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Laser surface alloying fabricated porous coating on NiTi shape memory alloy

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Abstract: Laser surface alloying technique was applied to fabricate a metallic porous coating on a solid NiTi shape memory alloy. By laser surface alloying a 40%TiH_2-60%NiTi powder mixture on the surface of NiTi alloy using optimized laser process parameters, a porous but crack-free NiTi layer can be fabricated on the NiTi substrate. The porous coating is metallurgically bonded to the substrate NiTi alloy. The pores are uniformly distributed and are interconnected with each other in the coating. An average pore size of less than 10 μm is achieved. The Ni content of the porous layer is much less than that of the original NiTi surface. The existence of the porous coating on the NiTi alloy causes a 37% reduction of the tensile strength and 55% reduction of the strain as compared with the NiTi alloy. Possible biomedical or other applications for this porous surface with good mechanical strength provided by the substrate are prospective.

Key words: laser surface alloying; NiTi shape memory alloy; porous coating; biomaterial

1 Introduction

The suitability of a metallic material to be used for bone replacement or bone fixation components such as plates and screws depends on many factors. The first is the osteointegrating capability of the material with the bone cell that affects the bonding or fixation strength between the implant and bone. The second is the risk of release of hazardous metallic ions into the body system that may cause allergic or even carcinogenic effect. The third is the difference of the strength between the metallic material and bone as the mismatch between the alloy and bone would induce stress shielding effect and subsequently bone degradation. Equal-atomic nickel titanium, NiTi shape memory alloy, a relatively new biomaterial, has attracted immense research interest because of its unique properties such as superelasticity, clamping capacity and shape memory effect. The superelastic property of NiTi is quite similar to that of human tissues such as tendon and bones and this similarity in stress—strain behaviour help reduce the stress shielding phenomenon and alleviate the bone degradation problem[1−4]. To enhance osteointegration of NiTi implants with bone, various methods have been researched[5−7]. A common approach is to coat the NiTi implant surface with a bioactive ceramic hydroxyapatite (HA) layer[8−10]. However, there have been concerns regarding the interfacial strength between the coating and the implant surface[5,11]. Another approach is to use bulk porous NiTi which allows the enhanced cell adhesion, migration, growth and proliferation[12]. Recently, the development of bulk porous NiTi to promote osteointegration by facilitating cell adhesion, migration, growth and proliferation has been reported[13−14]. However, bulk porous components may not be strong enough for load bearing applications as the strength of bulk porous material decreases linearly with the increase of porosity.

To overcome the above concerns, it is suggested to

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fabricate a metallic porous coating on a solid NiTi substrate. It is critical that the porous coating must have a metallurgical bond with the metal substrate, otherwise the interfacial strength would have posed a major problem. Plasma spraying and thermal spraying are coating techniques that can fabricate metallic porous coating on NiTi substrate but the interfacial bondings resulted are only physical ones. Laser surface alloying or cladding seems to be an ideal process for producing coating with metallurgical interfacial bonding. So far almost all publications concerning laser surface alloying or cladding are dealing with coatings without porosity.

In this study, porous NiTi shape memory alloy (SMA) coatings were fabricated on a compact NiTi substrate by using laser surface alloying technique.

2 Experimental

Hot rolled NiTi shape memory alloy plates with nominal compositions (mole fraction) of 49.2% Ni and 50.8% Ti were used as the substrate material. The samples with dimensions of 40 mm×25 mm×5 mm were cut by electro-discharge-machining from these plates. NiTi alloy powder (49.6%Ni and 50.4%Ti, mole fraction) with an average particle size of 43 μm and commercial pure titanium hydride (TiH_2) powder with an average particle size of 38 μm were used in the laser surface alloying.

The NiTi samples were polished with 600 grit SiC paper to remove the oxide scales and then sandblasted to achieve a roughened surface (R_a=0.2 μm) to enhance adhesion of the preplaced powder. The sandblasted samples were thoroughly cleaned using acetone and deionized water before powder preplacement.

