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Corrosion fatigue and electrochemical behavior of superelastic Ti-Nb-Ta alloy for medical implants under cyclic load conditions

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Abstract

The aim of the present work was to study corrosion and electrochemical behavior of Ti-22Nb-6Ta (at. %) superelastic alloy in comparison with commercially pure titanium (cp-Ti) under simulated service conditions of load-bearing bone implants, i.e. under cyclic load in simulated body fluid environment. Open circuit potential (OCP) measurements were carried out on wire samples in Hank's solution at 37°C applying bending load (maximum induced strain 0.8 %) up to 75×10^3 cycles or sample failure. It is shown that Ti-22Nb-6Ta alloy is superior to cp-Ti in terms of corrosion fatigue behavior. In particular, it possesses higher OCP values and its passive oxide film is more resistant to the impact of cyclic loading; fatigue life of the alloy is longer.

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Keywords: titanium alloys; superelasticity; martensitic transformation; biocompatibility; corrosion fatigue; oxide films

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1. Introduction

Titanium-based alloys have been widely used for many years as excellent materials for biomedical implants because of a unique combination of their properties: high strength, low stiffness and density, high corrosion resistance and biocompatibility [1].

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A material for intraosseous implants must meet stringent requirements of biomechanical and biochemical compatibility with bone tissue. It means that the material's mechanical properties must be close to those of bone (Young's modulus 10 – 40 GPa and superelastic behavior with recoverable strain not less than 2 %); it must contain only safe and medically approved elements, exhibit high corrosion resistance in various human body media.

These requirements are fully met by Ti-Nb-based alloys which exhibit superelastic behavior due to stress-induced reversible β (bcc) ↔ α'' (orthorhombic lattice) martensitic transformation [2,3].

One of the most common causes of load-bearing implant failure is corrosion fatigue failure [1,4]. Thus, corrosion and electrochemical studies under the conditions simulating the service mode of finished products are of a great practical relevance.

It has been shown earlier for superelastic Ti-22Nb-6Ta (at. %) alloy [5] that at high strain values (about 1 %), the process of corrosion fatigue crack propagation is restrained by crystals of strain-induced martensite that form at the crack tip during loading half-cycle. However, a valuable comparison of the corrosion fatigue behavior of Ti-Nb-Ta and conventional biomedical titanium was not conducted yet. In the present study, a slightly lower strain value (0.8 %) was chosen for the prolonged corrosion fatigue tests of Ti-22Nb-6Ta alloy and commercially pure titanium as reference material. The selected 0.8 % strain situates within the limits of the Ti-22Nb-6Ta alloy superelastic behavior, underlied by the mechanisms of reversible martensitic transformation, while for pure titanium, this strain value is known to cause plastic deformation.

2. Materials and methods

Biocompatible Ti-22Nb-6Ta (at. %) (hereinafter Ti-Nb-Ta) alloy was obtained by vacuum arc melting with consumable electrode. The ingot was hot-forged at 900 C and then subjected to a multistage thermomechanical treatment with final drawing to 0.7 mm-diameter wire and annealed at 600°C for 10 min. Commercially pure titanium (hereinafter cp-Ti) was tested for the comparison. The 10 cm-long samples were sanded to a diameter of 0.65 mm and ultrasonically cleaned in alcohol.

As-received surface layer was typical for natural oxide film on titanium alloys, with thickness below 10 nm, it consisted mainly of TiO2 with minor addition of alloying elements [1,6].

The simulated physiological medium was Hank's salt solution mimicking the inorganic component of osseous tissue and containing (concentrations, g/l): 8 NaCl, 0.4 KCl, 0.12 $Na_2HPO_4 \cdot 12H_2O$, 0.06 KH_2PO_4, 0.2 $MgSO_4 \cdot 7H_2O$, 0.35 $NaHCO_3$, 0.14 $CaCl_2$, H_2O (up to 1 l of solution); pH = 7.4.

Electrochemical tests were carried out with an IPC-Micro electronic potentiostat by open circuit potential (OCP) continuous measurement method. A two-electrode electrochemical cell was placed into a thermostat to maintain a test media temperature of (37 ± 1) °C. Saturated silver / silver chloride electrode (SSCE) served as a reference electrode. Before cycling, the samples were immersed in Hank's solution without loading for 15 hours in order to reach stable surface film conditions which were associated with a time-invariant OCP value.

Cyclic loading (0.8 % maximum strain, 1.1 Hz cycling frequency) was created using the originally designed experimental setup shown in Fig. 1a [5]. The wire samples (Fig. 1b) were placed in the test solution and mounted in two vertical organic glass crossbars. One of the crossbars was firmly fixed to the stationary stand, while another one was connected to the rod moved by an electrical motor.

