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Laser surface alloying of NiTi shape memory alloy with Mo for hardness improvement and reduction of Ni^{2+} ion release ☆

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Abstract

Interests in applying NiTi shape memory alloys as metallic implant materials have grown immensely in recent years due to their unique shape memory, super-elastic and corrosion resistance properties. However, concern has been raised for its long-term applications inside the human body because of the risk of release of Ni^{2+} ions. The sources of Ni^{2+} ion are the free nickel elements at the surface and the results of fretting wear and corrosion of the metal systems. This paper aims at investigating the feasibility of using molybdenum to alloy with the free Ni on the surface of NiTi alloys and in the mean time improving the surface hardness of NiTi. To introduce Mo into the surface of NiTi metallurgically, laser surface alloying is one of the most feasible route. The mechanical properties of the alloyed surface were examined. A single point wear test was used to study the wear resistance of the samples. It was found that the microhardness and the wear resistance of the laser-alloyed surface were better than the untreated ones. The Ni^{2+} ion release rate of the laser surface alloying specimen was found to be ten times lower than the untreated one. The corrosion rate of the alloyed surface was an order of magnitude lower than that of the untreated sample.

Keywords: Laser surface alloying; NiTi; Shape memory alloys; Ni ion release

1. Introduction

Due to their unique shape memory effect, high damping characteristics and super-elasticity, nickel–titanium (NiTi) shape memory alloys (SMA) have attracted a lot of research interests as they have good potential to be used as load-bearing implant materials. In fact, NiTi SMA alloys are already used in stent and dental applications. The major concern in applying NiTi inside the human body system is the risk of release of Ni^{2+} ions from the surface of the NiTi implant. Ni^{2+} ions cause allergic problems to the body system [1,2,3,4].

The existence of elemental nickel and nickel-rich compound at the surface of NiTi alloy provides the source for potential Ni^{2+} ions release. Corrosion and fretting wear at the implant surfaces enhance the release of these ions. Various surface treatment methods have been investigated in order to reduce the elemental Ni level at the surface. Man et al. applied laser surface melting to homogenize the surface of NiTi [5] and laser gas nitriding to produce a layer of TiN on NiTi [6] so as to reduce the elemental Ni level. Shabalovskaya et al. [7] used HF/HNO_3 to selectively etch out Ni^{2+} ions and form a homogeneous TiO_2 layer at the alloy surface. Others have used electropolishing [8] and H_2O_2 immersion [9] to achieve this aim.

This paper reports the results of an investigation on the possibility of laser surface alloying NiTi with a Ni stabilizer, molybdenum (Mo), for reducing the elemental Ni at the surface. Mo has been used to improve the resistance to pitting corrosion of AISI 316L stainless steel which has

