



# Is niobium more corrosion-resistant than commercially pure titanium in fluoride-containing artificial saliva?



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## ARTICLE INFO

### Article history:

Received 19 December 2016

Received in revised form 9 February 2017

Accepted 2 March 2017

Available online 6 March 2017

### Keywords:

Niobium  
Artificial saliva  
Fluoride  
Passivation  
Titanium

## ABSTRACT

In this work, commercially pure niobium (c.p. Nb) was selected to study its electrochemical behaviour in artificial saliva with several concentrations of fluoride ions ( $F^-$ ) over a range of 0–0.24 M. The chemical nature of passive layers on surface was characterised with x-ray photoelectron spectroscopy (XPS). The changes in surface topography due to  $F^-$ -induced corrosion were examined with scanning electron microscopy (SEM). For comparison, commercially pure titanium (c.p. Ti) was also investigated under identical conditions. Both c.p. Nb and c.p. Ti exhibit very good corrosion resistance in artificial saliva without  $F^-$  or with a low level of  $F^-$ , showing a low passive current density ( $j_{pass}$ ) and high polarisation resistance ( $R_p$ ). However, as the  $F^-$  concentration increases, c.p. Nb demonstrates a significantly greater corrosion resistance due to its stable passive film (mainly  $Nb_2O_5$ ) with a thickness of several nanometres, showing a much lower  $j_{pass}$  and higher  $R_p$ , with both values differing from those of c.p. Ti by over one order of magnitude. Significant differences in the corrosion behaviour between c.p. Nb and c.p. Ti can be understood from the thermodynamic perspective and the propensity of oxide dissolution. The advantage of niobium over titanium merits attention, as the c.p. Nb and Nb-based alloys are promising for further applications in dental prosthesis fabrication.

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## 1. Introduction

Commercially pure titanium (c.p. Ti, ASTM F-67) and titanium alloys (e.g. Ti-6Al-4V, ASTM F-136-02a; Ti-6Al-7Nb, ASTM F-1295-05) are widely used in restorative dentistry, such as in dental implants, orthodontic wire and dentures, due to their advantageous mechanical properties, corrosion resistance and biocompatibility [1–3]. As is well known, oral environments are very aggressive media with diverse corrosive substances. Both NaF and other fluoride compounds are frequently used in prophylactic dental treatments, including toothpaste, prophylactic agents and dental rinses, to prevent plaque formation and caries development. The concentration of fluoride ions ( $F^-$ ) in these products usually varies from ~1 ppm up to 22600 ppm, depending on the agents and therapies [4–6]. Under high levels of  $F^-$ , metallic service devices are required to have a high corrosion resistance. The challenge of  $F^-$ -induced corrosion in titanium-based alloys has been a long-standing concern [7–14]. Besides excessive metallic ion release by leaching, synergetic effects of corrosion and mechanical loading

can bring about stress corrosion cracking, delayed fracture and reduced fatigue strength of dental titanium alloys [12,15–17].

Based on the potential-pH (Pourbaix) diagram of the Ti- $H_2O$  system [18], it is well understood that titanium is thermodynamically reactive and easily passivated. In normal physiological media, the rate of corrosion is inhibited by the spontaneous formation of a passive film (mainly  $TiO_2$ ), as long as the film integrity is maintained. A  $F^-$ -containing acidic solution, however, has an exceptionally detrimental effect on the Ti surface, destroying the oxide layer even in the case of a low  $F^-$  concentration. In general, such deterioration of Ti is comparable to exposure to hydrofluoric acid [19–22]. As shown by Nakagawa et al. [19], there are well-defined critical  $F^-$  concentration and pH limits in artificial saliva, at which the Ti passive film is destroyed, accompanied by a transition from the non-corrosive to corrosive mode. The pH and  $F^-$  concentration in the solution exhibited an empirical relation, as follows,

$$pH = 1.49 \log(F) + 0.422 \text{ (anodic polarisation experiment)} \quad (1)$$

$$pH = 1.51 \log(F) + 0.237 \text{ (immersion experiment)} \quad (2)$$

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where  $\log(F)$  is the logarithm of  $F^-$  concentration in ppm. Characterising the electrochemical behaviour of a Ti-6Al-4V alloy in acidic  $F^-$ -containing artificial saliva, Huang et al. [21,23] showed the deterioration of passive film protectiveness with increasing NaF concentration. Anodic active polarisation took place when the NaF concentration exceeded 0.5%. For c.p. Ti immersed for 9 days in acidic artificial saliva containing 0.5% or 2.5% NaF, Mabilieu et al. [24] indicated that surface roughness was highly enhanced due to severe corrosion. It was also noted that the Ti surface passive layer (mainly  $TiO_2$ ) was greatly impaired, because of the transition of  $TiO_2$  to the soluble Ti-F complex  $TiF_6^{2-}$ . The reaction was proposed as follows [21,25,26]:



It is generally agreed that Ti suffers from a state transition from passivation to activation with increasing  $F^-$  concentration, which stems from the protective oxide film dissolution and consequent loss of protectiveness.

