Corrosion behaviour of titanium alloyed by molybdenum

L. Joska[1]*, J. Fojt[1], J. Veselý[2]

[1] *Institute of Chemical Technology, Department of Metals and Corrosion Engineering,*
Technická 5, 166 28 Prague 6, Czech Republic
[2] *UJP a.s., Nad Kamínkou 1345, 156 10 Prague 5, Czech Republic*

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Abstract

Titanium is a metallic biomaterial used for a long period of time. The current interest is focused on β titanium alloys; molybdenum is one of the elements that close the α region effectively. The objective of this work was to prepare titanium-molybdenum experimental alloys and to describe their corrosion properties in environments interesting from application in dentistry point of view.

The measurements were done using Ti grade 2, Ti15Mo and Ti30Mo alloys. Corrosion properties were studied in the physiological solution at three pH levels and fluoride ions content up to 5000 ppm. Measurements were done by standard electrochemical techniques.

Corrosion properties of the studied alloys were at higher pH values comparable with the properties of titanium. Decrease of pH and presence of fluorides resulted in the case of titanium in pronounced decrease of corrosion resistance. The change was not so sharp for alloys, alloying resulted in improvement of corrosion behaviour.

Key words: titanium, molybdenum, titanium β alloys, fluorides, corrosion

1. Introduction

Titanium is a metallic biomaterial that has been in the focus of attention over a long period of time. A major argument in support of its application was its mostly problem-free acceptance by the organism. The current development is focused on development of the so-called β alloys. In contrast to the hcp structure of α titanium, these materials have a bcc lattice; they are easy to process as compared with α or α + β alloys, and their elasticity-related characteristics place them the closest to the human bone of all metallic materials [1–3].

Molybdenum represents one of the elements that closes the α region very effectively, according to Oliveira et al. [4]; the β phase becomes the dominant structural component when the molybdenum content exceeds 10 wt.%. The Ti-Mo system has been studied from the metallurgical point of view by a number of authors [5–8]. A survey of the development of the Ti15Mo alloy is presented in Jablokov's study [9].

Alloying, by which the β structure is achieved, may lead to a change in corrosion properties. The carrier of titanium and titanium alloys corrosion properties is passivity, i.e. the existence of an oxide layer on the phase boundary between the metal and the body environment. In dentistry, which uses medical preparations combining low pH and a high content of fluoride ions, titanium-based products are exposed to rather aggressive environment. The negative corrosion effect of fluorides on titanium is generally known for a long time. In literature devoted to dental applications of titanium, attention is focused on this problem in the works, e.g. [10–14].

The effect of molybdenum on the corrosion properties of often complexly alloyed materials has been the subject of a few studies. Its positive effect in terms of passivity has been stated by Gonzalez et al. [15], a good corrosion resistance of TiMo alloys (4–20 wt.%) has been reported by Oliveira [4]. Alves Rezende disclosed the dominancy of the effect of low pH and the presence of fluoride ions over the effect of the alloying when he studied the corrosion behaviour of the Ti10Mo alloy [16]. Hashimoto has published a survey

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*Corresponding author: tel.: +420 220 444 204; fax: +420 220 444 400; e-mail address: joskal@vscht.cz

Table 1. Composition of the tested materials

Sample	Mo	O	N	Al	Fe	W	Ti
	(wt.%)						
Ti grade 2		0.23	0.01				rest.
Ti15Mo	15.1	0.18	0.044	0.37	0.044	0.18	rest.
Ti30Mo	29.4	0.15	0.032	0.63	0.051	0.073	rest.

article on the effect of molybdenum on the passive state of steels [17]. His conclusions are applicable to titanium-based alloys, particularly in a situation when the passive layer breakdown occurs.

The aim of this study was to prepare titanium-molybdenum experimental alloys with 15 wt.% and 30 wt.% molybdenum content and to describe their corrosion properties in an environment interesting from application in dentistry point of view.

2. Experimental

Measurements were done on specimens of titanium grade 2, Ti15Mo and Ti30Mo alloys. The specimens' composition is given in Table 1. An arc furnace L200 (Leybold-Heraeus) was used to prepare the alloys. They were melted in helium at a pressure of 3×10^4 Pa, with the use of a non-meltable wolfram electrode. Small ingots were 5 times remelted to improve homogeneity. The specimens were subsequently annealed at a temperature of 650 ℃ for 15 minutes in order to eliminate strain. In addition to the microstructure, the specimens were also evaluated in terms of hardness using the Vickers method. The structure was studied after etching in modified Kroll etching solution (3 ml HF, 8 ml HNO_3, 100 ml H_2O).