60%NiTi alloy and 40%TiH_2 powders were mixed manually using mortar and pestle. A paste was prepared by mixing the NiTi-TiH_2 mixture with a binder (4% polyvinyl alcohol, PVA) and then painted on the sandblasted samples. The powder mixture was pasted on the specimen and the paste thickness was controlled at 0.7 mm. The samples with pasted powder layers were baked at 80 ℃ for 4 h. The laser surface alloying of the specimen was carried out inside a gas tight chamber. Nitrogen with purity of 99.95% was flowed through the chamber to maintain a nitrogen atmosphere for the surface alloying and gas nitriding process.

Laser surface alloying was carried out using a high-power continuous wave Nd-YAG laser. The laser beam, delivered by optical fibre, was focused onto the sample by a ZnSe lens with focal length of 100 mm. Table 1 lists the optimum set of laser process parameters. Surfacing of the sample was achieved by 50% overlapping of successive melt tracks.

The porous macrostructure and microstructure of the cross-section of the samples were examined by optical and scanning electron microscopy (SEM JEOL JSM-6335F). The composition was determined by energy-dispersive spectroscopy (EDS, Leica Stereo Scan 440 SEM-EDX), and the phases present in the layer were identified by X-ray diffractometry (XRD, Bruker D8 Discover) using Ni filtered Cu K_α radiation generated at 40 mA and 40 kV, with a scanning rate of 1.5 (°)/min. For the tensile tests of the porous coated specimen, the specimen was first ground flat and polished by 1 μm diamond paste such that about 100 μm of the porous coating was removed. The 5 mm-thick specimen was then wire-cut from the back of the specimen such that the specimen for tensile test was only 1 mm in thickness which consisted of a porous coating with thickness of 200 μm. Fig.1 shows the sample for stress—strain test.

Table 1 Process parameters of laser surface alloying

Laser power/W	Diameter beam/mm	Scanning speed/($mm\cdot s^{-1}$)	Nitrogen gas flow/($L\cdot min^{-1}$)
600	3	25	30

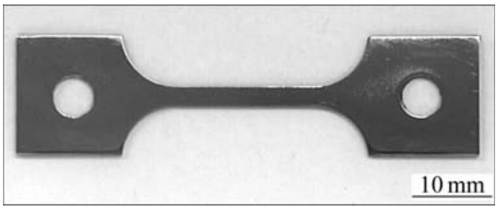

Fig.1 Sample for stress—strain test

3 Results and discussion

The integrity of the coated layer is affected by the processing conditions and the compositions of the powders. Generally, the constant processing conditions and low dilution between the coating and the substrate are required. During laser irradiation, the higher specific energy density, the higher the tendency of cracking of the coated layer. Fig.2 shows the micrograph of cross-section of overlapping sample. The surface is relatively smooth after overlapping.

The thickness of the laser alloying porous coating is

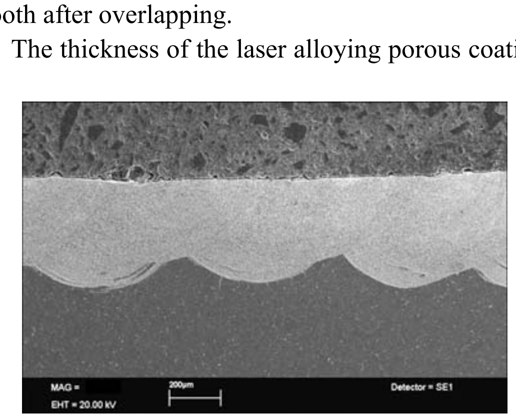

Fig.2 Micrograph of cross-section of laser alloyed overlapping sample

300 μm. Fig.3 shows SEM images of the cross-section of the porous coating. It can be seen that the porosities are evenly distributed along the thickness of the coating. The interface between the substrate and the coated layer is of metallurgical type and epitaxial growth of the dendrites at the interface is clearly shown in Fig.3.

