Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 253 (2007) 9426–9429
applied surface science
www.elsevier.com/locate/apsusc

Modification of medical metals by ion implantation of copper

Y.Z. Wan [a], G.Y. Xiong [b], H. Liang [a], S. Raman [c], F. He [a], Y. Huang [a,*]

[a] School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
[b] School of Mechanical and Electrical Engineering, East China Jiaotong University, Nanchang, Jiangxi 330013, PR China
[c] Department of Community Health and Epidemiology, Queen's University, Kingston, Ontario K7L 3N6, Canada

Received 25 July 2006; received in revised form 12 May 2007; accepted 3 June 2007
Available online 26 June 2007

Abstract

The effect of copper ion implantation on the antibacterial activity, wear performance and corrosion resistance of medical metals including 317 L of stainless steels, pure titanium, and Ti–Al–Nb alloy was studied in this work. The specimens were implanted with copper ions using a MEVVA source ion implanter with ion doses ranging from 0.5×10^{17} to 4×10^{17} ions/cm^2 at an energy of 80 keV. The antibacterial effect, wear rate, and inflexion potential were measured as a function of ion dose. The results obtained indicate that copper ion implantation improves the antibacterial effect and wear behaviour for all the three medical materials studied. However, corrosion resistance decreases after ion implantation of copper. Experimental results indicate that the antibacterial property and corrosion resistance should be balanced for medical titanium materials. The marked deteriorated corrosion resistance of 317 L suggests that copper implantation may not be an effective method of improving its antibacterial activity.

PACS : 87.68.+z; 68.55.Ln

Keywords: Ion implantation; Copper; Antibacterial activity; Corrosion resistance; Medical metals; Wear

1. Introduction

Metallic implants made from titanium and its alloys, stainless steel, cobalt-based alloys and so on, still dominate in the implant market on account of their high mechanical properties and ease of machining. However, implant-related infections are considered to be common clinical complications that cause high rates of mortality and morbidity in orthopaedic surgery, and the problem usually causes removal of the prosthesis and second operation, thus increasing health care costs. It is recognized that implants with antibacterial performance would be essential to prevent these bacterial infections. A number of surface modification techniques have been employed to confer metal surfaces with antibacterial property. Ion implantation has unique advantageous features compared to other surface modification techniques; these include high adhesive strength between the modified layer and the bulk materials, high reliability and reproducibility [1].

It has been commonly agreed that copper doping can increase the antibacterial effect of the materials [2–4]. However, copper doping may have an impact on the mechanical properties of metals crucial to implant safety, especially corrosion resistance and wear behaviour. In this work, copper ions were chosen to implant common medical metals including stainless steel, pure titanium, and titanium alloy. The objectives of the present work are to assess the effect of copper ion implantation on the antibacterial performance and the mechanical properties of the medical metals under study, as well as to assess the influence of ion dose on the observed effects.

2. Experimental procedures

2.1. Materials

The medical metals used in this work were a stainless steel (317 L) and two titanium materials (pure titanium and Ti–Al–Nb titanium alloy). Their chemical composition is presented in Table 1. Specimens with dimensions of $15 \times 15 \times 5$ mm^3 were mechanically polished with Al_2O_3 papers to 1000 grit. Plates

* Corresponding author. Tel.: +86 22 2740 5056; fax: +86 22 2740 5056.
E-mail address: tdtlltd@yahoo.com (Y. Huang).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2007.06.031

Table 1
Chemical composition of various materials used in this work

Materials	Elemental content (wt.%)								
317 L	Si $\leq$1.0	Mn $\leq$2.0	P $\leq$0.045	C $\leq$0.03	S $\leq$0.03	Cr 18–20	Ni 11–15	Mo 3.0–4.0	Fe (the rest)
Pure titanium	Fe $\leq$0.30	O $\leq$0.25	C $\leq$0.1	N $\leq$0.05	H $\leq$0.01	–	–	–	Ti (the rest)
Ti–Al–Nb	Fe $\leq$0.04	O $\leq$0.10	C $\leq$0.01	N $\leq$0.01	H $\leq$0.001	Al 6.0	Nb 7.0	–	Ti (the rest)

were ultrasonically washed with acetone and ethanol, and dried prior to ion implantation.

