The influence of anodic oxidation on NiTi/Ti6Al4V fretting corrosion behavior

E A Lukina
Department of Materials Science and Technologies of Materials Treatment, MAI (National Research University), 125993, Moscow, Russia
E-mail: lukinaea@mati.ru

Abstract. This work is aimed to evaluate the efficiency of creating of barrier insulating oxide layers using anodic oxidation at low (U = 50V) and high (U = 200V) voltages to prevent fretting corrosion damage of NiTi rods fixed in Ti6Al4V titanium pedicle screws. It has been revealed that the formation of nonporous amorphous oxide layer on the surface of titanium screws by low voltage anodic oxidation prevents NiTi rods damage under fretting corrosion conditions. On the other hand, the presence of porous oxide layer on Ti6Al4V surface that is created by high voltage anodic oxidation deteriorates corrosion resistance of NiTi significantly.

1. Introduction
Due to the presence of shape memory effect (SME) and superelasticity (SE) titanium nickelide based alloys (NiTi) are promising candidates for the manufacturing of rods for pedicle screw devices (figure 1a), used for the surgical treatment of scoliosis, traumas and degenerative diseases of the spine. The presence of shape memory effect facilitates the fixation of NiTi rods in the pedicle screws during the surgery, whereas low modulus of elasticity of NiTi rods prevents adjacent segment degeneration complication after the surgery, which makes it possible to avoid revision surgeries. Also, high wear resistance of NiTi in biological medium could prevent the development of metallosis in the tissues surrounding the implanted device [1–3]. However, there have been few reports recently that describe the discovery of extensive corrosion damage on several explanted NiTi rods in areas where they were in contact with Ti6Al4V alloy pedicle screws. Such damage was assumed to be the result of fretting corrosion development due to micro-movements of rods in the screws and could also be enhanced by galvanic interaction between them [4–5].

The aim of this work was to study the efficiency of creating of barrier insulating oxide layers using anodic oxidation to prevent the corrosion damage of NiTi rods fixed in Ti6Al4V pedicle screws in fretting corrosion conditions.

2. Materials and methods
NiTi rods (diameter 5.5 mm; 55.8 wt% Ni) had the temperature of shape recovery (A<sub>f</sub>) 20±2º and were in austenite state (B2) at the temperature of corrosion tests. Maximum Ti₆Ni₂O₄ inclusion size was 5 μm, average size 1.5±0.5 μm and their volume fraction evaluated at 500x magnification was 1.4±0.2%. Surface of the rods was electropolised.

The set-up for fretting corrosion tests is shown on figure 1b. Rods made of NiTi were fixed into pedicle screws made from Ti6Al4V titanium alloy. Some of the screws were in as-supplied state
Barrier oxide layers were created on the other part of the screws by anodic oxidation technique at a voltage of $U = 50$ V (group II) and at a voltage of $U = 200$ V (group III). The structure of oxide layers on the surface of Ti6Al4V screws was studied using X-ray diffraction analysis, scanning electron microscopy (SEM), EDAX analysis and Auger spectroscopy.

Figure 1. The pedicle screw device (a); set-up for fretting-corrosion tests (b).

A series of potentiostatic measurements of the fretting corrosion current was carried out at a sinusoidal cyclic load (100 N - 650 N, which corresponds to a bending moment of 6.5-7 Nm) using a 3-point bending scheme in 10% bovine serum in 0.9% NaCl. After testing, the surface of NiTi rods was studied using SEM and EDAX analysis and the content of metal ions in solution was studied using mass spectroscopy of secondary ions.

3. Results and discussion

It has been revealed that the anodic oxidation of Ti6Al4V screws at a voltage of 50 V (group II) leads to the formation of oxide layer of 2–2.5 μm thickness. The layer had an amorphous non-porous structure (figure 2a). Chemical composition of the layer was the following: 11÷13 Ti, 45÷46 O, 10÷14 Al, 3÷5 N, 14÷21 C, 4÷8 P, 1÷3 Si (at.%).

During anodic oxidation at a voltage of 200 V (group III), a porous oxide layer with a thickness of 25÷30 μm forms on Ti6Al4V pedicle screw (figure 2b). The porous structure of the oxide layer is typical for anodic oxidation carried out at voltages which exceed the breakdown voltage of the forming oxide [6–7]. The crystal structure of the layer is represented by rutile and anatase TiO$_2$ phases. Chemical composition of the layer was: 4÷9 Ti, 30÷35 O, 1 Al, 48÷59 C, 4÷8 P, 1÷3 Si (at.%).