Alloying has been a conventional approach to improve corrosion resistance of Ti under the  $F^-$ -containing oral environment. One route is to incorporate noble elements, such as silver, palladium and platinum [22,27,28]. This is based on the concept of accelerating cathodic reactions by microalloying, through which the corrosion potential of the alloy shifts to a level where the Ti is passivated. In other words, the noble elements enhance spontaneous passivation of the alloy, with respect to the unalloyed Ti. Another approach is to design alloys containing valve metals, including molybdenum, tantalum and niobium [10,29–31]. In these alloys, the oxides of alloying elements are incorporated into the surface passive layer, rather than monotonic Ti oxides. Consequently, the stability of the passive film is improved. Considering niobium as a representative valve metal, the role these elements have on such alloys can be understood from two aspects. Metikos̄-Huković et al. [32] suggested niobium cations located in the titanium oxide crystal lattice cause a decrease in the anion vacancies generated by lower titanium oxidation states,  $Ti^{3+}$  and  $Ti^{2+}$ , making the oxide film on the Ti alloy more stoichiometric and corrosion resistant. Furthermore, Yu et al. [33] showed that niobium enhances the resistance of Ti alloys to active/transpassive dissolution, attributed to formation of strong covalent-like bonding between neighbouring Ti and Nb atoms through the sharing of unpaired *d*-level electrons.

Apart from usage as a key component in Ti-based alloys, recently niobium and its alloys have received more interest as bio-implant candidate materials [34], due to their excellent biocompatibility and osteogenesis as compared to Ti [35–37]. O'Brien et al. [38,39] developed a new alloy for vascular stents, Nb-28Ta-3.5W-1.3Zr, to meet the requirement of magnetic resonance imaging (MRI) compatibility. Similarly, Li et al. [40] designed a new Nb-60Ta-2Zr alloy for MRI-compatible vascular stents. This alloy exhibited excellent corrosion resistance in simulated plasma solution and a haemocompatibility superior to the 316L stainless steels and L605 Co-Cr alloy [41,42]. Rubitschek et al. [43] showed that the ultrafine-grained (UFG) Nb-2Zr alloy had not only a high yield strength (677 MPa), but also higher fatigue resistance against crack growth in simulated body fluid, in comparison with Ti-6Al-4V. In addition, as indicated by Papakyriacou et al. [44], cold-worked commercially-pure niobium (c.p. Nb) is less sensitive to

the loss of fatigue strength under simulated inflammatory conditions. Several electrochemical studies [32,41,45–47] proved that Nb and its alloys are highly corrosion-resistant under simulated physiological environments, showing low corrosion rates and great polarisation resistance, without the pitting and transpassive behavior in the relevant potential region of the body ( $<1 V_{SCE}$ ). Such excellent corrosion resistance originates from the compact oxide surface film (predominantly  $Nb_2O_5$ ) spontaneously formed in physiological solutions.

From the dentistry perspective, it is of interest to understand if niobium and its alloys are expected to have a higher corrosion resistance under  $F^-$ -containing oral environments in comparison with Ti-based alloys. To our knowledge, however, few studies on this issue have been carried out so far. In the present work, c.p. Nb was selected to study its electrochemical behaviour in artificial saliva with several concentrations of  $F^-$ . The  $F^-$  concentration dependence of the stability of the surface passive film was characterised. For comparison, electrochemical behaviour of c.p. Ti under identical conditions was revisited in parallel. With x-ray photoelectron spectroscopy (XPS) and surface topography analyses, the chemical nature of the passive layers and the changes in surface topography due to  $F^-$ -induced corrosion were examined, respectively. Finally, physicochemical sources possibly responsible for the differences in corrosion resistance between niobium and titanium in  $F^-$ -containing oral environment are discussed.

## 2. Experimental

### 2.1. Materials and working electrolytes

The samples of Type 1 c.p. Nb (UNS R04200, ASTM B393) and Grade 2 c.p. Ti (UNS R50400, ASTM F67) were taken from commercial wrought rods, provided by the Ningxia Orient Tantalum Industry Co., Ltd, China and the Baoji Titanium Industry Co., Ltd, China, respectively. Their chemical compositions (in wt.%) are presented in Table 1.

For electrochemical measurements, cubic metallic specimens were prepared with dimensions of 10 mm × 10 mm × 10 mm. They were embedded into a cold-cure epoxy resin, making only one face exposed to the electrolyte. All samples were mechanically ground with SiC emery paper up to 2000 grit before electrochemical tests. The samples used for surface observations and XPS analyses were prepared with dimensions of 10 mm × 10 mm × 3 mm. Their surfaces were carefully polished using a 0.04 μm silica suspension to a mirror-like surface finish. Prior to the electrochemical tests and immersion, the specimens were ultrasonically cleaned with deionised water, acetone and ethanol, then dried using compressed air.

Fusayama-Meyer artificial saliva was used to mimic an oral electrolyte [48,49]. This solution is chemically composed of KCl (0.4 g L<sup>-1</sup>), NaCl (0.4 g L<sup>-1</sup>), CaCl<sub>2</sub>·2H<sub>2</sub>O (0.796 g L<sup>-1</sup>), NaH<sub>2</sub>PO<sub>4</sub>·2H<sub>2</sub>O (0.690 g L<sup>-1</sup>), Na<sub>2</sub>S·9H<sub>2</sub>O (0.005 g L<sup>-1</sup>) and Urea (1 g L<sup>-1</sup>). The solution was prepared using deionised water with a resistivity of 18.2 MΩ cm and certified reagents supplied by Alfa Aesar, USA. NaF (Sigma Aldrich, USA) was added to the artificial saliva solution to simulate different fluoride media. Covering the commercial fluoride agents frequently used by dentists and patients [4–6], three representative concentrations of  $F^-$  in artificial saliva were

**Table 1**  
Chemical compositions of commercially pure Nb and Ti used in this work.

Chemical composition/wt.%	Fe	C	N	H	O	Ta	Ti	Nb
c.p. Nb	0.0015	0.0006	0.003	0.0004	0.0043	0.05	–	bal.
c.p. Ti	0.03	0.08	0.03	0.014	0.25	–	bal.	–

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