2.2. Ion implantation

Copper ion implantation was performed by using an ion implantation machine (Beijing Normal University, Beijing, PR China) with a MEVVA ion source. Copper ions were implanted into one side of the plates with an acceleration energy of 80 keV and ion-beam current density of 14 μA/cm^2. The implantation dose was set at 0.5, 1, 2, and 4×10^{17} ions/cm^2. The vacuum in the target chamber was kept at 1×10^{-3} Pa.

2.3. Antibacterial tests

The plate-counting method was used to evaluate the antibacterial performance against *Staphylococcus aureus* (*S. aureus*) ATCC6538. All samples were sterilized by autoclave at 121 °C for 20 min. Solution of bacteria with a concentration of 10^5 CFU/ml was dripped onto the surface of the samples at a density of 0.02 ml/cm^2. The specimens with the bacterial solution were covered with an aseptic polyethylene film and incubated at 37 °C for 24 h. Then, the bacterial solution was collected and inoculated onto a standard agar culture medium. After incubation at 37 °C for 24 h, the active bacteria were counted in accordance with the National Standard of China (GB/T 4789.2) and the antibacterial effect was calculated using the following equation:

$$AE(\%) = \left(\frac{C - T}{C}\right) \times 100 \tag{1}$$

where AE is antibacterial effect (%), C is the average number of the bacteria on the control sample (CFU/sample), and T is the average number of bacteria on the testing samples (CFU/sample).

2.4. Wear tests

Wear performance of various samples was evaluated by sliding wear tests. The details of the experiments were described elsewhere [5]. Triple wear tests were conducted for each sample group. Average data are reported for all tests.

2.5. Corrosion measurement

The corrosion resistance in Hank's solution was examined by electrochemical methods using a PARSTAT2263 advanced electrochemical system. The reference electrode was a saturated calomel electrode. The specimen with exposed area of 10×10 mm^2 served as a working electrode. A platinum electrode was used as the reference electrode. Prior to the measurement, the samples were exposed to the test solution and stabilized for 5 min. The polarization in the anodic direction proceeded from a potential of -200 mV to a potential of 1500 mV at a scan rate of 0.5 mV/s.

3. Results and discussion

3.1. Influence of copper ion implantation on antibacterial performance

The results of antibacterial tests are presented in Table 2. Clearly, none of the control samples shows antibacterial effect. Note that antibacterial effect improves with the increase of ion dose in all cases. At low ion doses (0.5–2×10^{17} ions/cm^2), antibacterial effect is relatively low (smaller than 99%), which is not antibacterial as materials are considered antibacterial when the percentage of live bacteria is less than 1% after 24 h incubation according to JIS Z 2801 [6]. All three materials show strong antibacterial activity after copper ion implantation at 4×10^{17} ions/cm^2. Table 3 gives the concentration of copper on the surfaces of the three materials. As listed in this table, the concentration of copper enhances with ion dose, regardless of the nature of substrates. However, the level of copper concentration is dependent on the type of substrates, for example, higher concentrations were evident on titanium

Table 2
Effect of ion dose on the antibacterial effect (%) of various copper ion implanted materials

Samples	Ion dose (10^{17} ions/cm^2)	Antibacterial effect (AE)
317 L	0	0
	0.5	22
	1	69
	2	83
	4	99.7
Pure titanium	0	0
	0.5	31
	1	49
	2	90
	4	100
Ti–Al–Nb	0	0
	0.5	28
	1	42
	2	80
	4	99.9

Table 3
The concentration (wt.%) of copper on the surface of copper-implanted materials

	Ion dose (10^{17} ions/cm^2)			
	0.5	1	2	4
317 L	0.43	0.76	0.98	1.17
Pure titanium	0.92	1.69	3.05	4.70
Ti–Al–Nb	1.34	1.85	3.39	4.84

Table 4
A comparison of surface hardness (Hv 0.005) of control and copper-implanted (1×10^{17} ions/cm^2) materials

Materials	Unimplanted	Copper-implanted
317 L	316	373
Pure titanium	183	268
Ti–Al–Nb	238	329

materials than 317 L. It is interesting to note that the critical concentration of copper that demonstrates antibacterial activity against *S. aureus* is different among the three materials. For instance, a copper concentration of 1.17% enables 317 L to show strong antibacterial activity (99.7%) against *S. aureus*, while pure titanium and Ti–Al–Nb show lower antibacterial effects of 90 and 80% at higher concentrations of 3.05 and 3.35%, respectively. Since antibacterial activity of copper ions is related to the direct contact of copper ions with bacteria, the concentration of copper ions released from the surfaces of materials has an impact on the antibacterial activity [2,7]. The different critical copper contents with the three materials indicate that copper may exist in different states within different materials. This hypothesis will be addressed in future studies.

