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IMPROVING PROPERTIES OF SMART NI/TI DENTAL ALLOY

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ABSTRACT

It is well established that Ni/Ti is categorize as a shape memory alloy. They found great interesting application including aerospace, biomedical and so many others. However, there is possibility of corrosion of these alloys in physiological solution and dissolution of toxic Ni-ions. Laser surface treatment technique was adopted in this work. An improvement inNi-ion dissolution reduction of (310%) was obtained in Nd-YAG laser surface-treated samples. Great enhancement in corrosion resistance of (1549%) also occurred. A substantial improvement in hardness of (368%) was recorded in laser treated samples.

KEYWORDS: NiTi Shape, Nd-YAG, Toxic Ni-Ions

INTRODUCTION

The properties of shape memory alloys are well known today and exploited for many applications in different technological fields. The shape-memory effect (SME), i.e., the recovery of a “memorized” shape after a deformation, is due to a the rmoelastic martensitic transformation. The super elasticity, shape memory properties and its compatibility with biological tissues of equiatomic NiTi shape memory alloy make it a potential material for new biomedical applications [1].

The corrosion resistance, and thus the biocompatibility, seems to depend on the surface properties of the alloy, many surface treatments have been considered [1]. Surface engineering of metals could possibly provide a means to alleviate the corrosion problem. Various techniques and protocols have been used for surface treatments; among them mechanical and electrochemical treatments, chemical etching, heat treatments, conventional and plasma ion immersion implantation, laser and electron-beam irradiation, design of increase corrosion resistance and bioactive surfaces (2). Laser surface modification techniques are one of the important groups of surface engineering tools because of their characteristic features such as rapid heating and melting which facilitates the possibility of extended solid solution, fine microstructure, composition homogenization, excellent metallurgical interface etc(3).

In the LSM process, the absorbed energy is instantaneously transferred to the lattice and melt quickly the near surface regions. When the laser is removed, the metallic subsurface quenches quickly the melted layers, which provides refinement in the surface microstructure, chemical homogenization of the surface, removal of inclusions, and possible metastable phases. Over all the other surface treatments, Laser surface treatment (including laser surface melting and laser surface alloying) can produce a rapidly resolidified surface layer, in which both the microstructure and the distribution of the surface alloying elements can be greatly modified. Among other surface treatment techniques, laser surface melting presents the advantages of being a simple technique used to modify the surface without affecting the bulk properties by forming a well-adherent corrosion resistant layer.

EXPERIMENTAL

Materials and Preparation of Samples

Equiatomic NiTi (master mixture; 55 wt% Ni with 45 wt% Ti) was prepared by using powder metallurgy, which consists of mixing, compacting and sintering processes. The purity, the average particle size and origins of the powders (Alfa Aesar, A Johnson Matthey Company) used in this work are shown in Table 1.

Table 1: List of the Metals Used and the Purity, the Average Particle Size and Origins of the Powders

Metal (Powder)	Purity (%)	Average of Particle Size (µm)	Chemical Company
Ni	99.8	35	Alfa Aesar, A Johnson Matthey Company product No:44739
Ti	99.5	35	Alfa Aesar, A Johnson Matthey Company product No:43102

After mixing, all samples, each weighing (4.5) grams, were compacted at 800 MPa [4,5]. Pressing was done by a hydraulic pressing machine in a tool steel die of 15 mm in diameter Following the compaction, all of the samples were sintered at 950 °C for 7hours (the samples were allowed to heat up with the heating rate 10°C/min)using a vacuum furnace (GSL-1600x). The pressure of the vacuum furnace was 10^{-4} torr.

The specimen surface was mechanically polished (MP) down to 2000-grit SiC abrasive paper. All the specimens were first degreased with alcohol for 5 min, and then rinsed by distilled water and dried with blasting air.

Laser System

Pulsed Nd: YAG(HAN*S PB80 with moto man Robotics control) Laser (See Figure 1). The wavelength of the system is 1064 nm and the optimised parameters used to produce a melted surface after multiple tray. Different laser powers (400–500-600 W), beam diameters (2 mm), pulse duration time (3ms) and frequency (10 Hz).