For the purpose of electrochemical measurements, cylinders of ø 8×20 mm^2 were prepared with an inner thread allowing for their fixing in a holder according to ASTM G5-94, which was made solely of PTFE. The measurements were conducted in a physiological solution (9 g l^{-1} NaCl) of a temperature of 37.0 ± 0.2 ℃, with pH either non-adjusted or adjusted to values of 5.8 and 4.2 using a buffer solution [18]. The effect of fluoride ions, which are used in a number of medical preparations at a concentration of up to 10000 ppm (0.53 mol l^{-1}) and pH in the range of 3.2–7.7 [19], was modelled by the addition of sodium fluoride. Fluorides concentrations of 0.26 mol l^{-1} (5000 ppm) in a solution with non-adjusted pH, 0.053 mol l^{-1} (1000 ppm) in a solution with pH = 5.8, and 0.0053 mol l^{-1} (100 ppm) in a solution with pH = 4.2 were chosen in order for the specimens to be exposed in the region of titanium dioxide stability [12]. The content of 0.011 mol l^{-1} (200 ppm) at pH = 4.2 corresponds, according to Fovet et al. [12], to a boundary condition at which titanium dioxide ceases to be stable in an environment containing fluoride ions. The solutions were prepared using chemicals of the reagent grade purity and demineralized water of conductivity lower than 0.01 mS m^{-1}. The oxygen content in the electrolytes was not adjusted; it was in equilibrium with air.

Prior to measurements, the specimens were ground to the roughness of paper FEPA P1200, degreased in an ultrasound washer XB2 (Grant). Then they were sterilized in a standard way (120 ℃/20 min, saturated water vapour) (Ecosteri, BMT), and exposed after cooling in the air.

Electrochemical measurements were carried out using potentiostat FAS (Gamry). The potential is shown in relation to an Ag/AgCl/3 mol l^{-1} KCl (abbrev. SSCE) reference electrode RE 404 (Theta'90) with a potential of 0.207 V vs. standard hydrogen electrode. The measurements were conducted in a two-compartment thermostatic cell made of PTFE, with graphite auxiliary electrodes. The working electrolyte containing fluoride ions could get in contact only with polymer materials in the course of the specimens exposure.

The measurements proceeded as follows: At first the open circuit potential (E_{ocp}) was scanned for 11 hours, and it was always stabilized during this time. The measurement of polarization resistance followed and was always repeated twice, and the sequence was completed with the scanning of the potentiodynamic curve. The potential-current dependences needed for determining polarization resistance were measured in the range ±0.015 V from the open circuit potential at a rate of 0.1 mV s^{-1}. Potentiodynamic curves were scanned at a rate of 1 mV s^{-1} in the range from −0.05 V vs. E_{ocp} up to 1 V vs. SSCE.

3. Results

Titanium grade 2 is a material that is highly corrosion-resistant under the conditions of the human organism, and alloying should not have negative influence on this behaviour. The results of this corrosion study showed differences in the corrosion properties of titanium and its binary alloys with molybdenum.

Figures 1a and 1b show the microstructures of the alloys used in measurements. After rapid cooling, the