The conducted corrosion tests showed that the average value of the fretting corrosion current in case of NiTi rods testing in Ti6Al4V screws in as-supplied state (group I) was 5.8 μA, and erosion damage up to 200 μm and corrosion products in the form of titanium oxide Ti$_x$O$_y$ were detected on the surface of the rod in areas that were in contact with the screws (figure 3a). The content of Ni in the solution after testing increased 3 fold compared to its content in control solution that was not used for fretting corrosion testing (table 1). There was no statistically significant difference in the content of other elements (Ti, Al, V) in the solution before and after the test.

In the case of NiTi rods testing locked in group II screws, the fretting corrosion current decreased to 0.1 μA and no corrosion damage was observed on the surface of NiTi rods after the tests (figure 3b). Also, there was no Ni content increase in the test solution, which indicates that the creation of a porous
barrier insulating layer of titanium oxide on the surface of titanium screws improves the corrosion performance of NiTi rods in fretting conditions.

Figure 2. Morphology of Ti6Al4V pedicle screws after anodic oxidation at $U=50$ V (a) and $U=200$ V (b).

Figure 3. The surface of NiTi rods after fretting corrosion tests in pedicle screws made of titanium Ti6Al4V alloy: screws in as-supplied state (a); screws after anodic oxidation at 50 V (b); screws after 200 V (c).

On the other hand, in case of NiTi rods testing when locked in group III screws, the fretting corrosion current increased up to 53 $\mu$A and large erosions up to 800 $\div$ 1000 $\mu$m in size and
corrosion products were detected on the surface of the rods after the tests (figure 3c). The content of Ni in the test solution increased to 210 ppb. It can be assumed that the intensification of corrosion processes in this case is due to the porous structure of the oxide layer that forms at anodic oxidation at 200 V.

Table 1. The value of the fretting corrosion current ($I_{fret}$) and the content of metal ions in a corrosive environment (Ni, Ti, Al, V) after testing.

|               | $I_{fret}$, μmА | Ni, ppb   | Ti, ppb   | Al, ppb   | V, ppb    |
|---------------|-----------------|-----------|-----------|-----------|-----------|
| Control group | -               | 15±0,6    | 70±28     | 97±31     | 2±0,14    |
| Group I       | 5,8±3           | 44±4      | 78±23     | 106±32    | 2,6±0,7   |
| Group II      | 0,1±0,03        | 16±0,7    | 69±31     | 96±28     | 2±0,12    |
| Group III     | 53±42           | 210±23    | 90±34     | 126±43    | 2,9±0,6   |

4. Conclusions
The results of the work have demonstrated that the formation of nonporous amorphous oxide layer on the surface of titanium screws by low voltage anodic oxidation (U=50 V) prevents NiTi rods damage under fretting corrosion conditions. On the other hand, the presence of porous oxide layer on Ti6Al4V surface that is created by high voltage anodic oxidation (U=200 V) deteriorates corrosion resistance of NiTi significantly.

References
[1] Lukina E, Kollerov M, Meswania J, Mason P, Wagstaff P, Laka A and Blunn G 2015 Spine 40 1 17–24
[2] Lukina E, Laka A, Kollerov M, Sampiev M, Mason P, Wagstaff P, Noordeen H and Blunn G 2016 The Spine Journal 16 3 380–8
[3] Lukina E, Kollerov M, Meswania J, Panin P, Khon A and Blunn G 2017 Materials Today: Proceedings 4 3 4675–9
[4] Reigrut J, Schmidt D, Williams P and Schmidt J 2013 Tribo-Corrosion: Research, Testing, and Applications ed P Blau (ASTM International) 105–24
[5] Lukina E, Kollerov M, Meswania J, Khon A, Panin P and Blunn G 2017 Materials Science and Engineering: C 72 601–10
[6] Wang Y, Jiang B, Lei T and Guo L 2005 Applied surface science 246 1–3 214–21
[7] Borisov A, Krit B, Lyudin V, Morozova N, Suminov I and Apelfeld A 2016 Surface Engineering and Applied Electrochemistry 52 1 50–78