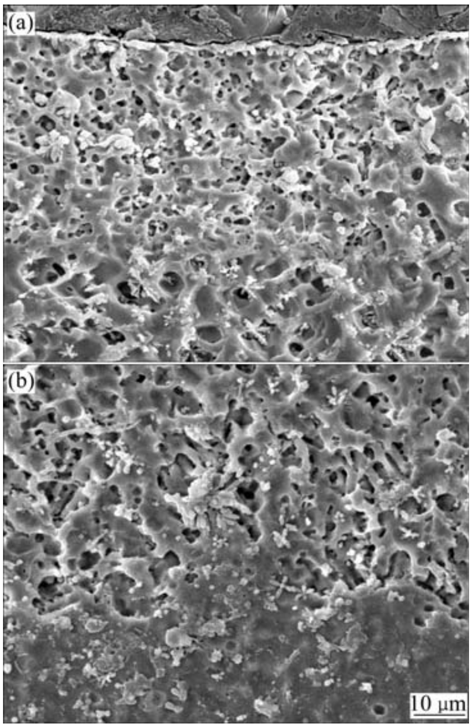

Fig.3 SEM images of cross-section of porous coating sample: (a) Top of porous coating; (b) Interface between porous coating and substrate

Fig.4 shows the XRD patterns of the NiTi alloy and porous coating samples. From Fig.4, the main phases in the NiTi alloy are NiTi and Ti_2Ni. After laser processing, porous coating sample shows that the main phases are Ti_2Ni, NiTi and TiN. Owing to the use of N_2 as the reactive and shielding gas and the high affinity of Ti with N, TiN is also present in the layer, in addition to Ti_2Ni and NiTi. During laser irradiation, the dissociated and nascent Ti has a tendency to react with nitrogen to form TiN phase which has the appearance of flower-like structure.

Fig.5 shows the micrograph of the top surface of porous coating sample. The top surface is ground flat and no chemical etching is carried out. It can be seen that the porosities are interconnected in a three dimensional manner. The size of the porosity is in the range of 1−5 μm.

Another advantage of fabricating the porous layer on NiTi substrate using the method developed from this work is the reduction of Ni content on the surface. A preliminary EDS analysis on the NiTi substrate and the laser alloyed layer, as shown in Fig.6, shows that the

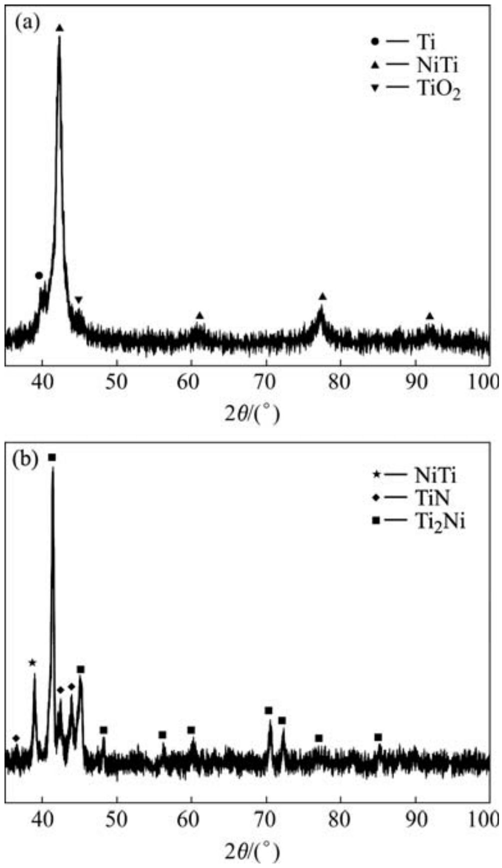

Fig.4 XRD patterns of NiTi alloy (a) and porous coating samples (b)

