health problems, stimulating the search of other alloys with better mechanical proprieties and with no potential damage to human health. As shown, Ti-15Mo is one of the most promising alloys, since it is not expected for molybdenum to have an adverse reaction in the organism. Also, as it was discussed in this review, it does present higher corrosion resistance than the mainly used titanium alloy in dentistry and has better mechanical properties. Adding these facts to the possible treatments that are listed, it is highly probable that Ti-15Mo becomes the material of choice to replace Ti-6Al-4V.

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