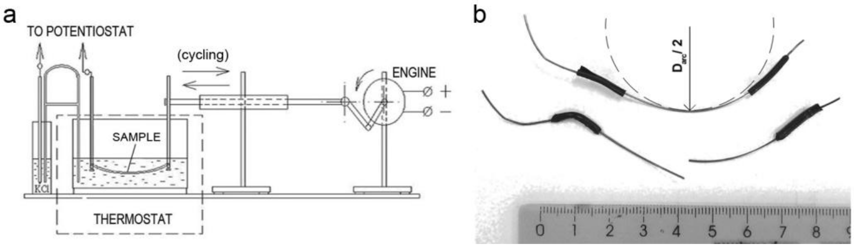

Fig. 1. (a) Experimental setup scheme; (b) Typical samples before and after failure; Darc is equal to the doubled curvature radius of the wire at a point of maximum stroke [5].

The strain value ε was calculated using to the following formula: $\varepsilon = d_w/D_{arc}$, where d_w is the sample (wire) diameter; D_{arc} is equal to the doubled curvature radius of the wire at a point of maximum stroke (in the vicinity of the sample center), corresponding to the point of maximum strain, see Fig. 1b.

The cycling was continued up to 75×10^3 cycles (about 18 hours of testing) or sample failure.

3. Results and discussion

Figure 2 shows two plots representing OCP as a function of the number of cycles (maximum strain ~0.8%) for Ti-Nb-Ta and cp-Ti samples immersed in Hank's solution.

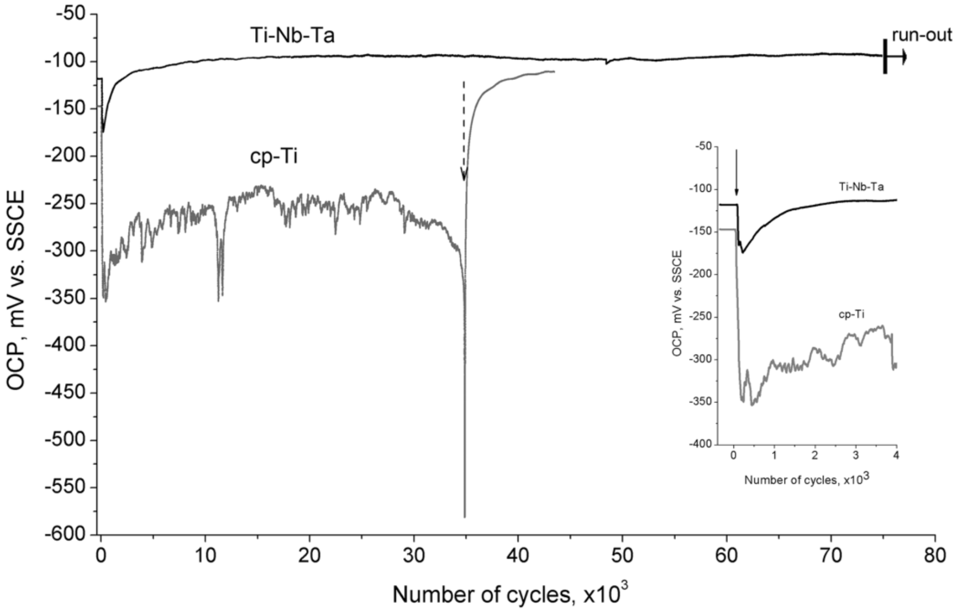

Fig. 2. Plots "OCP vs. number of cycles" for Ti-Nb-Ta and cp-Ti immersed in Hank's solution under cyclic dynamic load (strain value 0.8 %). Cycling start and cp-Ti sample failure are pointed by solid and dashed arrows, respectively; in the inset, a part of the entire diagram is enlarged, for clarity.

Dynamic cycling was started after the establishment of their time-invariant steady state OCP values which were close enough to each other (–118 and –147 mV for Ti-Nb-Ta and cp-Ti, respectively). The loading start was accompanied by an anticipated abrupt cathodic polarization (OCP shift towards more negative values), which was evidently connected with a local breakdown of passive oxide film. Subsequent OCP increase was observed for both materials. In the case of cp-Ti, this process was characterized by significant (20-30 mV) OCP fluctuations and, finally, did not lead to the restoration of the initial prior-to-testing potential value. At the same time, an OCP shift for Ti-Nb-Ta was featured by (a) a significantly smaller potential drop magnitude upon cycling start, (b) its smooth and gradual increase after the drop, and, what is more important, (c) reaching or even outreaching (by 25 mV) the initial state value.

The observed differences clearly indicate much higher rate of passive oxide film recovery in the case of Ti-Nb-Ta samples, its superior protective properties and, most significantly, higher resistance to the impact of dynamic mechanical cycling.

