

# Surface modification of TiNi alloy through tantalum immersion ion implantation

Y. Cheng\*, C. Wei, K.Y. Gan, L.C. Zhao

*School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China*

Received 30 December 2002; accepted in revised form 22 April 2003

## Abstract

TiNi alloy samples were implanted with tantalum at a dose of  $3.1 \times 10^{17}$  N/cm<sup>2</sup> by means of Plasma immersion ion implantation (PIII) method. The surface morphology, chemical composition was characterized by Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). The corrosion resistance, were determined by electrochemical methods in 0.9% NaCl solution at 37 °C. The results show that PIII treatment can increase the open-circuit corrosion potential ( $E_{\text{corr}}$ ) and decrease the corrosion current density ( $I_{\text{corr}}$ ). The pitting potential ( $E_{\text{br}}$ ) for the tantalum implanted TiNi alloy is approximately 810 mV, more than 200 mV higher than that of the unimplanted one. The corrosion hysteresis loop of the unimplanted TiNi alloy is larger than that of the implanted material, indicating improvement of the repassivating ability and pitting resistance of the TiNi alloys.  
© 2003 Elsevier Science B.V. All rights reserved.

*Keywords:* Plasma immersion ion implantation; Corrosion resistance; Tantalum; TiNi alloy

## 1. Introduction

TiNi shape memory alloys have found widespread applications in the medical field due to their unique shape memory effect, superelasticity [1–4], as well as biocompatibility [5–8]. However, as the Ni content in the alloy is more than 50 at.%, and the release of Ni ions in all metallic implants takes place during the corrosion process in the physiological environment [9,10], excesses of Ni ion may cause allergic reactions and promote carcinogenesis and toxic reactions [11,12]. The key to improve the TiNi alloys biocompatibility is closely related to the corrosion resistance of the material. To achieve this goal, various methods have been investigated including pulse high-energy density plasma [13], ion-nitrided [14], chemical and electrochemical passivation [15], thermal oxidation [16], excimer laser treatment [17], surface finishing [18], etc.

Plasma immersion ion implantation is an effective technique to modify the properties of biomedical materials without adversely affecting the bulk properties of materials. It has been found that many elements, such

as Cr, Ti, N, B, P and Ta are very useful for improving the corrosion resistance of metals [19,20]. In addition, as tantalum is almost completely immune to body fluids, non-irritating and has a high mass absorption coefficient, it has been widely used for making surgical appliance and implants. Up to date, to the best of our knowledge, there is no report in the literature about the modification of TiNi alloy surface with tantalum immersion ion implantation.

The aim of the present study is to characterize the surface of TiNi alloy implanted with tantalum, and to investigate the corrosion resistance in comparison with the unimplanted specimen in 0.9% NaCl solution.

## 2. Experimental

### 2.1. Substrate preparation

The composition of the test alloy is Ti-50.6 at.% Ni. Samples studied were plates of cold rolled TiNi alloys with the size of  $15 \times 15 \times 1.5$  mm<sup>3</sup>. One face was polished down to 1600 grit specification and then mirror polished with 1 μm diamond paste. Prior to implantation, the samples were cleaned ultrasonically in acetone followed by sputter cleaning in the ion implantation

\*Corresponding author. Tel.: +86-541-6412163; fax: +86-451-6413922.

E-mail address: [chengyan6607@yahoo.com](mailto:chengyan6607@yahoo.com) (Y. Cheng).