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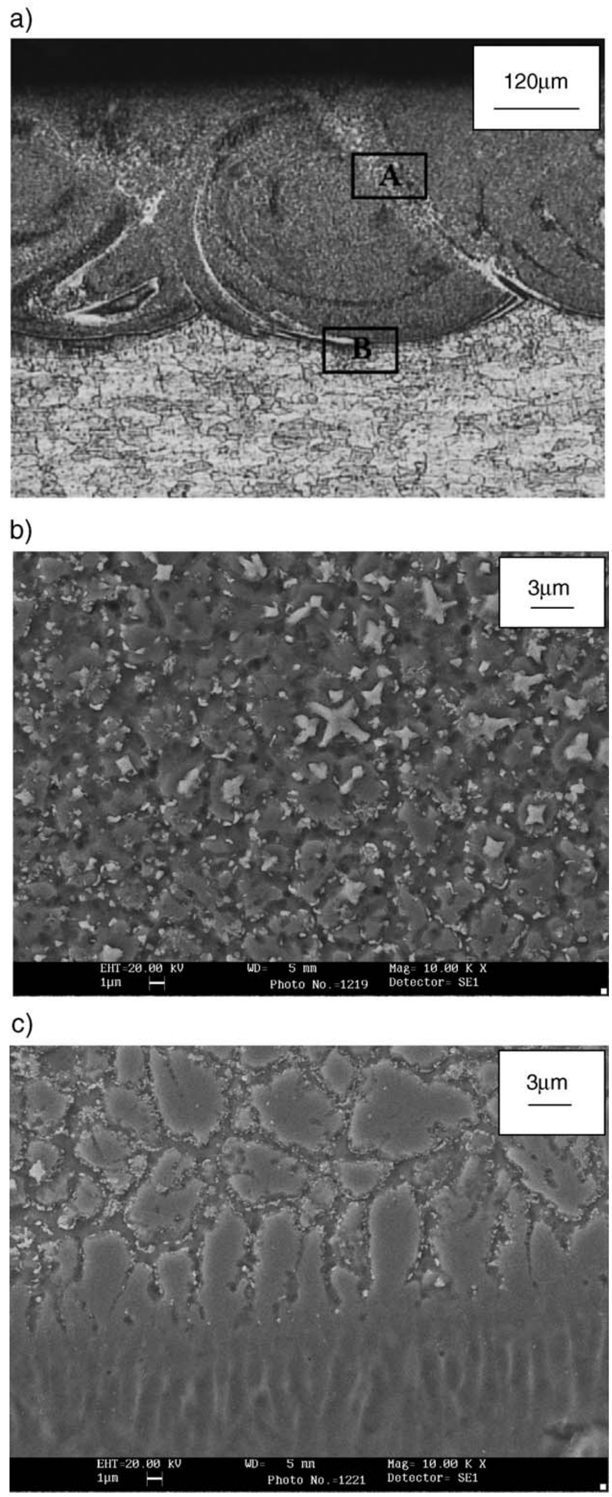

Fig. 1. (a) Microstructure of the overlapping tracks that form the alloyed surface (700 W, 30 mm/s), (b) SEM image of the middle region (area A of panel (a)), (c) SEM image of epitaxial grains at the interface (area B of panel (a)).

been used as a traditional implant alloy. Also, both the International Agency for Research on Cancer and the US Toxicology Program did not list molybdenum or molybdenum compounds as carcinogens [10]. Another reason that Mo is chosen as the alloying element is that it can improve the surface hardness of NiTi which in turn improves the wear resistance of this alloy.

2. Experimental details

Hot rolled plate of Ni–Ti SMA of composition of 50.1 wt.% Ni −49.9 wt.% Ti was used. The as-received alloy was cut into size of 35 mm × 30 mm × 2 mm and ground to remove the oxide layer. It was then sand-blasted for better adhesion with the pasted powder and reduced surface reflectivity to the laser beam. Finally, the specimen was ultrasonic cleaned in acetone to remove any surface residue.

Pure Mo powder of particle size of 1.5 μm to 3.5 μm was used in this work. The powder was mixed with polyvinyl alcohol (PVA) to form a paste which is then pasted on the NiTi surface. A paste thickness of 180 μm was applied. The specimen was then dried in an oven at 60 °C for 5 h.

Laser surface alloying (LSA) was carried out using a continuous wave 2 kW Nd-YAG laser. Argon gas was used as shielding gas to protect the melt pool from oxidizing. Individual LSA track was studied first in order to obtain the optimum process parameters. After that, a large surface was processed using the optimum process parameters by overlapping single tracks at 50% track width interval.

After laser surface alloying, the dilution ratio (DR) of the laser modified layer was calculated by the following equation.

$$DR = \left(1 - \frac{t}{d}\right)$$

where t is the thickness of powder paste coating (180 μm in this work) and d is the laser melt depth in the substrate. The ratio of DR is just used for the convenience of discussion and has no direct relationship with the changes of composition in the alloyed layer.

The microstructure, hardness and composition of the alloyed surfaces were examined. Potentiodynamic corrosion test was carried out to study the corrosion property. An

Table 1
Dilution ratio (DR) at different process parameters

Specimen no.	Power (W)	Scanning speed (mm/s)	Melt depth (μm)	Dilution ratio (DR)
1	500	30	261	0.31
2	500	35	202	0.11
3	600	30	397	0.55
4	600	35	383	0.53
5	700	30	459	0.61
6	700	35	441	0.59
7	800	30	514	0.65
8	800	35	472	0.62
9	900	30	590	0.70
10	900	35	558	0.68
11	1000	30	627	0.71
12	1000	35	578	0.69