Applied Surface Science 254 (2008) 6725–6730

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Corrosion and wear properties of laser surface modified NiTi with Mo and ZrO_2

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ARTICLE INFO

Article history:
Received 10 October 2007
Received in revised form 15 April 2008
Accepted 15 April 2008
Available online 29 April 2008

Keywords:
NiTi shape memory alloys
Laser surface alloying
Molybdenum
ZrO_2
Corrosion resistance
Electrochemical impedance spectroscopy
Wear resistance

ABSTRACT

Because of its biocompatibility, superelasticity and shape memory characteristics, NiTi alloys have been gaining immense interest in the medical field. However, there is still concern on the corrosion resistance of this alloy if it is going to be implanted in the human body for a long time. Titanium is not toxic but nickel is carcinogenic and is implicated in various reactions including allergic response and degeneration of muscle tissue. Debris from wear and the subsequent release of Ni^+ ions due to corrosion in the body system are fatal issues for long-term application of this alloy in the human body.

This paper reports the corrosion and wear properties of laser surface modified NiTi using Mo and ZrO_2 as surface alloying elements, respectively. The modified layers which are free from microcracks and porosity, act as both physical barrier to nickel release and enhance the bulk properties, such as hardness, wear resistance, and corrosion resistance. The electrochemical performance of the surface modified alloy was studied in Hanks' solution. Electrochemical impedance spectroscopy was measured.

1. Introduction

Nickel titanium shape memory alloy (SMA) is a relatively new biomaterial that has attracted immense research interest for biomedical application. The desirable and superior properties such as good strength and ductility with shape memory effect, superelasticity, and good biocompatibility [1–4] are most suitable for medical applications [5,6]. The alloy can be applied for the manufacturing of equipment and devices used for medical applications in orthopaedics and dentistry, such as stents, compression staple and knee joints [7,8]. However, there are still concerns on the wear resistance and nickel ion release of this alloy if it is going to be implanted for a long time [9–11]. Nickel release can be attributed to the breakdown of the passive TiO_2 film due to localized corrosion, fretting wear and fretting corrosion [12–16]. Nickel ion is carcinogenic and also causes allergic response and degeneration of muscle tissue. Debris from fretting wear and the subsequent release of Ni^+ ions into the body system are fatal issues for long-term application of this alloy in the human body.

To improve the long-term biocompatibility and corrosion properties of NiTi, different surface treatment techniques have been investigated by many researchers [17–25]. Laser surface alloying technique is a popular method to modify the surface characteristics of many alloys. In order to reduce the risk of nickel release of NiTi in the human body, one possible way is to lower the Ni^+ content at the surface and in the mean time increase the wear resistant property of the alloy. This can be achieved by fabricating a wear resistant barrier coating and also diluting the concentration of Ni content at the surface. This paper investigates the feasibility of laser surface alloying NiTi with the aims to reduce the nickel concentration at the surface and in the mean time provide a wear and corrosion resistant barrier coating. Mo and ZrO_2 are chosen to be the surface alloying elements because of their good biocompatibility and non-toxicity feature. Molybdenum (Mo) is classified as the non-toxic materials with high hardness. According to phase diagram, it forms solid solution with titanium and provides the solution hardening effect. Mo has being used as one of the alloy materials for medical material such as stainless steel without any negative response. Zirconium oxide is a ceramic and is bioinert.

2. Experiment details

2.1. Sample preparation and laser surface alloying

The substrate material used in this study was the NiTi (hot-rolled Ni-55%, Ti-45%) alloy. The specimen was cut into size of 50 mm × 30 mm × 5 mm. The samples were ground to remove the thick oxide scale and then ultrasonically cleaned in acetone, alcohol and distilled water successively and dried. It was then sand-blasted for better adhesion with pasted alloy metal powders.

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0169-4332/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2008.04.076

molybdenum (Mo) and zirconium dioxide (ZrO_2) powders were mixed with polyvinyl alcohol (PVA) to form a paste, respectively which is then pasted on the NiTi surfaces. A paste thickness of 0.1 mm and 0.3 mm of Mo and ZrO_2 were applied on NiTi blocks, respectively. The specimens were then dried in an oven at 60 °C for 5 h. A continuous wave 2-kW Nd-YAG laser was used to perform the laser surface alloying process. The melt pool at the laser interaction point was shielded by nitrogen in a gas tight chamber with a transparent glass window. Different processing parameters such as laser power (600–1100 W), laser beam diameter (3–5 mm), beam scanning speed (10–25 mm/s) and nitrogen gas flow rate (30 L/min) were systematically varied and optimized to produce defect-free single tracks. After that, a large surface was processed using the optimum process parameters by overlapping single tracks at 50% track width interval.

2.2. Metallographic and microstructural examination

After laser surface alloying, the samples were sectioned, mounted, polished and etched with reagent (HF10%, HNO_3 40%, H_2O 50%) for metallographic examination. Composition profile along the depth of the surface layer was acquired by energy-dispersive spectrometry (EDS, Oxford EDX System). Microstructural characterization in terms of the phases was analyzed by X-ray diffractometry (XRD, Philips model PW3710). The radiation source used was Cu Kα generated at 40 kV and 35 mA, with a scan rate of $1.5^\circ\ min^{-1}$.