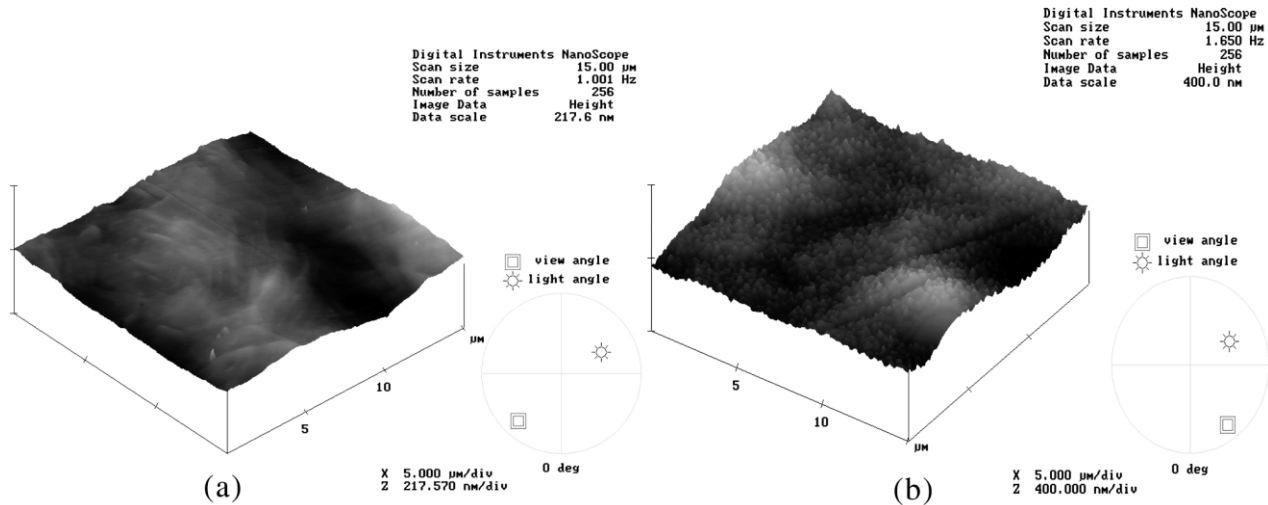


Fig. 1. The AFM images of the surface of TiNi alloy (a) before and (b) after implanted with tantalum.

chamber using energetic ions from argon plasma to remove any residual surface contaminants.

### 2.2. Tantalum immersion ion implantation

The experiment was conducted using a plasma immersion ion implanter. A 13.56 MHz, 2 kW RF plasma source was positioned on top of the chamber to produce RF plasmas of high density and high purity. Four sets of MEVVA plasma sources were located around the chamber to introduce metallic ions into the plasma. Electrons emitted from four sets of multifilament electron guns were used to ignite the vacuum discharge plasma, and a set of RF antennae in the chamber enhances the radial and axial uniformity of the plasma. Tantalum ion was implanted on the TiNi surface with the ion doses of approximately  $3.1 \times 10^{17}$  ions/cm<sup>2</sup>.

### 2.3. Characterization of the deposited films

A Nano-ScopeIII Atomic Force Microscopy (AFM), Digital Instruments, Inc. was used for surface observations. Surface elemental composition, were determined by X-ray photoelectron spectroscopy (XPS) using a ESCA PHI500 spectrometer with a Mg K $\alpha$  X-ray source.

### 2.4. Electrochemical tests

Electrochemical experiments were carried out with a standard three-electrodes system. A saturated calomel electrode (SCE) was used as the reference electrode with a platinum counter electrode. The potentiodynamic experiment was carried out using a computer-controlled potentiostat (EG and G Princeton Applied Research, model 273). The corrosion resistance was examined in 0.9% NaCl solution at  $37 \pm 0.5$  °C (pH 7.4). The

solution was deoxygenated with nitrogen gas, while carrying out the electrochemical studies. Polarization experiments started after the specimen immersed in the experimental solution for half an hour under open-circuit conditions and performed at a rate of 20 mV/min. The open circuit potential was measured immediately after immersion. After the corrosion measurements, the samples were washed with de-ionized water and dried in air.

## 3. Results and discussion

### 3.1. Surface morphology

As the microtopography is an important factor in determining material stability and cellular responses between ultra smooth surfaces and porous structures, and changes in surface roughness will affect the biocompatibility. So the surfaces of the implanted and unimplanted with tantalum were investigated using atomic force microscopy (AFM). Fig. 1 shows a three-dimensional view of the surfaces of TiNi alloys implanted and unimplanted with tantalum. It is clearly seen that the surface obtained after implanting tends to be compact and homogeneous and quite different from that of the unimplanted one, and nano-particles are dispersed evenly throughout the modified surface, and the surface roughness ( $R_a$ ) is approximately 8.231 nm, whereas no such small particles appear on the unimplanted sample.