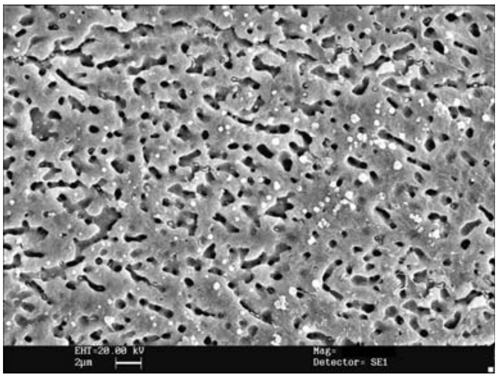

Fig.5 Micrograph of top surface of porous coating sample

mole fraction of Ni in the alloyed layer is about 12.5%, which is significantly lower than that in the substrate (about 49.2%). Because of the extra supply of Ti from TiH_2, the stable compound formed on the surface is mostly Ti_2Ni. EDS results indicate that the mole fraction of Ni is reduced from 49.2% to 12.5% on the outmost surface. Thus, TiH_2 can facilitate the formation of a porous structure and also reduces the Ni content in the layer. The reduction will greatly alleviate the potential release of Ni into the body fluid system. In the near future, the high Ni content of NiTi SMA will be a concern to clinicians due to the allergic and toxic nature of Ni in the human body.

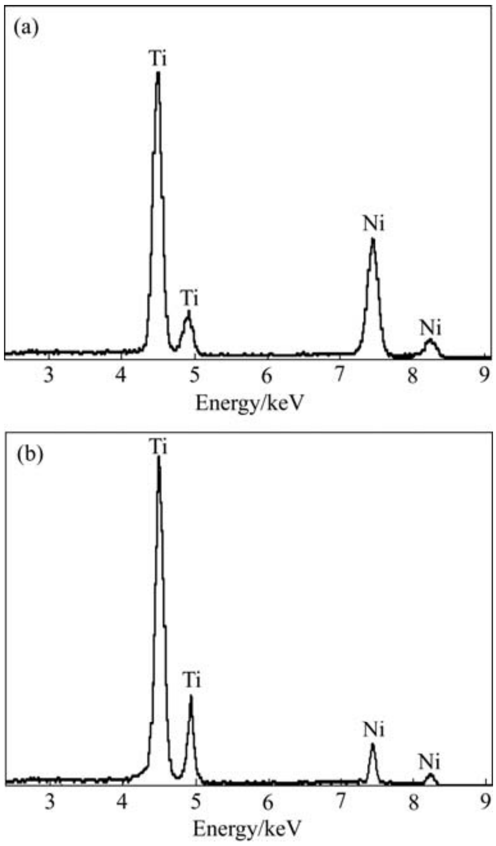

Fig.6 EDS analysis of NiTi substrate (a) and surface of porous coating samples (b)

Table 2 lists the stress—strain behavior of NiTi alloy and laser alloyed samples. It can be seen that the strength and strain of the porous coated NiTi are 63% and 45% of those of the NiTi, respectively. Thus, NiTi substrate with a porous layer combines the desirable properties of both bulk NiTi and those of porous materials, being capable of providing good mechanical strength together with enhanced osseointegrative characteristics.

Table 2 Stress—strain behavior of NiTi substrate and porous coated NiTi

Specimen	Tensile strength/MPa	Elongation at break/%
NiTi substrate	719	52
Porous coated NiTi	458	23

4 Conclusions

1) By laser surface alloying a 40%TiH_2-60%NiTi powder mixture on the surface of NiTi alloy at optimised laser process parameters, a porous but crack-free NiTi layer can be fabricated on the NiTi substrate. The metallurgical interface between the porous layer and the substrate assures excellent bonding strength between them.

2) The pores, in the range of 1−5 μm, are interconnected three dimensionally.

3) The Ni content of the porous layer is much less than that of the original NiTi surface. The existence of the porous coating on the NiTi causes a 37% reduction of the tensile strength and 55% reduction of the strain as compared with the NiTi alloy.

4) Possible biomedical or other applications for this porous surface with good mechanical strength provided by the substrate are prospective.

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