2.3. Hardness and pin-on-disc abrasive wear

The hardness along the depth of the cross-section was obtained using a microhardness tester (Buehler Micromet II) at a load of 200 g and a loading time of 15 s. The wear properties of the specimens were investigated using a pin-on-disc abrasive wear device. The specimen for wear test was cut into 10 mm × 10 mm × 5 mm square and then inserted in the slot of the pin. In order to have a consistent surface to start with the wear test, the specimens were ground to a consistent surface roughness using Grade 600 SiC abrasive paper after they were laser treated. About 0.2 mm of the outmost surface was removed. The specimen was held stationary on the top against a rotating abrasive disc. The required load of 150 g was applied through the pin [11]. Grade 500 SiC grits abrasive papers was used on the rotating disc in the test. The disc was rotated at 150 rpm and the pin was located at a radial distance of 150 mm from the rotating axis. Water was used in the test for washing out the ploughing abrasive particles. For every 5 min, the specimen was taken out and cleaned in an ultrasonic machine to remove the worn out debris and abrasive particles. The specimen was then dried and weighed to ±0.001 mg accuracy. A fresh abrasive paper was used after every measurement.

2.4. Corrosion tests

Potentiodynamic corrosion test and electrochemical impedance spectroscopy (EIS) of the alloyed surfaces were carried out to study the corrosion property. Samples for corrosion study were mounted in epoxy to expose a surface area of 1 cm^2. Hanks' solution (composition given in Table 1) is used as the electrolyte and an electrolyte temperature of 37 ± 1 °C was applied. Potentiodynamic polarization measurements were performed conforming to ASTM Standard G5-94 [26] with a potentiostat (EG&G Princeton Applied Research; model 273A, M352 software with a standard three-electrode system). All potentials were expressed with respect to the SCE electrode. Before any data were recorded, an initial time delay of 1800 s was set to allow the specimens to achieve equilibrium in the solution at open potential. The scanning started at a potential of about 400 mV below the open circuit potential of each sample with a scanning rate of 1 mV/s. For EIS (Impedance Analyzer Model 6310, EG&G Instruments) study, the instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system. A small amplitude signal of 10 mV is applied to the specimens over a frequency range of 0.01 Hz to 100 kHz recoding with 50 points.

Table 1
Chemical composition of Hanks' solution

Component	Concentration (g/l)
NaCl	8.0
$CaCl_2$	0.14
KCl	0.4
$NaHCO_3$	0.35
Glucose	1.0
$MgCl_2{\cdot}6H_2O$	0.1
$Na_2HPO_4{\cdot}2H_2O$	0.06
KH_2PO_4	0.06
$MgSO_4{\cdot}7H_2O$	0.06

3. Results and discussions

3.1. Surface characterization

The cross-section microstructure of Mo-alloyed layer and ZrO_2-alloyed layer are shown in Figs. 1 and 2, respectively. The optimum set of laser parameters for Mo-alloyed layer were 800 W laser power, 10 mm/s scanning speed and 3 mm beam diameter while these were 600 W, 10 mm/s and 3 mm for ZrO_2-alloyed layer. It can be seen that a laser alloyed surface layer of Ni–Ti–Mo alloy is about 500-μm thick where the Ni–Ti–ZrO_2 layer is approximately 750-μm thick. The interface is of metallurgical nature and no crack nor porosity was found in both layers. The alloyed elements, Mo and ZrO_2, appear to form solid solution with NiTi matrix.

The composition profiles (Figs. 3 and 4) along the depth of the cross-section indicate that Mo and ZrO_2 can successfully reduce the amount of Ni content on the surface of NiTi. There is a 36% and 50% reduction of Ni content on the surface for Mo-alloyed layer and ZrO_2-alloyed layer, respectively. The composition profiles are consistent with the laser-treated thickness. The profiles started from 500-μm thick and 750-μm thick for both layers are mainly consists of NiTi.

Preliminary investigation on the phases existed as the alloyed layers were carried out by XRD. Fig. 5 shows the XRD pattern of the Mo surface-alloyed specimen. According to the pattern, Mo did not form any intermetallic compound with Ni and Ti. When Mo was alloyed in the surface of NiTi, the alloyed layer consists of mainly the austenitic phase NiTi and the Mo solid solution. Fig. 6 shows the XRD pattern of the ZrO_2-surface-alloyed specimen. The alloyed layers are mainly composed of austenitic phase of NiTi and ZrO_2 in significant amount. No new phase was identified. The standard enthalpy of ZrO_2 is $-1100.56\ kJ\ mol^{-1}$ which is more negative than TiO_2. ZrO_2, therefore, is more stable [29].

3.2. Hardness and wear resistance

The hardness values of the Ni–Ti–Mo and Ni–Ti–ZrO_2 layers are 660 Hv and 720 Hv, respectively while the hardness for NiTi substrate is 220 Hv. The hardness profile along the depth of the layer is shown in Fig. 7.

It is obvious that the hardness of NiTi can be greatly improved by laser surface alloying with Mo and ZrO_2. A pin-on-disc wear test was carried out to compare the wear resistance between the as-