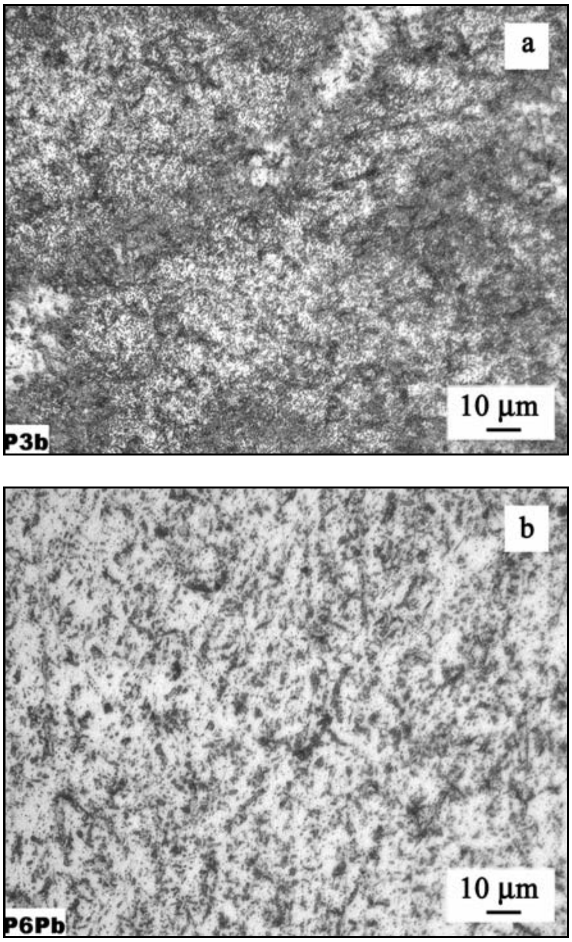

Fig. 1a,b. Microstructure of the tested alloys.

material containing 15 wt.% of molybdenum had β structure with precipitated globular particles of the metastable α phase denoted as ω (Fig. 1a). With the molybdenum content increased to 30 wt.%, the structure of the alloys did not change, and it was again formed by phase β with precipitated particles of phase ω (Fig. 1b). However, the origin of this phase was strongly suppressed. The heat treatment of the specimens, which was aimed to eliminate strain in the casting structure, did not have any significant effect on the structure.

The time dependences of the open circuit potential of the specimens in the studied environments were very similar, and therefore only selected typical courses are shown in Fig. 2 ((a) Ti grade 2, (b) Ti15Mo, (c) Ti30Mo, valid for Figs. 2 and 3).

The values of the stabilized open circuit potential at the end of the eleventh hour of exposure in solutions containing fluoride ions are summarized in Table 2. The measured data range in three regions, as is also obvious from Fig. 2. The shape of potentiodynamic curves, which are summarized in Fig. 3, corresponds in most cases to the passivity of the specimens. The level of pH played only a limited role. The addition of fluoride ions to the physiological solution led generally to a decrease in the potential, its value being due primarily to their content.