### 3.2. Surface chemical composition

Fig. 2a shows a typical X-ray photoelectron spectroscopy (XPS) survey spectrum of the unimplanted surface of a mechanically polished to mirror-finish. The dominant surface elements are titanium and oxygen. The main contaminant is carbon. This result is similar to

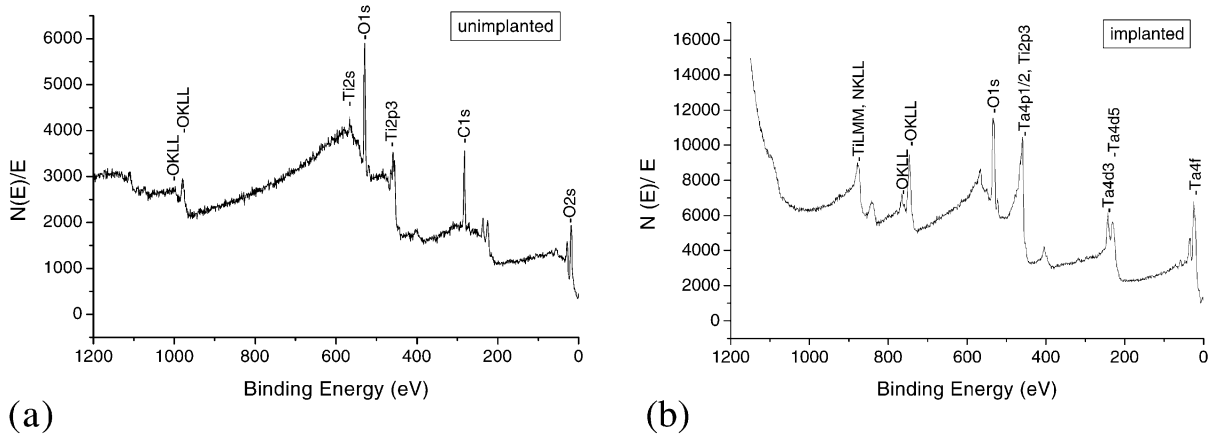


Fig. 2. Typical XPS survey spectrum of the surface of the TiNi samples (a) unimplanted and (b) implanted with tantalum.

that obtained by Shabalovskaya [21]. Fig. 2b is the XPS survey spectrum of the surface of the TiNi sample implanted with tantalum. Ta, Ti and O signals are detected on the implanted samples, and no other elements are observed, including the absence of contamination within the detection limits. It is reasonable as the contamination is removed after argon ion sputtering.

The depth profile of TiNi alloys implanted with Ta is shown in Fig. 3. It can be seen that the tantalum content is approximately 12 at.% in the maximum. The part of the film closer to the surface contains approximately 60–70% oxygen, presumably from the incorporation of Ta and Ti. Ti element distribution is approximately 25 at.% throughout the sputtering time, and Ni is found after 12 min sputtering, indicating no Ni element exists in the outmost layer of the modified sample.

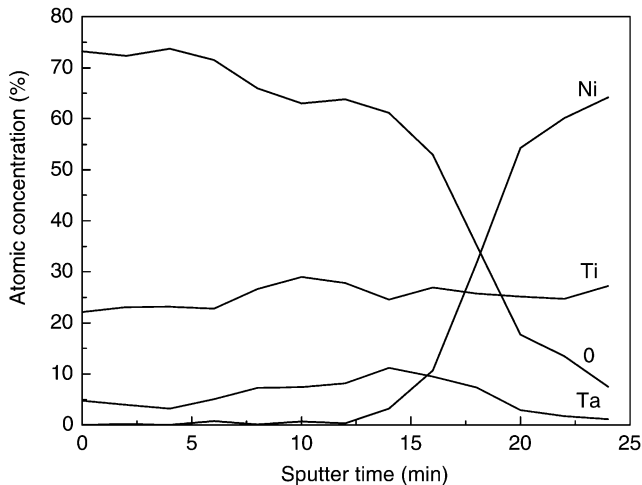


Fig. 3. XPS depth profile of TiNi alloys implanted with Ta.

### 3.3. Electrochemical behaviour

#### 3.3.1. Open-circuit potential

In order to obtain more information on the evolution of the corrosion behaviour, the free corrosion potentials  $E_{corr}$  transients for both unimplanted and implanted TiNi specimens, were investigated as shown in Fig. 3. It is noted that the corrosion potential of the unimplanted and Ta-implanted TiNi alloys stabilize at  $-310$  and  $35$  mV, respectively. The continuous increase in  $E_{corr}$  indicates the passivation of the surface. It can be explained by the fact that both titanium and tantalum are easily passivated in water-contained solution.

