J Mater Sci: Mater Med (2008) 19:1553–1557
DOI 10.1007/s10856-008-3374-9

Surface preparation of bioactive Ni–Ti alloy using alkali, thermal treatments and spark oxidation

W. Chrzanowski · E. A. Abou Neel ·
D. A. Armitage · J. C. Knowles

Received: 4 September 2007 / Accepted: 4 January 2008 / Published online: 24 January 2008

Abstract The primary aim of this study was to compare different surface treatments used for bioactivation of pure titanium surfaces—thermal, alkali treatment and spark oxidation, and to assess their suitability as treatments for Ni–Ti alloys. This was considered by examining the surface properties, calcium phosphate precipitation from a physiological solution, and nickel ion release. Additionally, changes in the transformation temperature were measured for thermally treated samples. These studies indicate that the native surface of Ni–Ti alloy is highly bioactive when assessing the precipitation of calcium phosphates from Hank's solution. Low temperature heat treatments also produced promising surfaces while high temperature treatment resulted in a very low rate of Ca and P precipitation. Alkali treatment and spark oxidation resulted in some bioactivity. Nickel ion release was greatest for alkali treated and sparks oxidized samples, and the rate of its release from these two samples was on the verge of daily safe dose for adolescent human. The other analyzed samples revealed very low rates of nickel ion release. Heat treatment at 400°C resulted in significant increase in the transformation temperatures, and a further increase of the treatment temperature up to 600°C caused a drop of the transformation temperature.

1 Introduction

Nickel titanium alloys (Ni–Ti or Nitinol) are commonly manufactured as implants used for different biomedical purposes such as: cardiologic, urologic stents, dental and maxillofacial implants and orthopaedic devices [1–7]. Each of these applications requires different properties with respect to surface chemistry, energy or wear. To date, different surface treatments have resulted mainly in formation of an oxide layer—TiO_2, Ni_2O_3 [6, 8–12]. It was shown also that titanium oxides have bioactive properties, and they can cause HAP formation on the surface. Noteworthy is the fact that alkali treatment of titanium in NaOH resulted in precipitation of a large amount of Ca–P on the surface when immersed in a physiological solution [13–15]. Several authors presented variety of methods to enhance bioactivity and the most effective were methods that gave porous, complex 3D topography to the surface [2, 16–18]. It was also proved by cell culture examination that those kinds of surfaces are more likely to trigger biological activity [19–22]. The complex surface topography could be beneficial to form apatite nuclei and increase adherence between the coating and substrates. However, in regards to the Nitinol bioactivation, the release of nickel ions must be considered. It is known that ingesting nickel above a threshold of 200–300 μg/day can cause serious health problems, and even trace release from implant materials can result in significant ion concentrations in the surrounding tissues. Furthermore, the increasingly common hypersensitivity to nickel as a result of nickel-plating on jewellery is also a major cause for concern.

The primary aim of this study was to compare different surface treatments used in the bioactivation of pure titanium surfaces—thermal, alkali treatment and spark oxidation and assess their suitability as treatments for Ni-Ti alloys by examining the surface properties.

W. Chrzanowski (✉) · E. A. Abou Neel · J. C. Knowles
Division of Biomaterials and Tissue Engineering,
Eastman Dental Institute, University College London,
256 Gray's Inn Road, London WC1X 8LD, UK
e-mail: w.chrzanowski@eastman.ucl.ac.uk

D. A. Armitage
Department of Engineering, University of Leicester,
Leicester LE1 7RH, UK

2 Materials and methods

In the study, nickel titanium alloy 50Ni–50Ti was used in the superelastic form (Johnson Matthey, Inc.). Flat samples were ground on SiC paper to 4000 grit, cleaned, then soaked in 37.5% HNO_3 for 10 min, and finally cleaned again. There were four sample groups. Three different types of treatment and a control:

- Thermal—at 400, and 600°C in air for 1 h—400, 600,
- Alkali—in 10 M NaOH (24 h, 80°C), then heat treatment in 600°C in air [14, 23]—BNT,
- Plasma electrolysis—spark oxidized in H_2SO_4, H_3PO_4, 250 mA, 1 min [24–26]—SP.
- The reference cpTi samples ground to mirror finish were used.