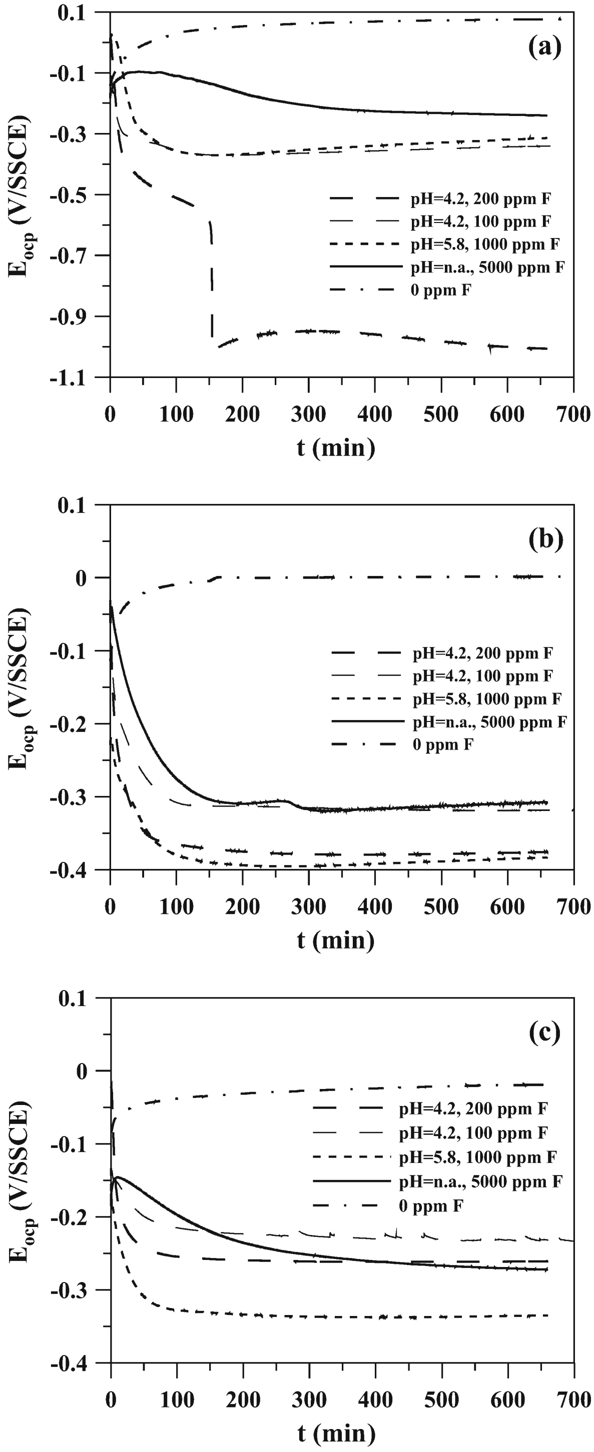

Fig. 2a,b,c. Time dependences of the open circuit potential.

Current densities read from potentiodynamic curves at a potential of 0.2 V/SSCE, which is approx-

Table 2. Open circuit potential in the end of 11th hour of exposure

Sample	pH	F^- conc.	E_{ocp}
		ppm	V (SSCE)
Ti rade 2	n-a	5000	−0.240
	5.8	1000	−0.314
	4.2	100	−0.339
	4.2	200	−1.005
Ti15Mo	n-a	5000	−0.307
	5.8	1000	−0.383
	4.2	100	−0.319
	4.2	200	−0.379
Ti30Mo	n-a	5000	−0.273
	5.8	1000	−0.335
	4.2	100	−0.234
	4.2	200	−0.262

imately the highest oxidation-reduction potential in the oral cavity and thus represents the boundary potential that a material may achieve in the mouth [20], are summarized in Table 3.

The polarization resistances are summarized in Table 4. The differences in corrosion behaviour between titanium grade 2 and the tested alloys is the most important at pH = 4.2.

4. Discussion

The addition of molybdenum into titanium rapidly closes the α region under equilibrium conditions. The maximum solubility of molybdenum in a solid α solution at 695 °C is 0.8 wt.%. At this temperature and Mo concentration of ~ 12 wt.%, eutectoid transformation occurs [21]. At higher molybdenum concentrations, the β phase becomes the dominating structural component. From the practical point of view, this fact signifies good cold formability.

Minor changes in the structure of the tested alloys occurring with increasing molybdenum content corresponded with the noted changes in their hardness. In the Ti15Mo alloy, the mean hardness value was 295 ± 12 (S.D.) HV, in the Ti30Mo alloy it was 282 ± 15 HV. The slight decrease in hardness was within the limits of the measurement variance, the differences were not statistically significant at $p = 0.05$, yet it may correspond to a lower share of phase ω in the matrix. The hardness was compared with hardness of titanium grade 2. It was 157 HV, i.e. markedly lower than that of the TiMo alloys.

