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LETTER

Surface modification of NiTi alloy with tantalum to improve its biocompatibility and radiopacity

Y. Cheng · W. Cai · H. T. Li · Y. F. Zheng

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Nickel–titanium alloy, with the features of shape memory effect, superelasticity and biocompatibility offers many unique advantages for the biomedical application. These applications have included everything from surgical tools to permanent implants [1–3]. However, many researchers highlighted the selective dissolution of Ni ion from the NiTi alloy during the corrosion process, which could lead to potential danger [4–6]. Different surface treatments have been investigated to improve the corrosion resistance of NiTi implants [7–10]. In modern medicines, to analyze the motion of implants, it is necessary to estimate the 3D position and orientation of each component using radiography [11]. When small stents, guidewires and catheter are quite thin and space farther apart, the detection of the implantable devices or tools become very difficult [12, 13]. The methods to enhance the visibility under X-ray include adding a mark of noble metals and coating with gold, etc. Although gold plating of nitinol components to improve the radiopacity has been achieved by means of electroplating technique, problems such as risks of galvanic corrosion, biocompatibility and hydrogen embrittlement still exist [14].

Tantalum metal has successfully been used for implants for half a century [15]. Since the galvanic potentials of tantalum and nitinol are very similar, the galvanic corrosion effect is almost immeasurable and complete failure of the implants is impossible [16]. Tantalum and tantalum oxide particles are often used to improve radiopacity of other materials [17, 18]. No problems have been reported concerning its biocompatibility [19–22]. It has been found that tantalum coatings are 100% pinhole-free and show great potential within both industrial and medical applications [23]. Tantalum coating with a very ductile nature is suitable where a product can be improved by combining material characteristics of the substrate with an exceptional corrosion-resistant surface [24, 25]. As a result, tantalum is an excellent candidate for usage as coatings for NiTi alloys to improve its anti-corrosion property and radiopacity.

For coating applications, a good bonding strength between the coating and the substrate is required in order to ensure the lifetime service in the implanting environment [26]. The multi arc ion-plating technique, with the feature of high packing density and good adhesion, can satisfy this requirement [27]. Accordingly, the purpose of the present study is to develop a novel biocompatible and radiopaque Ta coating on NiTi alloy by multi-arc ion plating technique, the surface characterization, corrosion behavior and hemocompatibility are investigated.

The chemical composition of the experimental alloy was Ti-50.6 at%. All samples were mechanically polished to 1 μm and then ultrasonically cleaned in acetone, alcohol and distilled water successively, then dried and loaded into the deposition chamber. The tantalum coatings were deposited by multi arc ion-plating technique [27]. Prior to deposition, the surfaces of the NiTi alloy substrates were further cleaned by Ar ion bombardment with energy of 1100 eV for 10 min. And the temperature of the NiTi alloy substrates was held to be 300 °C. The substrate bias voltages were controlled to be −300 V with an arc current be 75 A, deposition pressure

Y. Cheng · Y. F. Zheng (✉)
Department of Materials and Nanotechnology, College of Engineering, Peking University, Beijing 100871, China
e-mail: yfzheng@pku.edu.cn

W. Cai · H. T. Li
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

be 1.5–2.0 Pa. The deposition time is 100 min except for the stents. The as-deposited samples were annealed at 900 °C for 60 min in air.

A S-570 Scanning Electron Microscope (SEM) was utilized to investigate the cross-sectional morphology of the tantalum coatings.

The release of nickel ion was determined by measuring the nickel ion content in the 0.9% NaCl solution after 1, 7, 14, and 49 days, respectively. All samples were entirely immersed in sealed 0.9% sodium chloride solution and maintained at 37 ± 0.5 °C. The nickel ion release was measured by a graphite-furnace atomic absorption spectrometry (GFAAS) (AA6501F, Shimadzu, Japan). The thromboresistant property of the materials was evaluated using an adult volunteer fresh blood by the kinetic clotting method. In vitro platelet adhesion test was subsequently performed to identify the blood compatibility of the tantalum coatings according to the method presented in the paper [28], The samples were incubated in the plasma in an atmosphere for 30 min.

Figure 1 is a typical SEM micrograph showing the cross-sectional morphology of the NiTi alloy specimen coated with tantalum (the negative bias voltage is −300 V, and deposition time is 100 min). A uniform tantalum coating can be observed on the surface of the NiTi alloys.