Atomic force microscopy (AFM) (PSIA XE-100) in non-contact mode was used to examine the topography of the samples surfaces. *X-ray photoelectron spectroscopy (XPS)* (Thermo Escalab 220iXL) measurements was performed to examine the chemical composition of the sample surfaces using an Al Kα monochromated X-ray source and quantified in CasaXPS (Casa software Ltd). *Contact Angle (CA)* (KSV Cam200) measurements were also carried out using ultrapure water to assess the wetting ability of the surfaces after treatments. In this test, droplets of approximately 5 µl of ultra-pure water were placed on the samples surface using a manual syringe. To assess the ability for *calcium and phosphorous precipitation* on their surfaces, samples were immersed in Hanks' balanced salt solution (HBSS, Gibco) for 3 h, 24 h and 7 days at 37 ± 1°C. Chemical compositions of the surfaces were also examined using XPS and topographic information provided by AFM. The transformation behavior and the characteristic temperatures of the Nitinol samples treated at 400 and 600°C were determined using a *Pyris Diamond DSC* (Perkin-Elmer Instruments) and compared with the non treated ground samples. For DSC, discs ($n = 3$) of each sample were heated from -50 to 150°C at 10°C min^{-1}, and the transformation temperature was calculated by the onset of change in the endothermic direction (upwards) of the heat flow of the heating ramp. All tests were carried out under nitrogen purge. Nickel ion release was evaluated using *inductively coupled plasma mass spectrometry (ICP-MS)* (Spectromass 2000, Spectro). Samples for the ion release evaluation were soaked in ultrapure water for 3 h, 24 h and 7 days. Two isotopes (^{58}Ni and ^{60}Ni) were measured, and the results were considered by taking the average of three repeat. The instrument was calibrated in the range 1ppb to 1ppm using a single element standard (Fluka, TraceCERT^{TM} Ultra).

3 Results and discussion

Heat treatment slightly increased the roughness of the surface as measured by AFM, and this roughness increased with increasing heat treatment temperature—Table 1. The alkali treatment; however, produced sample surfaces with more complex structure (Fig. 1c) and greater roughness than those of heat treated samples at 600°C (Fig. 1b). The spark oxidized (Fig. 1d) samples had a rough layer and exhibited a pitted structure.

The XPS are compiled in Table 1. Thermal treatment resulted in gradual increase in thickness of the oxide layer with increasing temperature. For example, the samples treated at 600°C were composed of titanium dioxide and nickel oxides. Whilst the samples treated at 400°C contained some amount of metallic nickel and titanium which may suggest that the oxide layer is thinner. Not only the oxide layer thickness but also the surface roughness increased with temperature. The alkali treatment resulted in increased Na content within the surface layer that showed a very low contact angle i.e. high wettability. However, the very high Ni/Ti ratio obtained with these samples causes concern. On the other hand, the spark oxidized surface was composed mostly of titanium dioxide with very little nickel oxide. The samples exhibited high roughness and a significant quantity of phosphorous at the surface. The contact angle values for spark oxidized samples suggest that the bioactivity may be high. For thermally treated samples, the wettability increased with temperature but still was significantly lower than untreated, alkali and spark oxidized samples.