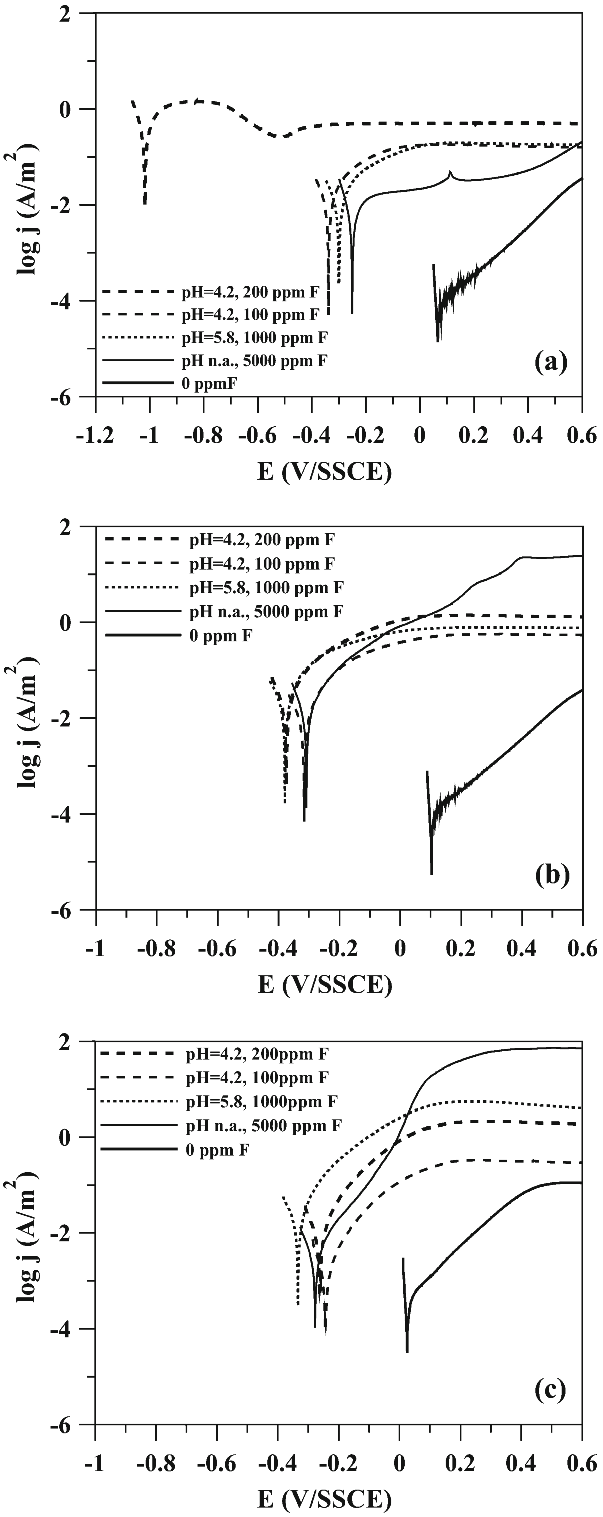

Fig. 3a,b,c. Potentiodynamic curves.

Titanium grade 2 offers only limited formability. Forming must be done in the region of cubic modification stability, i.e. at temperatures over 900 °C. In contrast, the formability of alloys with the β structure is very good. Cold rotational forging helped us to achieve an up to 85 % reduction of the cross section of cylindrical rods without any damage. The strength of

Table 3. Potentiodynamic curves-current density at 0.2 V/SSCE

	pH n-a 5000 ppm F^- j (A m^{-2})	pH = 5.8 1000 ppm F^- j (A m^{-2})	pH = 4.2 100 ppm F^- j (A m^{-2})	pH = 4.2 200 ppm F^- j (A m^{-2})
Ti grade 2	0.021	0.17	0.17	0.54
Ti15Mo	0.86	0.66	0.37	1.1
Ti30Mo	1.1	2.4	0.12	0.77

Table 4. Polarization resistances

	pH n-a		pH = 5.8		pH = 4.2		
ppm F	0	5000	0	1000	0	100	200
	(Ω m^2)		(Ω m^2)		(Ω m^2)		
Ti grade 2	1558	2.83	1283	1.99	1109	1.74	0.044
Ti15Mo	957	1.17	1091	0.87	1020	1.75	0.865
Ti30Mo	370	4.91	396	0.89	385	5.13	1.72

these alloys may be up to doubled by way of forming. Physical properties of the titanium-molybdenum system may be also changed by way of heat treatment. In the range of temperatures 300 to 450 °C, precipitation of dispersely scattered ω particles occurs. The choice of a suitable regime of hardening annealing may help increase hardness up to three times. A drawback rests in difficulties concerning the homogeneity of the chemical composition, which requires the inclusion of homogenization annealing and remelting operations in the process of production.

In addition to corresponding mechanical properties, and particularly good formability which is necessary for the production of complicated shapes of stomatological components, alloys considered for application in this field must also satisfy requirements relating to their corrosion resistance and cell tolerance. Titanium grade 2 is a material that is highly corrosion-resistant under the conditions of the human organism, and alloying should not have any negative effect on this behaviour.

Regardless of the specimens' composition, the open circuit potential in a pH non-adjusted physiological solution stabilized at 0.034 V/SSCE (confidence interval of 0.021 V at $p = 0.05$), without any obvious trend as a consequence of alloying. This fact allows us to assume that the corrosion behaviour of the specimens under these conditions was governed primarily by titanium and its capability to form the passive layer effectively. This is due among other things to the fact that titanium dioxide is more stable than molybdenum oxides – standard Gibbs energy of TiO_2 formation is –889 kJ mol^{-1} at 298 K as compared with –668 kJ mol^{-1} in the case of MoO_3 and –533 kJ mol^{-1} in the case of MoO_2 [18].