3.2. Influence of copper ion implantation on wear behaviour

Wear behaviour of 317 L stainless steel, pure titanium, and Ti–Al–Nb implanted at different ion doses were evaluated in the present work. Fig. 1 shows the wear rate as a function of ion dose for the three medical metals. Clearly, the wear rate is ion dose (surface copper content) dependent for all the three materials. The lowest wear rate is observed at 1×10^{17} ions/cm^2, suggesting the materials implanted at 1×10^{17} ions/cm^2 show the best wear performance. Note that the copper-

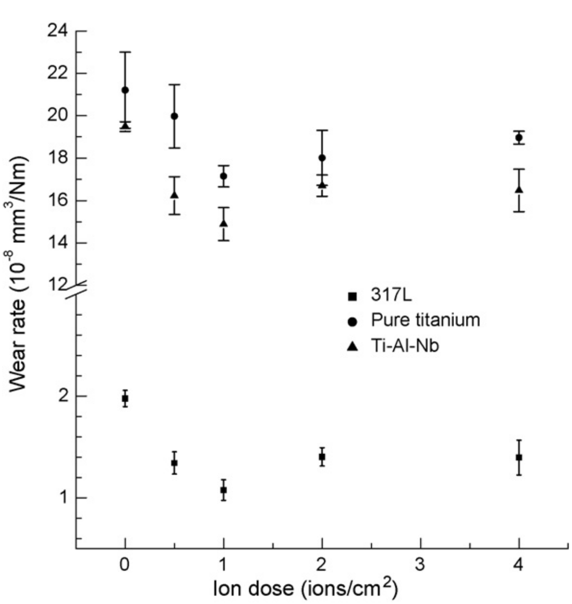

Fig. 1. Wear rate of different copper-implanted samples.

implanted 317 L, pure titanium, and Ti–Al–Nb at 4×10^{17} ions/cm^2 show 30, 11, and 15%, respectively, lower wear rate than their control samples, suggesting copper ion implantation into 317 L, pure titanium, and Ti–Al–Nb can concurrently improve their antibacterial performance and wear property. The hardness given in Table 4 (using DUH-W201/W201S Dynamic Ultra Micro Hardness Tester, Shimadzu, at 50 mN) may indicate that the improvement of wear behaviour is, at least partially, due to the enhanced surface hardness for the medical metals. Previously, Yoshinari et al. found that F^+-implanted specimens, significantly inhibited the growth of both *Porphyromonas gingivalis* ATCC 33277 and *Actinobacillus actinomycetemcomitans* ATCC 43718 than the unimplanted pure titanium while Ca^+- and N^+-ion implanted specimens did not show any inhibition of the growth of either bacteria [8]. This suggests that although ion implantation usually improves wear resistance of biomedical titanium and its alloys [9,10], the type of implanted element controls the antibacterial properties of the resultant implanted materials.

3.3. Influence of copper ion implantation on corrosion resistance

In addition to wear and antibacterial properties, corrosion resistance is of crucial importance for medical metals. Hence, comparisons among control and various ion-implanted samples were made in terms of anodic polarization curves from which the inflexion potential was obtained by determination of the point of the sudden rise of anodic current density. The value of this potential indicates the corrosion resistance, where increasing values of the inflexion potential indicates improved corrosion resistance. The results of electrochemical examinations are presented in Table 5. Clearly, copper ion implantation affects the corrosion resistance of all medical metals studied in this work. Furthermore, the inflexion potential obtained for copper-implanted samples is lower than that from control samples. In the cases of pure titanium and Ti–Al–Nb, the

Table 5
Effect of copper ion implantation on the inflexion potentials (mV) for various medical materials