#### 3.3.2. Electrochemical potentiodynamic polarization behavior

The open-circuit potential measurement alone does not provide sufficient information for assessing corro-

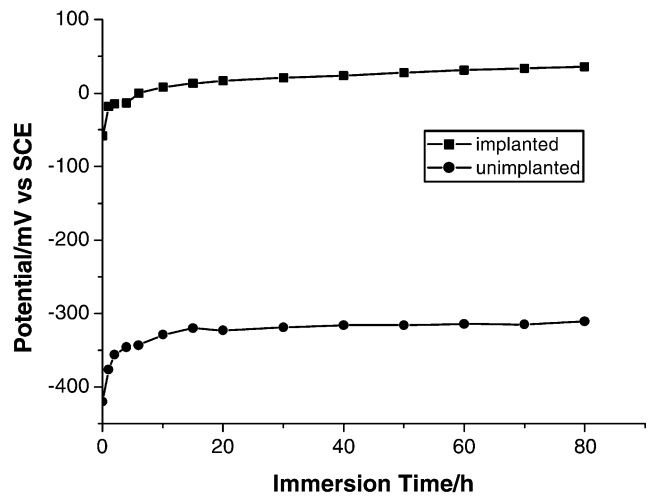


Fig. 4. Open-circuit potentials vs. immersion time in 0.9% NaCl solution.

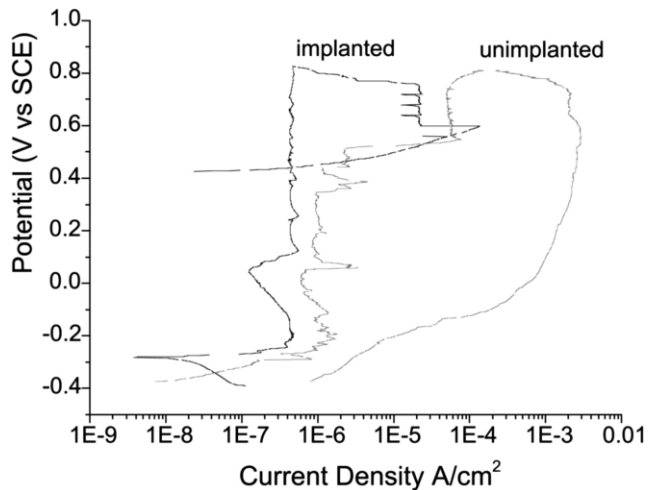


Fig. 5. Cyclic potentiodynamic polarization curves in 0.9% NaCl solution.

sion resistance. Other techniques, such as cyclic polarization curve were used for further investigation. Fig. 4 plots the typical anodic polarization curves of the tantalum-implanted and unimplanted TiNi alloys in 0.9% NaCl solution. Typical hysteresis loops and second passivation phenomenon appear in the curves of tantalum-implanted and the unimplanted sample, indicating surface passivation process happened on both cases. It is well known that the pitting corrosion represents the potential above, which a pre-existing passive film breaks down, and pits originate on the free surface of the specimen. The pitting potential ( $E_{br}$ ) for the tantalum-implanted TiNi alloy is approximately 810 mV, more than 200 mV higher than that of the unimplanted one. The corrosion hysteresis loop of the implanted TiNi alloy is smaller than that of the unimplanted one, indicating improvement of the repassivating ability and pitting resistance of the TiNi alloy. Moreover, the passive current density is approximately  $4.5 \times 10^{-7}$  A/cm<sup>2</sup>, lower than the corresponding values for the unimplanted specimen  $1 \times 10^{-6}$  A/cm<sup>2</sup>. As discussed above, we can come to the conclusion that Ta ion implanted TiNi alloys can improve the corrosion resistance of TiNi alloys in the 0.9% sodium chloride solution Fig. 5.

The reason for the improvement of corrosion resistance of TiNi alloys may be as follows:

Firstly, the formation of tantalum oxide film resulting from a saturation of the valence forces of the atoms in the metal surface by combined oxygen can strengthen the passive film of TiNi alloys. The co-existence of Ta, Ti and O verified by the XPS survey spectrum has demonstrated it. Secondly, from a molecular orbital calculation for d-electron in Ti–Ta system, tantalum is a  $\beta$ -phase stabilizer for titanium, thus it can enhance

the covalent bonds between Ti and Ta, and results in suppression of the dissolution of titanium. And the last, the hydrogen overvoltage of tantalum is larger than that of titanium and leads to the decrease of cathodic current density.