As the film as-deposited was composed of a metastable tetragonal h-Ta which is hard, brittle, thermally unstable, and can transform into a-phase tantalum through annealing. The effect of annealing temperatures on the microstructure of as-deposited films is shown in Fig. 2. XRD results reveal that all the metastable tetragonal h-Ta transform into body-centered cubic a-Ta with body-centered cubic structure after annealing.

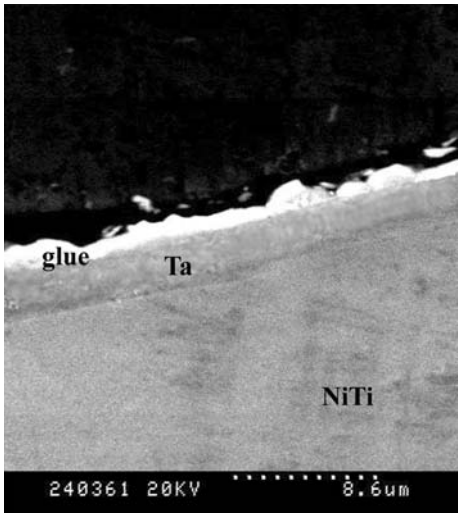

Fig. 1 SEM cross-sectional morphology of the TiNi alloy coated with tantalum

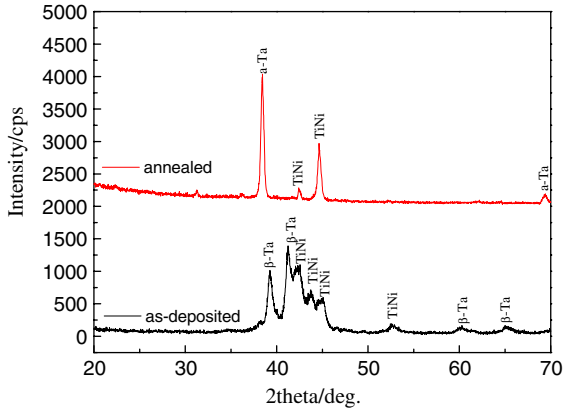

Fig. 2 XRD pattern of the as-deposited and annealed Ta coatings on TiNi alloy

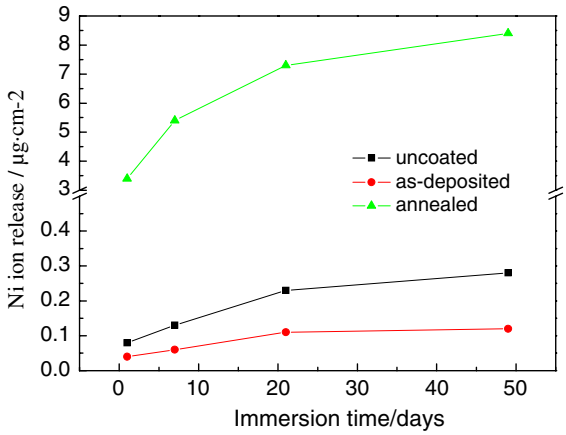

Fig. 3 The amount of Ni ion release from different specimens

The release of Ni ion takes place during the corrosion process in the physiological environment. Fig. 3 illustrates the variation curves of the amount of Ni ion release with the immersion time for different samples immersed in 0.9%NaCl solution. Clearly, the amount of Ni ion released from the as-deposited samples reduces significantly in comparison with that of the uncoated sample. On the other hand, the annealing treatment can further decrease the ion release for the as-deposited samples. All the specimens have the same tendency that the Ni release rate decreases with the immersion time. This experiment shows that the tantalum coating effectively suppresses the release of Ni ion. The amount of the released Ni ion from the as-coated NiTi alloy sample is as about 1/30 times as that from the uncoated NiTi alloy sample after immersing in the 0.9%NaCl solution for 49 days, which can attributed to the improvement of the anti-corrosion properties and the barrier effect of the tantalum coating that prohibits the Ni ion release into the immersion solution.