	Ion dose (10^{17} ions/cm^2)				
	0	0.5	1	2	4
317 L	1.141	0.302	0.173	0.233	0.335
Pure titanium	1.481	1.325	1.241	1.246	1.183
Ti–Al–Nb	1.401	1.304	1.279	1.237	1.103

potential values decrease with the increase of ion dose. The greatest decrease of the potential is noted for 317 L. The potential of the copper-implanted 317 L at 4×10^{17} ions/cm^2 is found to be only 29% of its control sample, while for pure titanium and Ti–Al–Nb, the corresponding values are 80 and 79%, respectively, for pure titanium and Ti–Al–Nb. The decline of corrosion resistance of copper-implanted samples is likely to be attributed to the increased surface flaws such as vacancies, dislocations, and interstitial atoms and to the damage of inactive passive films that cover the surfaces of 317 L, pure titanium, and Ti–Al–Nb as a result of bombardment during ion implantation. The investigation of the detailed mechanisms of these changes is underway.

It should be mentioned that the observed trend of corrosion resistance differs from the change of antibacterial effect with ion dose. In other words, the improved antibacterial activity is offset by the decreased corrosion resistance. It is well recognized that good corrosion resistance is the basic requirement for any metallic materials used *in vivo* and that titanium materials are more favorable than stainless steels due to their better corrosion resistance. From this viewpoint, data shown in Table 5 suggests that copper ion implantation into medical 317 L is not recommended as considerable decrease in corrosion resistance is observed even at a low ion dose of 0.5×10^{17} ions/cm^2.

4. Conclusions

Copper ion implantation improves the antibacterial property of 317 L, pure titanium and Ti–Al–Nb. The antibacterial activity increases with copper ion dose, regardless of the type of the substrates. The copper-implanted materials with an ion dose of 4×10^{17} ions/cm^2 show the highest antibacterial activity in all cases. However, different trends are observed for the changes of wear behavior and corrosion resistance with ion dose. The wear resistance of the copper-implanted materials with the highest ion dose is lower than that with 1×10^{17} ions/cm^2. Furthermore, the corrosion resistance declines with copper ion implantation for the three medical metals studied. The corrosion resistance of 317 L decreases sharply after copper ion implantation at each ion dose; while pure titanium and Ti–Al–Nb experience a gradual decline in corrosion resistance with increasing ion dose. It is believed that copper ion implantation to 317 L is not reasonable due to the resulting marked decrease in corrosion resistance. In the case of titanium materials, a trade-off should be considered between the antibacterial capabilities and corrosion properties when copper ion implantation is employed to improve their safety and efficacy for medical use.

Acknowledgment

This work was supported by the Tianjin Municipal Science and Technology Committee through Grants No. 05YFSYSF01800, No. 043111511 and No. 07ZCKFSF01100.

References

[1] F.Z. Cui, Z.S. Luo, Surf. Coat. Technol. 112 (1999) 278.
[2] I.T. Hong, C.H. Koo, Mater. Sci. Eng. A 393 (2005) 213.
[3] A. Top, S. Ulku, Appl. Clay Sci. 27 (2004) 13.
[4] F. Heidenau, W. Mittelmeier, R. Detsch, M. Haenle, F. Stenzel, G. Ziegler, H. Gollwitzer, J. Mater. Sci.-Mater. Med. 16 (2005) 883.
[5] Y.Z. Wan, G.C. Chen, S. Raman, J.Y. Xin, Q.Y. Li, Y. Huang, Y.L. Wang, H.L. Luo, Wear 260 (2006) 933.
[6] Antimicrobial Products—Test for Antimicrobial Activity and Efficacy, Japanese Standards Association, Japanese Industrial Standard, 2000.
[7] E.A. Neel, I. Ahmed, J. Pratten, S.N. Nazhat, J.C. Knowles, Biomaterials 26 (2005) 2247.
[8] M. Yoshinari, Y. Oda, T. Kato, K. Okuda, Biomaterials 22 (2001) 2043.
[9] M. Yoshinari, Y. Oda, T. Kato, K. Okuda, A. Hirayama, J. Biomed. Mater. Res. 52 (2000) 388.
[10] F. Alonso, M. Rinner, A. Loinaz, W. Ensinger, B. Rauschenbach, Surf. Coat. Technol. 93 (1997) 305.