After 3 h soaking in HBSS, a gradual increase of calcium and phosphorous (mainly present as phosphate) precipitation on the surfaces was observed for all the samples. The highest Ca/P ratio was observed for ground and heat treated at 400°C (0.90 and 1.17). Soaking for 24 h, however, resulted in further increase of the Ca and P concentrations. The increase of the calcium and phosphate content was significant for ground Ni–Ti and reference titanium, and it was slightly lower for thermally, alkali treated and spark oxidized samples. Significantly lower content of Ti on the BNT surface could be the main reason for lower calcium and phosphate precipitation. Titanium seems to be responsible for higher bioactive properties of other samples that contained greater amount; predominantly as TiO_2. In addition very small changes of the roughness of BNT samples could suggest that a very thin apatite layer was growing uniformly on the surfaces. After 24 h, Ca/P ratio was close to 1.30 for: ground, treated at 400°C and alkali treated. These values were close to the reference titanium. In spite of the relatively quick increase of Ca and P on cpTi the ratio was far from that found in

Table 1 Results of XPS analysis (calcium, phosphorous, Ca/P and Ni/Ti ratio), contact angle measurement (CA) and AFM roughness measurement for the samples after surface treatment and soaking in HBSS for 3 and 24 h

Sample	Ca (wt. %)	P (wt. %)	Ca/P	Ni/Ti	CA (°)	R_a^{AFM} (nm)
Ti	0.16 ± 0.04	0.62 ± 0.06	0.25 ± 0.05	n/a	47.18 ± 0.42	5.67 ± 1.14
Ti 3 h	0.41 ± 0.23	0.97 ± 0.24	0.41 ± 0.14	n/a	n/a	7.53 ± 1.02
Ti 24 h	10.31 ± 0.35	7.78 ± 0.53	1.33 ± 0.05	n/a	n/a	30.32 ± 6.21
NiTi	0.00	0.00	0.00	0.44 ± 0.14	32.71 ± 0.44	10.28 ± 1.24
NiTi 3 h	0.35 ± 0.15	0.39 ± 0.15	0.90 ± 0.049	0.44 ± 0.02	n/a	11.56 ± 1.67
NiTi 24 h	9.42 ± 0.71	6.72 ± 0.42	1.40 ± 0.02	0.16 ± 0.15	n/a	68.45 ± 7.87
400°C	0.16 ± 0.05	0.00	0.00	0.31 ± 0.09	55.77 ± 8.09	7.06 ± 0.87
400°C 3 h	0.31 ± 0.05	0.27 ± 0.02	1.17 ± 0.24	0.26 ± 0.04	n/a	9.62 ± 4.35
400°C 24 h	4.75 ± 0.76	3.63 ± 0.27	1.31 ± 0.11	0.63 ± 0.32	n/a	113.56 ± 3.53
600°C	0.00	0.00	0.00	0.09 ± 0.01	45.13 ± 1.84	22.88 ± 2.11
600°C 3 h	0.33 ± 0.11	0.77 ± 0.03	0.42 ± 0.12	0.05 ± 0.01	n/a	19.51 ± 3.53
600°C 24 h	0.23 ± 0.14	0.61 ± 0.08	0.36 ± 0.18	0.09 ± 0.02	n/a	30.51 ± 2.12
BNT	1.23 ± 0.27	0.00	0.00	16.63 ± 2.40	14.52 ± 3.09	64.11 ± 10.80
BNT 3 h	0.42 ± 0.12	0.74 ± 0.52	0.69 ± 0.32	72.55 ± 41.22	n/a	42.54 ± 2.82
BNT 24 h	3.56 ± 0.40	2.94 ± 0.93	1.25 ± 0.26	14.77 ± 3.94	n/a	42.00 ± 2.11
SP	0.36 ± 0.22	10.93 ± 0.22	0.03 ± 0.01	0.59 ± 0.09	12.25 ± 6.20	142.11 ± 24.48
SP 3 h	2.85 ± 0.18	11.67 ± 0.72	0.25 ± 0.03	0.31 ± 0.01	n/a	281.53 ± 10.60
SP 24 h	4.77 ± 0.34	11.14 ± 0.04	0.43 ± 0.03	0.33 ± 0.04	n/a	216.51 ± 20.50