#### 4. Conclusions

In summary, we have successfully demonstrated a new method of modifying TiNi alloy surfaces with tantalum by means of Plasma immersion ion implantation (PIII). This study has shown that TiNi alloys implanted with tantalum cannot only change the surface morphology, chemical composition, but also influence the corrosion behaviour compared with TiNi alloys. When the implanted TiNi alloys are immersed in 0.9% NaCl solution at 37 °C, the modified surface of TiNi alloys can increase the open-circuit corrosion potential and decrease the corrosion current density. The pitting potential for the tantalum implanted TiNi alloy is approximately 810 mV, more than 200 mV higher than that of the unimplanted samples. The corrosion hysteresis loop of the implanted TiNi alloy is smaller than that of the unimplanted one. All of these suggest that PIII technique is an efficient method to improve the corrosion resistance of TiNi alloys.

#### References

- [1] T. Duerig, A. Pelton, D. Stockel, *Mater. Sci. Eng.* A273–275 (1999) 149.
- [2] S.K. Wu, H.C. Lin, *Mater. Chem. Phys.* 64 (2000) 81.
- [3] J.G. Binch, *Proceedings of the First European Conference on Shape Memory and Superelastic Technologies*, Antwerp Zoo, Belgium, 1999, 154.
- [4] P. Philippe, F. Domimique, M.K. Clemens, *Proceedings of the First European Conference on Shape Memory and Superelastic Technologies*, Antwerp Zoo, Belgium, 1999, 165.
- [5] F. Widu, D. Drescher, R. Junker, C. Bourauel, *J. Mater. Sci.: Mater. Med.* 10 (1999) 275.
- [6] D.J. Wever, A.G. Veldhuizen, J.D. Vires, H.J. Busscher, D.R.A. Uges, J.R.V. Horn, *Biomaterials* 19 (1998) 761.
- [7] G. Rondelli, B. Vicentini, *Biomaterials* 20 (1999) 785.
- [8] S.A. Shabalovskaya, *Bio-Med. Mater. Eng.* 12 (2002) 69.
- [9] W.Y. Jia, M.W. Beatty, R.A. Reinhardt, T.M. Petro, D.M. Cohen, C.R. Maze, et al., *J. Biomed. Mater. Res.* 48 (1999) 488.
- [10] K. Endo, R. Sachdeva, Y. Araki, H. Ohno, *Proceedings of the First International Conference on Shape Memory and Superelastic Technologies*, Pacific Grove, California, USA, 1994, 197.
- [11] M. Uo, F. Watari, A. Yokoyama, H. Matsuno, T. Kawasaki, *Biomaterials* 20 (1999) 747.
- [12] C. Shin, S. Lin, K. Chung, Y. Chen, Y. Su, S. Lai, et al., *J. Biomed. Mater. Res.* 52 (2000) 395.
- [13] Y. Ying, X.F. Wu, Y. Wang, B. Li, S.Z. Yang, *Appl. Surf. Sci.* 157 (2000) 167.
- [14] S.K. Wu, C.L. Chu, H.C. Lin, *Surf. Coat. Technol.* 92 (1997) 206.
- [15] B. O'Brien, W.M. Carroll, M.J. Kelly, *Biomaterials* 23 (2002) 1739.

- [16] X.X. Wang, Z.Y. Mao, Z.W. Cao, Proceedings of the Second International Conference on Shape Memory and Superelastic Technologies, Pacific Grove, California, USA, 1997, 621.
- [17] F. Villermaux, M. Tabrizian, L.H. Yahia, M. Meunier, D.L. Piron, *Appl. Surf. Sci.* 109/110 (1997) 62.
- [18] S. Trigwell, G. Selvaduray, Proceedings of the Second International Conference on Shape Memory and Superelastic Technologies, Pacific Grove, California, USA, 1997, 383.
- [19] J.P. Hirvonen, D. Ruck, S. Yan, A. Mahiout, P. Torri, J. Likonen, *Surf. Coat. Technol.* 74–75 (1995) 760.
- [20] Y. Sugizaki, T. Yasunaga, H. Tomari, *Surf. Coat. Technol.* 83 (1996) 167.
- [21] S.A. Shabalovskaya, J.W. Anderegg, *J. Vac. Sci. Technol.* A13 (5) (1995) 2624.