The optical densities versus time curves of different samples are shown in Fig. 4. The optical density represents

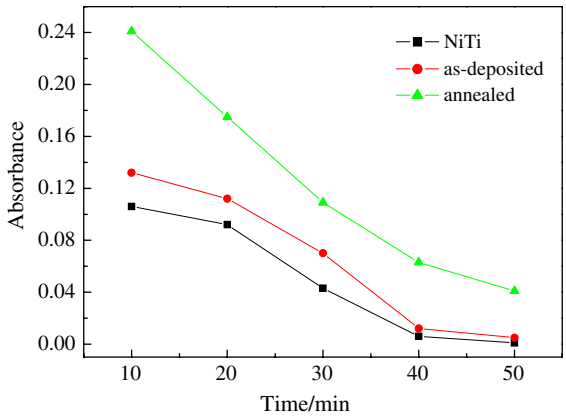

Fig. 4 Optical density versus time curves and amount of platelet on the surface of different samples

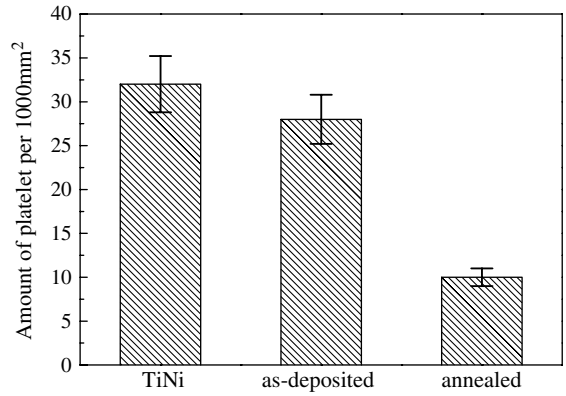

Fig. 5 Amount of platelets on the surface of different samples

the relative concentration of the hemolyzed hemoglobin when a material contacts with the blood for a predetermined time. The higher the absorbance is, the better the thromboresistance is. Clearly, it can be seen that the clotting tendency of the as-coated NiTi alloy sample after annealing is the lowest compared with other samples, and the uncoated NiTi alloy specimen behaves the poor thrombo-resistant ability in all experimental samples.

As platelet activation can elicit a variety of physiologic cellular responses including shape change, release of granule contents and initiation of aggregation, platelets have been extensively studied due to their role in thrombogenesis when the blood makes contact with the surface of sample. In the present study, we use in vitro platelet adhesion experiment to evaluate the preliminary hemocompatibility of Ta coating. Figure 5 shows the amount of platetlets adhered on the different samples. Obviously, the amounts of platelets on the surface of uncoated NiTi alloy sample are higher than that of the other samples. The Ta-coated sample after annealing has the lowest amount of adhered platelets.

The X-ray photographs of NiTi alloy wire and pure Ta wire both with the same diameter of 0.6 mm are shown in Fig. 6a. It can be seen that the image of the tantalum wire is much bright and clear compared to that of the NiTi alloy wire, which indicates that Ta has a better X-ray visibility than the NiTi alloy, and we can make use of Ta to improve the radiopacity.

Figure 6b illustrates the X-ray photographs for NiTi alloy mesh stents, weaved by a single 0.12 mm diameter NiTi alloy wire and coated by Ta for different times. Obviously, the uncoated NiTi alloy stent is quite dark and unclear in comparison to all Ta-coated NiTi alloy stents. And for the Ta-coated samples, the higher the deposition time is, the brighter the image of NiTi alloy stent under X-ray is.

For the implant materials, especially for the thin and small stent, improving its X-ray visibility is an essential requirement. This can help the surgeons or cardiologists to determine the location and orientation of the implanted device more accurately. The radiopacity of a material is related to the following Equation [29]

$$I = I_0 \, e^{-mx}$$

I is the strength of X-ray after transmission, I_0 the strength of X-ray before transmission, m absorption coefficient of material for X-ray and x the material thickness.Clearly, the higher the atomic number and the specific gravity of material are, the weaker the strength of X-ray after transmission is, and the clearer its X-ray visibility is. Our results indicate that the tantalum coating can efficiently improve the radiopacity of the NiTi alloy stent.In summary,