The shape of potentiodynamic curves (Fig. 3) was distinctly influenced by the addition of fluoride ions to the physiological solution. Severe influence of fluoride ions addition was recorded at pH lowered to 4.2. The open circuit potential of titanium was always in this environment the most negative while that of the Ti30Mo alloy was the most positive. This difference was at a level of 100 mV in an environment containing 100 ppm F^-. However, the value of the open circuit potential of titanium was in the region of TiO_2 stability. The sharp decrease of the titanium grade 2 potential in an environment containing 200 ppm F^- represented an essential change in its corrosion behaviour. An increase in the concentration of fluoride ions to this level led after some time of exposure to a jump decrease of the potential to about –1 V/SSCE, which roughly corresponded to Ti/TiO_2 equilibrium [22]. The open circuit potential of alloys stayed under these conditions practically unchanged in the case of Ti30Mo, while shifting by –60 mV in the case of Ti15Mo. Both values fall within the region of oxides stability of both molybdenum and titanium in water environment [22].

Potentiodynamic curves of titanium grade 2 and both the tested alloys were mostly of a very similar shape in the studied environments. In a pH non-adjusted electrolyte without any fluorides content, the curves lie in the region of very low current densities. Corrosion potentials are on the boundary of the maximum oxidation-reduction potential in the oral cavity [20], while the anodic parts of the curves are outside this region. Alloying with molybdenum led to a slight shift in potentiodynamic curves towards more negative potentials and higher current densities.

In all cases, the presence of fluoride ions in a corrosion environment resulted in a distinct shift of the corrosion potential in the negative direction, and an increase of current densities by orders of magnitude. In an environment of pH = 4.2 containing 100 ppm F^-, the position of titanium grade 2 and the Ti15Mo alloy curves in the corrosion potential region is comparable. However, the curve for Ti15Mo lies lower on the current axis. Current densities become balanced at a potential of –0.030 V/SSCE. With an increasing oxidation power of the environment, the current in the Ti15Mo alloy grows more rapidly than in titanium grade 2. Essentially different is the behaviour of the Ti30Mo alloy. Its curve is shifted towards lower values on the current axis and in the positive direction on the potential axis. It achieves the same current level as titanium grade 2 only at a potential of 0.260 V/SSCE.

Just as in the case of the open circuit potential, an essential change occurred in the course of the potential-current dependence of titanium grade 2 in the most aggressive electrolyte with 200 ppm F^- and pH = 4.2. In addition to a distinct shift of the curve in the negative direction and an increase in current densities, the curve shows a clear passivation peak with a passivation potential of –0.63 V/SSCE, and a current density of 1.4 A m^{-2} in the peak. The course of the potentiodynamic curve makes it clear that the oxide layer was strongly attacked by fluorides under these conditions, and only an increasing potential – the oxidation power of the environment – allowed for its effective restoration. The behaviour of both binary alloys shows considerable differences under these conditions. The anodic parts of the curves lie in the region of potentials which is by over 0.6 V more positive than in the preceding case. The anodic currents become balanced at potentials of 0.05 V/SSCE (Ti15Mo) and 0.15 V/SSCE (Ti30Mo). It is evident that alloying with molybdenum increased the corrosion resistance of the studied materials in wide range of potentials (oxidation power of the environment).

Current densities read from potentiodynamic curves at a potential of 0.2 V/SSCE (Table 3) are in most cases the lowest in the case of titanium grade 2. The current density of 0.54 A m^{-2} determined on the curve measured in an environment with pH = 4.2 and 200 ppm F^- nevertheless corresponds to a corrosion rate calculated with the assumption of the origin of a compound with titanium in an oxidation state of 4+, 0.47 mm a^{-1}. This statement is not surprising from the corrosion point of view. The measured data clearly show that pH in the acidic region combined with the presence of fluorides and higher level of oxidation-reduction potential of the environment leads to a considerable increase in the corrosion rate and consequently to higher burdening of the organism with released corrosion products.