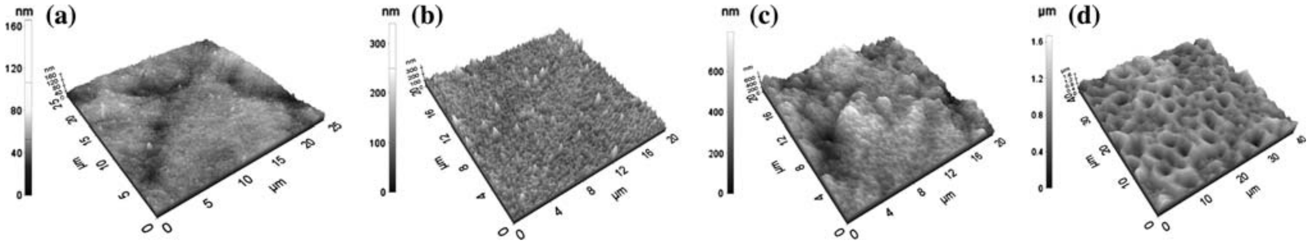

Fig. 1 AFM images of the (**a**) ground—NiTi, (**b**) thermally treated at 600°C, (**c**) alkali treated—BNT and (**d**) spark oxidized—SP

hydroxyapatite (HAP). For the samples treated at 600°C, there were no significant changes with soaking; the amount of the Ca and P remained very low. The fastest growth rate of the layer thickness was observed for ground NiTi, and this rate was similar to the cpTi. For heat treated at 400°C, spark oxidized, and alkali treated Ni–Ti samples, the increase rate was slightly lower.

In the literature it was demonstrated that alkali treatment had a very positive effect on bioactivity of cpTi. Unexpectedly this treatment did not change significantly the bioactive properties of NiTi. It is assumed that the main reason for this is the chemical composition of the top layer which was in contact with the media. Alkali treatment removed titanium from the surface. Therefore, the layer was very rich in nickel (not showing bioactive properties).

XPS analysis of samples soaked for 7 days in HBSS did not bring any further information due to the fact that the surfaces of all the samples were covered with layer that was thicker than the depth of the XPS analysis. On the surface, only C, Ca and P were observed. Therefore, it was suggested that all the samples possessed bioactive properties and the difference in the bioactivity rate could be detected only up to 24 h using XPS. Beyond that point, however, other techniques such as; wavelength dispersive X-ray (WDX), X-ray powder diffraction (XRD), and glow discharge spectroscopy (GDS) could be used to evaluate the apatite layer formation rate.

Nickel ion release was at very low levels for ground and thermally treated samples (Fig. 2). After 7 days, the amount of released nickel did not exceed 0.22 μg l^{-1} mm^{-2}. The alkali treated samples and spark oxidized samples showed significantly higher release. The amount of nickel, detected in the water, was approximately 6.2 and 11.5 μg l^{-1} mm^{-2} for alkali treated and spark oxidized respectively. This demonstrated that these two types of surface preparations require further modification before they can be considered