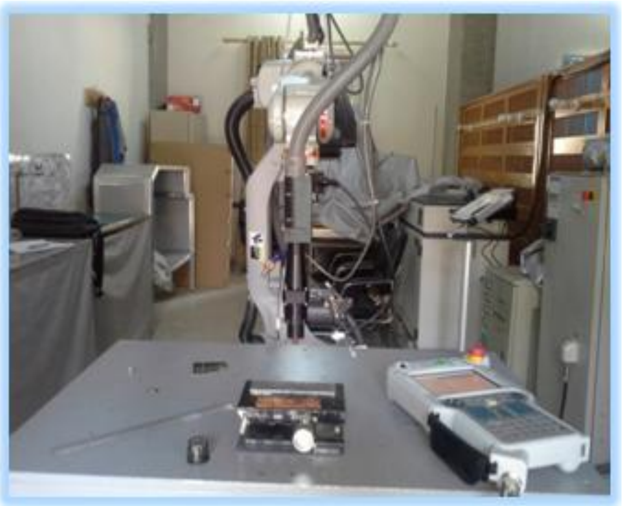


Figure 1: Nd: YAG (HAN*S PB80 Laser)

Microstructure

The microstructure for the laser treated and untreated NiTi samples was observed by optical microscopy (OM), scanning electron microscopy (SEM).and the surface was also analysis by X-ray energy dispersive spectroscopy (EDX).

Corrosion Test

The corrosion-resistant properties of the laser treated and untreated samples in artificial saliva solution at 37°C were evaluated by potentiodynamic anodic polarization measurements (type is X MTD-2MA) with a standard three-electrode. The composition of artificial saliva is shown in table 2.

Table 2: Artificial Saliva for Mulation[5]

Component	Quantity(mM)
KH2PO4	2.5
Na2HPO4	2.4
KHCO3	15
NaCl	10
MgCl2	1.5
CaCl2	1.5
CitricAcid	0.15

Vickers Hardness

Vickers hardness was also measured using the digital micro hardness Vickers Hardness Tester TH714. where the average of 10 readings was taken. All hardness values were taken at a load of 2.94 N.

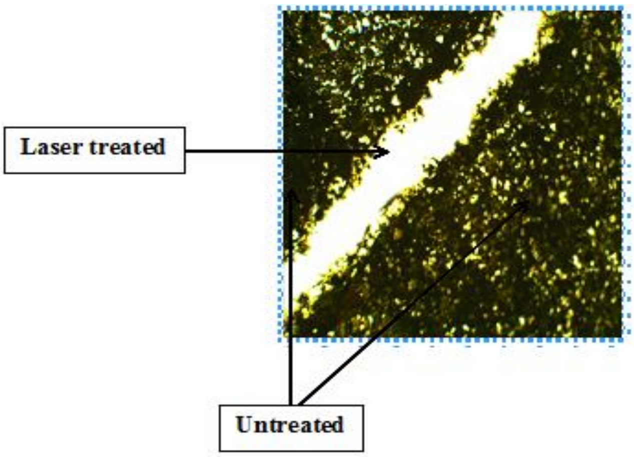
Atomic Absorption Spectrometry

Atomic absorption spectrometry (AA-6300) was used to determine the release rate of nickel out of NiTi in artificial saliva at 37 °C. The test samples were immersed in individual flasks with 100 ml of solution, and then after a specific period of time (15 days), the solution was collected and stored for analysis.

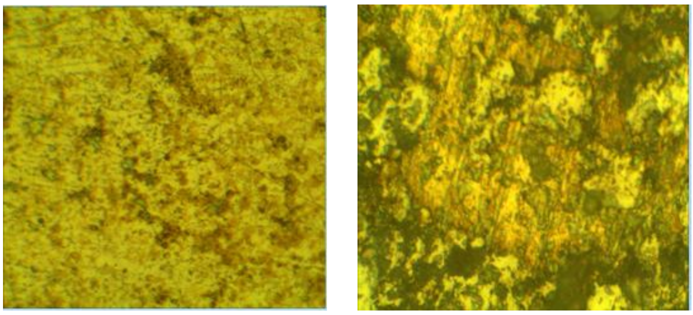
RESULTS

Microstructure

The microstructure of the surface observed by OM for the untreated(M) and laser treated (LT) NiTi samples is shown in figure 2. Many inclusions were observed during this work in the substrate of NiTi. However, only few inclusions were found in the laser treated layer. The surface topography of the laser treated NiTi and untreated samples are shown by SEM figure 3. The appearance of all laser treated samples is mainly an oxide film which is quite uniform and free of cracks. Thicker layers are desirable for enhancement of corrosion resistance, uniformity and compactness of the oxide film.

