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Characterization and corrosion study of NiTi laser surface alloyed with Nb or Co

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ABSTRACT

The interest in NiTi alloys for medical applications has been steadily growing in recent years because of its biocompatibility, superelasticity and shape memory characteristics. However, the high Ni content in NiTi alloys is still a concern for its long-term applications in the human body. The release of Ni ion into the human body might cause serious problems, as Ni is capable of eliciting toxic and allergic responses. In view of this, surface modification to reduce the surface content of Ni and to improve the corrosion resistance, both of which would reduce Ni release, is an important step in the development of NiTi implants. In the present study, NiTi was surface alloyed with Nb or Co by laser processing. The fine dendritic structure characteristic of laser processing has been described in terms of rapid solidification. The amount of surface elemental Ni was reduced to 10% and 35% for the Nb-alloyed and Co-alloyed layer, respectively. The corrosion resistance in Hanks' solution (a simulated body fluid) was increased as evidenced by a reduced passive current density and a higher pitting potential for both the Nb- and Co-alloyed specimens. The composition and hardness profiles along the depth of the modified layer were correlated with the distribution of the dendrites. The microhardness of the alloyed layers was around 700–800 Hv, which was about four times that of the untreated NiTi specimens.

1. Introduction

Nickel Titanium (NiTi) shape memory alloy (SMA) has been increasingly used in the medical devices industry. The shape memory effect, superelasticity, and good biocompatibility [1–4] were the driving forces for the early introduction of NiTi for medical applications [5,6]. The alloy has been used for the manufacturing of equipment and devices in cardiology, orthopedics and dentistry, such as stents, compression staple and knee joints [7,8]. The presence of high concentration of Ni in NiTi is a concern because it is well known that if the amount of Ni in the human body exceeds a certain threshold value, it will cause allergic, toxic and carcinogenic reactions [9,10]. Thus reduction of Ni release from implants into the human body is of paramount importance for long-term applications.

Surface modification is an attractive technique to improve the surface properties while retaining the bulk mechanical properties of the substrate. Many surface modification techniques, including physical vapor deposition (PVD) [11], chemical treatment [12] and electropolishing [13] have been suggested to tackle the nickel release problem of NiTi, each with its own merits and limitations. For PVD the main limitation is the low interfacial adherence of the coating and the substrate. Electropolishing and chemical treatment could only produce a limited protection due to the formation of a thin oxide layer. Other techniques such as chemical vapor deposition (CVD) [14] and ion implantation [15] also do not form a modified layer that is thick enough against wear.

Recently laser surface modification has been employed for enhancing the surface properties of NiTi [16–23]. Laser modification is becoming popular because of its flexibility, high precision rate and intense beam profile [24]. More importantly, laser surface modification also has the advantage of creating a metallurgical bond between the coating and the substrate. The application of laser surface treatment for improving corrosion properties of various alloys have been widely reported [25–29]. Yet no work has been conducted on the use of laser surface alloying technique for improving the corrosion resistance of NiTi. By virtue of the extremely high solidification rate characteristic of laser surface treatment, laser surface alloying is capable of producing an alloyed layer with extended solubility of the alloying elements, in addition to a homogeneous and fine microstructure.

The present paper investigates the feasibility of applying laser surface alloying technique to improve the corrosion resistance of NiTi in simulated body fluid. NiTi was alloyed with Nb or Co powders by CO_2 laser. Nb was selected as the surface alloying element because of its biocompatibility and stable intermetallic compounds formation upon solidification [24]. Co could also improve mechanical strength and corrosion resistance [30]. The microstructure of the alloyed layer was investigated by scanning-electron microscopy (SEM), energy-dispersive spectrometry (EDS) and X-ray diffrac-

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tometry (XRD) and the corrosion resistance was studied using potentiodynamic polarization.

2. Experimental details

2.1. Specimen preparation and laser surface alloying

Hot-rolled 5-mm-thick Ni(55 wt.%)Ti shape memory alloy (SMA) specimens of 50 mm × 30 mm × 4 mm in size were mechanically ground with 120 grit SiC paper to remove the oxide layer. The specimens were then ultrasonically cleaned in acetone and distilled water, and sand-blasted for better adhesion with paste of Niobium (Nb) and Cobalt (Co) powders. Nb and Co powders of particle size of 1.5–3.5 μm were separately mixed with polyvinyl alcohol (PVA) to form a paste and then painted on the NiTi surface. A paste thickness of 0.3 mm was used on the NiTi plates. The specimens were then dried in an oven at 60 °C for 5 h. A continuous-wave 3-kW CO_2 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. The nitrogen gas flow rate was 30 L/min. With the laser spot diameter kept at 1.5 mm, various sets of laser processing parameters were tried out to obtain alloyed tracks of depth around 500 μm. For Nb, this could be achieved at a laser power of 700 W and a beam scanning speed of 600 mm/min, while for Co, 600 W and 1200 mm/min. A large surface was processed using these parameters by 50% overlap of the single tracks.