The polarization resistances are summarized in Table 4. In an environment free from any fluoride ions, the corrosion current density calculated from Rp of titanium grade 2 is 4.2×10^{-5} A m^{-2}, that of the Ti15Mo alloy is 5.3×10^{-5} A m^{-2}, and the Ti30Mo alloy shows 14×10^{-5} A m^{-2}. The given values correspond to corrosion rates of the order of 10^{-5} mm a^{-1}. The differences in corrosion resistance between titanium grade 2 and the tested alloys are apparently insignificant under the given conditions. The addition of fluoride ions in the amount of 5000, 1000 and 100 ppm at a corresponding pH was chosen in order for titanium to be exposed in the region of stable passivity. The destruction effect of fluorides is clearly expressed by a decrease in polarization resistances by orders of magnitude as compared with an environment free from fluoride ions. Even under these conditions, however, the corrosion properties of the tested alloys are comparable with titanium grade 2. In an environment with 100 ppm F^-, the measured polarization resistance of the Ti30Mo specimen was higher than that of titanium grade 2. An essential change in the polarization resistance, reflecting the course of the open circuit potential and evident from the position of the potentiodynamic dependence, was noticed for titanium grade 2 in an environment with pH = 4.2 and 200 ppm F^-. For this material the given combination of pH and a low concentration of fluoride ions are evidently critical. Polarization resistances of the tested binary alloys are under these conditions on a relatively low level, yet they are higher by two orders of magnitude as compared with titanium.

In the absence of fluorides, the corrosion rate of titanium calculated from the polarization resistance is 3.6×10^{-5} mm a^{-1}. This corresponds to the rate of titanium release in the oxidation state 4+ at the level of 0.002 μg cm^{-2} h^{-1}. With a polarization resistance 1.99 Ω m^2 (current density of 2.7×10^{-2} A m^{-2}), the rate of release is 1.2 μg cm^{-2} h^{-1}. A polarization resistance 0.044 Ω m^2 (current density of 1.2 A m^{-2}) represents a rate of release of 55 μg cm^{-2} h^{-1}, and the corrosion rate is 1.1 mm a^{-1} in this case.

The main objective of alloying titanium with molybdenum was to achieve the β structure of the alloys. In the case of titanium-based products, the highest corrosion resistance may be expected for the non-alloyed titanium. The corrosion behaviour of this non-noble metal (the standard potential of the reaction $Ti^{2+} + 2e \rightarrow Ti$ is −1.63 V [23]) is due to its easy passivation and high stability of its homogeneous passive layer. If the alloying elements participate in the formation of the passive layer, a change in the passive layer homogeneity and possibly also deterioration of corrosion properties may be expected. The data measured in the presented study confirm the effect of molybdenum in the mechanism of binary alloys passivation. Their open circuit potential was always in the region of stability of both molybdenum and titanium oxides. At a potential of 0.2 V/SSCE, the current densities of the tested alloys read from potentiodynamic curves were on the same or somewhat higher level than in the case of titanium. It is evident that the presence of molybdenum did not have any substantial negative effect on the corrosion properties even at a potential corresponding to the boundary oxidation conditions in the oral cavity. On the contrary, the positive effect of molybdenum could be seen in the case of the alloy containing 30 % molybdenum at pH = 4.2. The corrosion current density of the Ti30Mo alloy in a solution containing 100 ppm fluoride ions was three times lower than that of titanium grade 2. The open circuit potential of the alloy remained practically unchanged when the concentration of fluoride ions was doubled, and it stayed in the region of stability of the oxides of both components. The corrosion current density of the alloy increased under these conditions but this change was only minimal in view of the change in the corrosion current density of titanium grade 2. The calculated rate of corrosion products release was 40 times lower in the case of Ti30Mo alloy than for titanium grade 2. Under these conditions, the alloying with molybdenum prevented a decrease of the potential and most likely led to the stabilization or a more effective restoration of titanium oxides.

5. Conclusions

Both experimentally prepared titanium-molybdenum binary alloys have a β structure with precipitated particles of the ω phase. In terms of practical application, both alloys promise good formability combined with the possibility of affecting their mechanical properties by way of hardening or strain hardening.

