Available online at www.sciencedirect.com
ScienceDirect
Acta Biomaterialia 4 (2008) 1969–1984
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

Effect of surface treatment on the bioactivity of nickel–titanium

Wojciech Chrzanowski [a,c], Ensanya Ali Abou Neel [a], David Andrew Armitage [b], Jonathan Campbell Knowles [a,*]

[a] *Division of Biomaterials and Tissue Engineering, UCL Eastman Dental Institute, 256 Gray's Inn Road, London WC1X 8LD, UK*
[b] *De Montfort University, Leicester School of Pharmacy, The Gateway, Leicester LE1 9BH, UK*
[c] *The Silesian University of Technology, Faculty of Mechanical Engineering, ul. Konarskiego 18a, 44-100 Gliwice, Poland*

Received 16 January 2008; received in revised form 23 April 2008; accepted 9 May 2008
Available online 9 June 2008

Abstract

In this paper, the bioactive properties of Ni–Ti alloy after different surface treatments were evaluated in different media (Hanks' balanced salt solution, Dulbecco's modified Eagle's medium and osteogenic). Evaluation was performed on the basis of X-ray photoelectron spectroscopy and atomic force microscopy studies after immersing samples for up to 24 h in the relevant media. This allowed assessment of the kinetics of Ca^{2+} and P^{5+} precipitation and early interaction of the media with surfaces. In addition, the surface free energy was measured and the influence of heat treatment on phase transformation temperatures and rate of nickel and titanium ion release was investigated. The most favourable bioactive properties were observed for simply ground Ni–Ti samples when evaluated in HBSS, which showed similar properties to reference positive samples (BioactiveTi). On the other hand, samples heat-treated at 600 °C showed very low levels of precipitation of Ca and P. Most interestingly, evaluation in the media containing organic components (protein, vitamins, antibiotics and drugs) revealed that bioactivity for all the samples was at the same level (except for the reference negative) irrespective of the surface preparation method. It demonstrated that organic components interact with the surface rapidly, forming a thin protein layer, and this altered the surface properties of the samples, making them bioactive. No significant difference in kinetics of the Ca^{2+} and P^{5+} precipitation were observed. Nevertheless, further ion release and chemical composition evaluation revealed that alkali treatment and spark oxidation cannot be considered as a useful for biomedical application due to very high levels of Ni in the top layer (alkali-treated) and high rate of Ni release (spark-oxidized and alkali-treated).

Keywords: Bioactivity; Nitinol; Nickel–titanium alloy; Heat treatment; Spark oxidation

1. Introduction

Titanium and its alloys have been important materials in the production of implants for hard tissues for several years. This is as a result of their mechanical properties (which are more favourable than those of stainless steel), very good tissue response and enhanced osseointegration. It is also possible to make the implant inert, which was demonstrated to be important for retrieving the implant and reducing the adherence of soft tissues (e.g. tendon) that could alter their functions [1]. However, there is a considerable difference between the elastic properties of the metal compared to bone, and this difference plays a very important role during fracture healing for many types of fixations. It must be highlighted that it is not the mechanical properties of the material that are the most important but rather the properties of the entire construct which bears the load. Ideally, the fixator should replicate the natural rigidity of intact bone at the interface. This is because metal implants have a completely different shape and structure than tissue so its "shape" rigidity must be fitted to the tissue. Nevertheless, among the titanium alloys, one has exceptional mechanical properties including superelastic properties and shape memory effects; this is the nominally

* Corresponding author. Tel.: +44 (0)207 915 1189; fax: +44 (0)207 915 1227.
E-mail address: j.knowles@eastman.ucl.ac.uk (J.C. Knowles).

1742-7061/$ - see front matter
doi:10.1016/j.actbio.2008.05.010

equiatomic Ni–Ti alloy (Nitinol), and these properties may improve the performance of some devices. The current fairly low popularity of Ni–Ti is caused by high material cost and very high content of Ni, which is known to be carcinogenic [2]. However, it has been demonstrated that its mechanical properties make this material especially attractive for bone fixators (bone clamps, plates, wires and pins), dental and laparoscopic devices. The biological properties of Nitinol can be improved by different surface treatments; it has also been shown that the negative effects of Ni can be eliminated by the same types of treatments [2–9]. For Nitinol, treatments such as oxidation, nitriding, different types of coating (e.g. carbon, hydroxyapatite and polymers), chemical etching, polishing and electrochemical methods [4,8,10–19] have been proposed. These treatments have been successfully used for commercially pure titanium (cpTi) and its alloys (Ti6Al4V, Ti15Zr4Ta4Nb, Ti6Al7Nb, Ti13Zr13Nb). Each of these methods can lead to different degrees of bioactivation or conversely passivation.