The essential results revealing the advantages of Ti-Nb-Ta alloy are those obtained after 30×10^3 cycles of continuous testing (Fig. 2). While OCP value for Ti-Nb-Ta remained almost constant during the immersion, it lowered during further cycling for cp-Ti and, after 34.9×10^3 cycles, the sample failed at the point of a maximum bending stroke, which was accompanied by a drastic potential drop. The cause of failure was stress localization in the zone of the initial breakdown of the passive film; this area acts as a zone of the primary fatigue crack nucleation. The passive film recovery on the renewed surface progresses due to the transition of metallic atoms close to the film failure area into oxidized state. This process must evidently lead to the specific mechanical stress increase resulted from the decrease of apparent cross section area caused by the growth of the fatigue crack cycle after cycle. After-failure behavior exhibiting considerable OCP increase up to the initial value corresponded to the formation of passive film on the freshly formed active surface (cross section) of the sample.

In contrast with cp-Ti, the ongoing cycling of Ti-Nb-Ta did not lead to any notable changes in its electrochemical behavior even after more than 76.2×10^3 cycles, which gives evidence of the enhanced stability of the passive layer as well as the alloy in general, in terms of its resistance to corrosion fatigue failure at a certain strain value.

The origin of such characteristics involves the reversible martensitic transformation which takes place under the considered deformation strain (0.8 %). Martensite crystals formed in the loading half-cycle act as effective mechanical barriers for crack propagation [7,8]. In the unloading half-cycle, the recovery of the alloy's initial structural state proceeds via reverse martensitic transformation and, therefore, does not trigger the dislocations-related deformation mechanisms and, therefore, allow stress relaxation without plastic deformation [9]. It is obvious that the reversible martensitic transformation under cyclic load in this alloy has a stabilizing influence implying the maintaining or enhancing the plastic properties of surface layers (chemomechanical effect [10]) resulting from the barrier effect of the martensite crystals, which hamper dislocation yield in the near-surface area.

In summary, comparing the OCP evolution of the Ti-Nb-Ta and cp-Ti wire samples subjected to repetitive bending in Hank's solution makes it possible to suggest that superelasticity of the first material, and the underlying phenomenon of reversible martensitic transformation, plays a determinant role in its higher corrosion fatigue resistance.

4. Conclusion

The in situ open circuit potential (OCP) measurements under strain (0.8 %) were conducted on superelastic Ti-22Nb-6Ta (at. %) alloy and reference cp-Ti, in Hank's solution. It is shown that at an equal strain magnitude, Ti-Nb-Ta alloy possesses higher OCP values (increased chemical stability) under continuous cycling conditions. The oxide film on the alloy exhibits higher resistance to the destructive impact of applied cyclic load, which is evident from smooth, gradual and minor OCP variations compared with cp-Ti. The fatigue life of Ti-Nb-Ta alloy is at least two times longer than that of cp-Ti and is directly influenced by superelastic properties of the material. Therefore, Ti-Nb-Ta alloy significantly surpasses cp-Ti in terms of corrosion fatigue resistance. This fact allows considering this alloy as a prospective material for load-bearing implants.

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References

[1] D.M. Brunette, P. Tengvall, M. Textor, P. Thomsen, Titanium in medicine: material science, surface science, engineering, biological responses and medical applications, Springer, 2001.
[2] S. Miyazaki, H.Y. Kim, H. Hosoda, Mater. Sci. Eng. A 438-440 (2006) 18–24.
[3] V. Brailovski, S. Prokoshkin, M. Gauthier, K. Inaekyan, S. Dubinskiy, M. Petrzhik, M. Filonov. Mater. Sci. Eng. C 31 (2011) 643–657.
[4] C. Fleck, D. Eifler, Int. J. Fatigue 32 (2010) 929–935.
[5] Y.S. Zhukova, Yu.A. Pustov, A.S. Konopatsky, M.R. Filonov, S.D. Prokoshkin, J. Mater. Eng. Perform. 23 (2014) 2677–2681.
[6] Y.S. Zhukova, Yu.A. Pustov, A.S. Konopatsky, M.R. Filonov, J. Alloy Compd. 586 (2014) S535–S538.
[7] S. Yi, S. Gao, Int. J. Solids Struct. 37 (2000) 5315–5327.
[8] S.W. Robertson, A. Mehta, A.R. Pelton, R.O. Ritchie, Acta Mater. 55 (2007) 6198–6207.
[9] V. Brailovski, S. Prokoshkin, P. Terriault, F. Trochu, Shape memory alloys: fundamentals, modeling and applications. Montreal: ETS Publ., 2003.
[10] E.M. Gutman, Mechanochemistry of materials, Cambridge International Science Publishing, 1998.