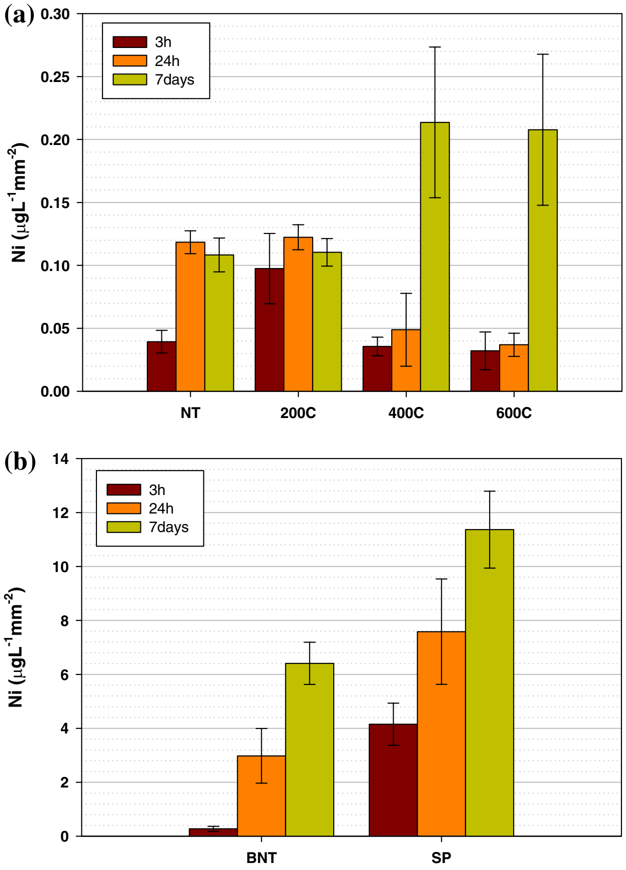

Fig. 2 ICP-MS results of nickel release form the samples (**a**) NiTi 400°C, 600°C, and (**b**) BNT and SP

for biomedical applications. The release of nickel at levels approximating the recommended daily amount for ingestion is of concern as release from a biomaterial is likely to result in far higher local concentrations than ingested nickel.

The DSC analysis revealed the difference in the transformation temperature after thermal treatment—Fig. 3. The highest temperature (49.4°C) was observed for the samples annealed at 400°C. It was about 30°C higher than the ground samples. A reduction in the transformation temperature to 30.6°C was observed with increasing the annealing temperature to 600°C. These results suggest that heat treatment has an influence on structure of the Nitinol in the body temperature, and this should be taken into account during treatment selection for certain applications. Cold work is frequently used by manufacturers to alter the phase transformation energetics and hence change in the transformation temperatures. Therefore, the changes on heat treatment may be due to thermal recovery in the crystal structure. Analyzing the heat treated samples showed that the highest calcium and phosphorus precipitation was observed for the treatment at 400°C. It can suggest that austenitic structure could be more prone to trigger precipitation of the elements and is more bioactive. However, this statement is contradicted by the ground sample which had the highest Ca/P ratio and also had significantly higher wettability that is considered an important factor for bioactivation.

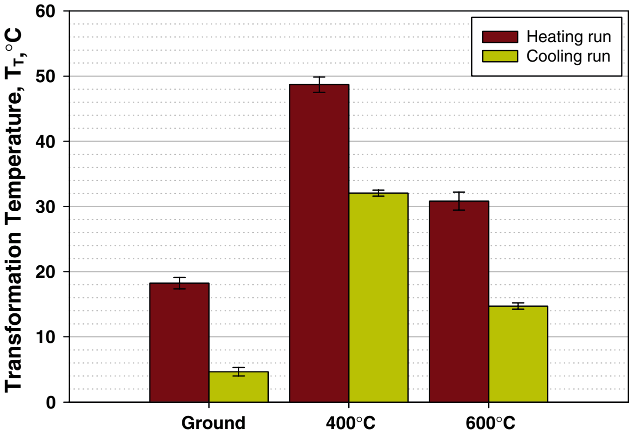

Fig. 3 Transformation temperature of heat treated nickel titanium alloy at temperatures 400 and 600°C

4 Conclusions

Significant differences in topography, chemistry and wetting ability of modified Ni–Ti surfaces were observed by altering the surface treatment. The alkali treatment used in the bioactivation of titanium produced a very high Ni/Ti ratio. Careful control of oxidation in air was found to reduce both the Ni/Ti ratio and contact angle values. Bioactivity study showed a gradual increase of the calcium–phosphorous film for all the samples except those thermally treated at 600°C. However, differences in Ca/P ratio for different surface preparation were observed. The rate of the film growth and Ca/P ratio was the most favorable for ground Ni–Ti, alkali treated and reference cpTi. No growth of the layer was noticed for samples heat treated at 600°C. For thermally treated samples and ground samples, a very low rate of nickel release was observed. However, for alkali and spark oxidized samples, the rate was very high and would be a major cause for concern when these treatments considered as implant materials. DSC analysis revealed that heat treatment at 400°C significantly increased the transformation temperature. Ni–Ti alloy treated at this temperature had a different crystallographic structure at body temperature than the other analyzed samples. Further increase of the treatment temperature caused a drop of the transformation temperature.