The bioactive properties of materials can be interpreted in different ways. In general, the term bioactivity is related to the ability of the material to trigger a biological action, and the authors linked this term to cell response or more commonly to the formation of an apatite layer from simulated body fluid (SBF) [10,14,20–22]. To date, in the literature, there is little agreement as to how to evaluate bioactivity, and many authors follow Kokubo's approach, immersing samples in SBF for 14 days and measuring the chemistry of the formed film using energy-dispersive X-ray analysis and X-ray diffraction [22,23]. However, this evaluation does not involve consideration of immediate interactions of the surface with the fluids that were found to be the most important for cell response, i.e. for cells to "recognise" the surface, attach to it and proliferate. Most of the cell studies have been carried out over time periods ranging between a few hours and several days [24–26]. For the same reason evaluation of bioactivity should be performed over a similar period. Bioactivity evaluation after immersion for 14 days does not yield detailed information about the kinetics of apatite film formation. Nevertheless, most of the studies used zeta potential measurements, ion release or ion depletion from the solution as a means to characterize the bioactivity; these parameters enable better analysis of the bioactive behaviour of the material.

Bioactivity can be altered by several different methods that change the topography, chemistry, wetting ability and surface energy. All these features were found separately and in combination to have an influence on Ca and P precipitation [4,15,27–30].

In this paper, the influence of surface treatments, heat, alkali treatment, and spark oxidation on the bioactive properties of Nitinol were evaluated. The results were compared with reference samples that were reported to be bioactive and passive in SBF. A new approach to evaluate bioactivity in medium containing not only inorganic but also organic components such as peptides, antibiotics, proteins and vitamins on the basis of X-ray photoelectron spectroscopy (XPS) examination was proposed.

2. Material

In the study 50 at.% Ni–50 at.% Ti alloy (also called Ni–Ti or Nitinol) in superelastic form was used (Johnson Matthey Inc./SMA). Three types of the surface treatments were chosen to alter the surface reactivity of the alloy with SBF: heat treatment, alkali treatment and spark oxidation (plasma electrolysis). These types of treatments were demonstrated to have a positive effect on bioactivity of Ti and Ti-based alloys such as Ti6Al4V and Ti6Al7Nb [4,16,17,19,23]. Prior to the treatments, Ni–Ti samples of dimensions $8 \times 8 \times 0.8$ mm, were ground to a mirror finish and cleaned in isopropanol and ultrapure water. They were then soaked in 60% nitric acid, and finally ultrasonicated in ultrapure water (18 MΩ cm) and dried in compressed air.

Heat treatment for Ni–Ti samples was carried out at three different temperatures (200, 400 and 600 °C in air), followed by cooling to room temperature. Alkali treatment was conducted in 10 M NaOH. Samples were immersed in the solution for 24 h at 80 °C then rinsed with water, dried and heat-treated at 600 °C in air. Spark oxidation was carried out in a solution with a ratio of two parts of 85% phosphoric and three parts of 25% sulphuric acid. During treatment, the temperature was controlled and kept at 25–35 °C. Oxidation was done using direct current (current density 2 mA cm^{-2} for 1 min), and a Ti mesh electrode coated with Pt was used as a cathode. In total, six types of surfaces were produced:

- heat-treated—samples denotated 200, 400 and 600;
- alkali-treated—BNT;
- spark-oxidized—SP;
- ground to a mirror finish and cleaned—NT.

As reference samples, cpTi was used. The surface of the cpTi was prepared by:

- grinding to a mirror finish—Ti, called reference negative (−ve);
- alkali treatment: 10 M NaOH for 24 h at 80 °C then rinsed with water, dried and heat-treated at 600 °C in air—BioactiveTi (BTi) (23), also called reference positive (+ve).

3. Methods

For all of the Ni–Ti and reference samples, topography, roughness, surface chemistry, structure and surface energy were investigated and related to the bioactivity evaluation results. These factors have been reported to alter the behaviour of the material in contact with body fluids. The experiments were conducted on triplicate samples.