2.2. Metallographic and microstructural examination

After laser surface alloying, the specimens were sectioned, mounted, polished and etched with reagent (HF 10%, HNO_3 40%, H_2O 50%) for metallographic examination. The microstructure after laser alloying process was examined using scanning-electron microscopy (SEM, Leica Stereoscan 440). The composition profile along the depth of the surface layer was acquired by energy-dispersive spectrometry (EDS, Oxford EDX System). The phases present were analyzed by X-ray diffractometry (XRD, Philips model PW3710) at 40 kV and 35 mA, with a scan rate of 1.5 °/min.

2.3. Hardness and corrosion tests

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. Potentiodynamic corrosion test of the laser alloyed specimens was carried out to study the corrosion property. Specimens for corrosion study were mounted in epoxy to expose a surface area of 1 cm^2. Hanks' solution (composition given in Table 1) was used as the electrolyte at a temperature of 37 ± 1 °C. Potentiodynamic polarization measurements were performed conforming to ASTM Standard G5-94 [31] with a potentiostat (EG & G Princeton Applied Research; model 273A, M352 software with a standard three-electrode system). A pair of graphite rods served as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference 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-circuit potential. Scanning started at a potential of 400 mV below the open-circuit potential with a scanning rate of 1 mV/s.

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 discussion

3.1. Microstructure in the alloyed layer

The alloyed region of the Nb-alloyed layer is free of porosity and cracks and the thickness of the alloyed layer is around 400–500 μm, as shown in Fig. 1a. Melting and Maragoni flow of the melt pool promoted homogenization of the composition in the surface layer. The alloying element Nb appears to form a dendritic phase with the NiTi matrix in the alloyed layer. Laser processing develops a large temperature gradient of the order of 10^2–10^4 K/mm between the centre of the melt pool and the cooler solid/melt interface [24], and this results in the formation of fine dendrites. The size of the dendrites and its amount vary with the depth. By comparing the

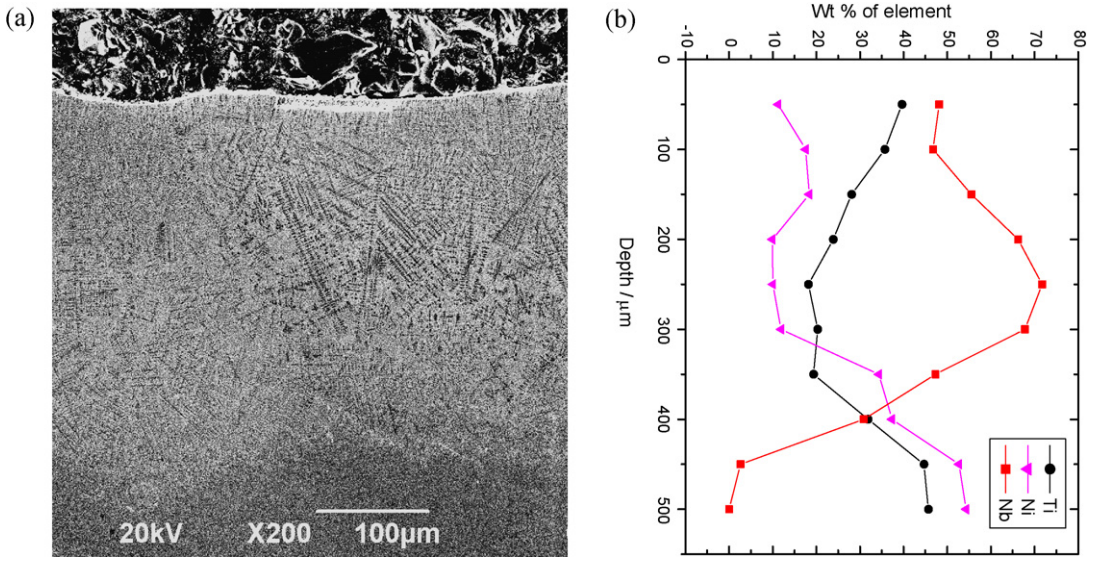

Fig. 1. (a) Cross-sectional SEM micrograph of the Nb-alloyed specimen, (b) EDS composition profile along the depth of the Nb-alloyed specimen.