Acknowledgements This work was supported by EU FP6, IEF Marie Curie action, and EPSRC.

References

1. M.F. Chen, X.J. Yang, R.X. Hu et al., Mater. Sci. Eng. C **24**, 497–502 (2004)
2. P. Filip, J. Lausma, J. Musielak, K. Mazanec, Biomaterials **22**, 2131–2138 (2001)
3. N. Shevchenko, M.-T. Pham, M. F. Maitz, Appl. Surf. Sci. **235**, 126–131 (2004)
4. C.L. Chu, C.Y. Chung, P.H. Lin, S.D. Wang, J. Mater. Process. Technol. **169**(1), 103–107 (2005)
5. B. Grosgogeat, E. Jablonska, J.M. Vernet et al., Mat. Sci. Eng.: C **26**(2–3), 267–272 (2006)
6. A. W. Hassel, Minim. Invasive Ther. Allied Technol. **13**(4), 240–247 (2004)
7. Y.F. Zheng, B.M. Huang, Shape memory materials and its applications. Mater. Sci. Forum **394**(3), 57–60 (2001)
8. Y. Cheng, Y.F. Zheng, Mat. Sci. Eng.: A **438–440**, 1146–1149 (2006)
9. X. Ju H. Dong, Surf. Coat. Tech. **201**(3–4), 1542–1547 (2006)
10. J. Ryhanen, *Biocompatibility evaluation of nickel–titanium shape memory alloy*, (OulunYliopisto, Oulu, 1999)
11. L. Tan, R.A. Dodd, W.C. Crone, Biomaterials **24**, 3931–3939 (2003)
12. J.H. Yi, C. Bernard, F. Variola et al., Surf. Sci. **600**(19), 4613–4621 (2006)
13. T. Kokubo, F. Miyaji, H.M. Kim, J. Am. Ceram. Soc. **79**, 1127–1129 (1996)
14. T. Kokubo, Acta Mater. **46**(7), 2519–2527 (1998)
15. T. Kokubo, Mat. Sci. Eng. C **25**, 97–104 (2005)
16. S. Fujibayashi, M. Neo, H.-M. Kim et al., Biomaterials **25**, 443–450 (2004)
17. C. Garcia, S. Cere, A. Duran, J. Non-Cryst. Solids **352**(32–35), 3488–3495 (2006)
18. S.F. Hulbert, S.J. Morrison, J.J. Klawitter, J. Biomed. Mat. Res. **6**, 347–374 (1976)
19. V.C. Dinca, S. Soare, A. Barbalat et al., App. Surf. Sci. **252**, 4619–4624 (2006)
20. T.J. Flatley, K.L. Lynch, M. Benson, Clin. Orthop. **179**, 246–252 (1983)
21. X.X. Wang, S. Hayakawa, K. Tsuru, A. Osaka, J. Biomed. Mater. Res. **52**, 172–178 (2000)
22. D.J. Wever, A.G. Veldhuizen, M.M. Sanders et al., Biomaterials **18**, 1115–1120 (1997)
23. M.F. Chen, X.J. Yang, Y. Liu et al., Surf. Coat. Technol. **173**, 229–234 (2003)
24. W. Chrzanowski, J. AMME **18**(1–2), 67–71 (2006)
25. W. Chrzanowski, J. Szewczenko, J. Tyrlik-Held et al., J. Mat. Proc. Technol. **162–163**, 163–168 (2005)
26. A.L. Yerokhin, X. Nie, A. Leyland et al., Surf. Coat. Technol. **122**(2–3), 73–93 (1999)