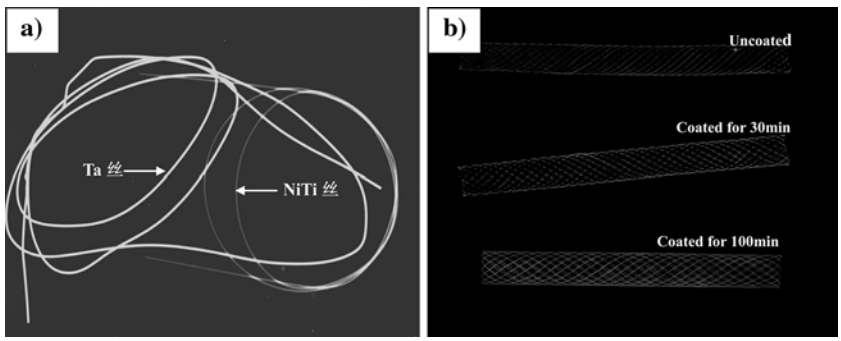

Fig. 6 X-ray photographs of Ta and TiNi wires with the same diameter (**a**) and stents of the uncoated and coated for different deposition time (**b**)

tantalum coatings have been successfully deposited on the surface of Ti-50.6 at.% Ni alloy samples by the multi arc ion-plating technique. The tantalum coating effectively suppresses the release of Ni ion. The amount of the released Ni ion from the as-coated NiTi alloy sample is as about 1/30 times as that from the uncoated NiTi alloy sample after immersing in the 0.9%NaCl solution for 49 days. The hemocompatibility of the NiTi alloy coated with tantalum is better than that of the uncoated one, and after annealing treatment, the hemocompatibility of the Ta-coated sample behaves the best. The tantalum coating can efficiently improve the radiopacity of the NiTi alloy stent.

References

1. Duerig T, Pelton A, Stockel D (1999) Mater Sci Eng (A) 273–275:149
2. Thompson A (2000) Inter Endo J 33:297
3. Fatiha EF, Gaetan L, Michel F, Diego M (2002) Adv Eng Mater 4:91
4. Shabalovskaya SA (2002) Bio-Med Mater Eng 12:69
5. Wever DJ, Veldhuizen AG, Vriesv J, Busscher HJ, Uges DRA (1998) Biomaterials 19:761
6. Putters JL, Kaulesar SD, De Zeeuw GR, Besselink PA (1992) Euro Surg Res 24:378
7. Starosvetsky D, Gotman I (2001) Biomaterials 22:1853
8. Villermaux F, Tabrizian M, Yahia LH, Meunier M, Piron DL (1997) Appl Surf Sci 109/110:62
9. Cheng Y, Cai W, Gan KY, Zhao LC (2004) Surf Coat Technol 176:261
10. Cheng Y, Cai W, Li HT, Zheng YF, Zhao LC (2004) Surf Coat Technol 186:346
11. Imai S, Higashijima K, Ishida A, Fukuoka Y, Hoshino A, Minamitani H (2003) Med Eng Phys 25:419
12. Duerig TW, Tolomeo DE, Wholey M (2000) Min Invas Ther Allied Technol 9:235
13. Kastrati A, Mehili J, Dirschinger J (2001) Circulation 103:2816
14. Steegmueller R, Wagner C, Fleckenstein T, Schuessler A (2002) Mater Sci Forum 394–395:161
15. Gardner WJ (1946) Cleve Clin Q 13:72
16. Venugolapan R, Trepanier C (2000) Mini Invasive Therapy Allied Tech 9:67
17. Chan DC, Titus HW, Chung KH, Dixon H, Wellingoff ST, Rawls HR (1999) Dent Mater 15:219
18. Warren A (1970) Radiology 97:327
19. Kovacs P, Davidson JA (1996) In: Brown SA, Lemons JE (eds) Chemical, electrochemical aspects of the biocompatibility of titanium and its alloys. Medical applications of titanium and its alloys: the material and biological issues. Philadelphia, p 163
20. Jaschke W, Klose KJ, Strecker EP (1992) Cardiovascular Intervent Radiol 15:356
21. Johasson CB, Hansson HA, Albreksson T (1990) Biomaterials 11:277
22. Hironobu M, Atsuro Y, Fumio W, Motohiro U, Takao K (2001) Biomaterials 22:1253
23. Lee SL, Cipollo M, Windover D, Rickard C (1999) Surf Coat Technol 120–121:44
24. Sartwell SD, Natishan PN, Donovan EP, Bunker SN, Armini AJ (1996) Surf Coat Technol 83:183
25. Macionczyk R, Gerold B, Thull R (2001) Surf Coat Technol 142–144:1084
26. Ashrafizadeh F (2000) Surf Coat Technol 130:186
27. Randawa H, Johnson PC (1987) Res Devel 2:173
28. Huang N, Yang P, Leng YX, Chen JY (2003) Biomaterials 24:2177
29. Feinstein LG, Hutteman RD (1973) Thin Solid Films 16:129