Comparison with the values recorded for titanium grade 2 shows that alloying with molybdenum does not have any essential effect on the corrosion behaviour in the presence of fluoride ions within the studied pH range if titanium and molybdenum oxides are the stable corrosion products. In a situation when the titanium passive layer is significantly destroyed by the effect of fluoride ions and titanium open circuit potential corresponds to the active state, the potential of the tested alloys is more positive by hundreds of milivolts and the corrosion current densities are lower by orders of magnitude. Based on the results we may conclude that molybdenum represents a suitable alloying element for the development of titanium β alloys for dentistry both in view of the effective closure of the α region and in view of the positive changes in the corrosion behaviour of alloys exposed in an environment with increased aggressiveness.

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References

[1] ELIAS, L. M.—SCHNEIDER, S. G.—SCHNEIDER, S.—SILVA, H. M.—MALVISI, F.: Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing, *A432*, 2006, p. 108.

[2] YANG, G.—ZHANG, T.: Journal of Alloys and Compounds, *392*, 2005, p. 291.

[3] HANADA, S.—MATSUMOTO, H.—WATANABE, S.: International Congress Series, *1284*, 2005, p. 239.

[4] OLIVEIRA, N. T. C.—ALEXIO, G.—CARAM, R.—GUASTALDI, A. C.: Materials Science & Engineering A, *A452–A453*, 2007, p. 727.

[5] LIN, D. J.—CHERN LIN, J. H.—JU, C. P.: Biomaterials, *23*, 2002, p. 1723.

[6] BANERJEE, R.—NAG, S.—STECHSCHULTE, J.—FRASER, H. L.: Biomaterials, *25*, 2004, p. 3413.

[7] NAG, S.—BANERJEE, R.—FRASER, H. L.: Materials Science & Engineering, C: Biomimetic and Supramolecular Systems, *C25*, 2005, p. 357.

[8] YU, Z.—ZHOU, L.: Materials Science & Engineering, A: Structural Materials: Properties, Microstructure and Processing, *A438-A440*, 2006, p. 391.

[9] JABLOKOV, V. R.—NUTT, M. J.—RICHELSOPH, M. E.—FREESE, H. L.: Journal of ASTM International, *2*, 2005, 8.

[10] BOERE, G.: Journal of Applied Biomaterials, *6*, 1995, p. 283.

[11] NAKAGAWA, M.—MATSUYA, S.—SHIAIRSHI, T. —OHTA, M.: Journal of Dental Research, *78*, 1999, p. 1568.

[12] FOVET, Y.—GAL, J. Y.—TOUMELIN-CHEMLA, F.: Talanta, *53*, 2001, p. 1053.

[13] SCHIFF, N.—GROSGOGEAT, B.—LISSAC, M.—DALARD, F.: Biomaterials, *23*, 2002, p. 1995.

[14] ROBIN, A.—MEIRELIS, J. P.: Journal of Applied Electrochemistry, *37*, 2007, p. 511.

[15] GONZALEZ, J. E. G.—MIRZA-ROSCA, J. C.: Journal of Electroanalytical Chemistry, *471*, 1999, p. 109.

[16] ALVES-REZENDE, M. C. R.—AVES, A. P. R.—CODARO, E. N.—DUTRA, C. A. M.: Journal of Materials Science: Materials in Medicine, *18*, 2007, p. 149.

[17] HASHIMOTO, K.—ASAMI, K.—KAWASHIMA, A. —HABAZAKI, H.—AKIYAMA, E.: Corrosion Science, *49*, 2007, p. 42.

[18] The Handbook of Chemistry and Physics. 88th edition. On line edition. CRC Press, http://www.hbcpnetbase.com/

[19] TOUMELIN-CHEMLA, F.—ROUELLE, F.—BURDAIRON, G.: Journal of Dentistry, *24*, 1996, p. 109.

[20] YONTCHEV, E.—HAKANSSON, B.—HEDEGARD, B.—VANNERBERG, N. G.: Journal of Oral Rehabilitation, *13*, 1986, p. 365.

[21] Phase Diagrams of Binary Titanium Alloys. Ed.: Murray, J. L. Metals Park, Ohio, ASM International 1987.

[22] POURBAIX, M.: Atlas of Electrochemical Equilibria in Aqueous Solutions. Houston, NACE 1974.

[23] Standard Potentials in Aqueous Solution. Eds.: Bard, A. J., Parsons, R., Jordan, J. New York, Marcel Dekker 1985.