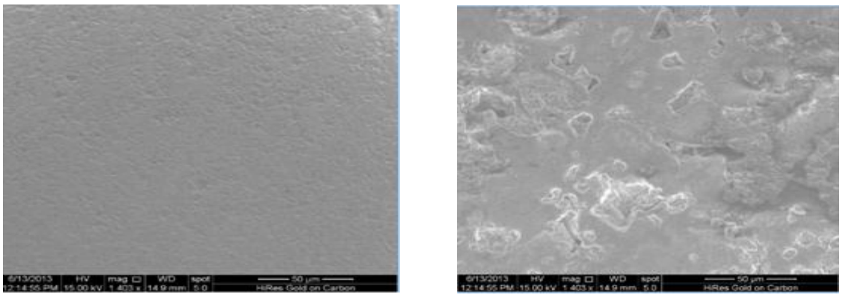


(a)



(b) (c)

Figure 2: Optical Microstructure Shown Difference between Laser Treated and Untreated Sample where (a) Shown the Two Region in 160x (b) Laser Surface Treated Layer at 1600 X (c) Un Treated Layer at 1600x



(a) (b)

Figure 3: Scanning Electron Microscopy Shown the Topography of the Surface for (a) Untreated (b) Laser Treated Sample

CORROSION TEST RESULTS

Corrosion is probably the most destructive factor for these shape memory alloys. Corrosion test was carried out by using Tafel extrapolation method in artificial saliva at 37°C for all laser treat (LT) samples and untreated sample(M). The results are represented graphically.

Corrosion current of the untreated sample is (24.79 µA).The lowest corresponding current of laser treated specimen is (1.6 µA). This means that, an improvement of (1549%) is introduce by laser treatment figure 4.

However it appears that, a further improvement was produce by the increase of laser power. Higher the laser power lower the corrosion current. For instance this increase of laser power from (0.4 KW to 0.6 KW) causes a decreases of (9.82 to 1.6 µA), i.e. An improvement of (613%) was obtained.

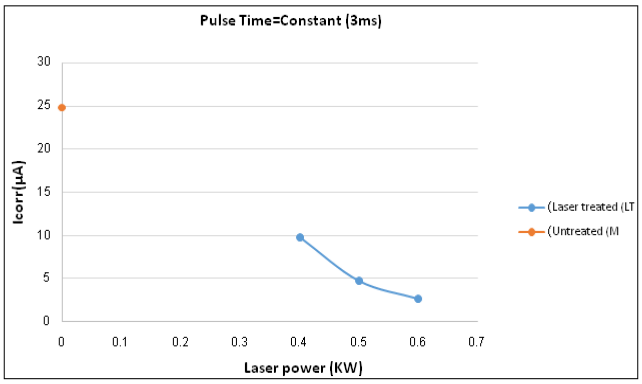


Figure 4: Corrosion Current Values for the Master Sample and the Laser Treated Sample with Various Laser Power at the Same Pulsed Time (3ms)

Vickers Hardness

The measurement of hardness was carried out for all samples by taking the average of 10 reading. Result obtained are presented graphically.

Measurement hardness value of untreated sample is (241.33HV); the high corresponding value of laser treatment specimen is (888.07HV). This mean that an improvement of (368%) is introduce by laser treatment, Figure 5.

However it appears that a further of improvement was obtained by the increase of laser power. High laser power higher the hardness value. Therefore the increase of power from (0.4KW to 0.6KW) causes an increase of (630HV to 8880. 7HV), i.e. an improvement of (141%) was obtained

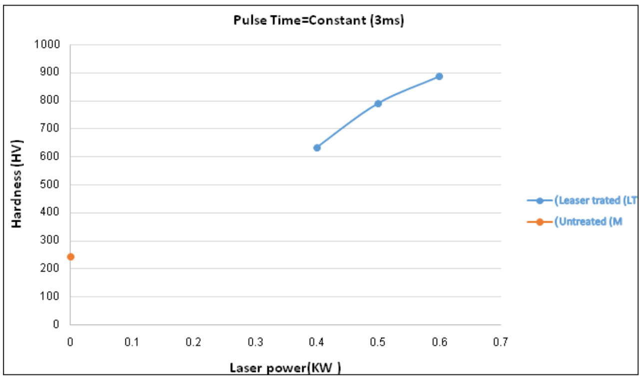


Figure 5: Hardness Values for the Master Sample and the Laser Treated Sample with Various Laser Power at the Same Pulsed Time (3ms)

Nickel Ion Release and Chemical Composition

Though Ni is an essential element for the human body, it is allergenic and toxic when present at elevated levels. Nickel ion release were measured for laser treated and untreated samples by using atomic absorption spectrometry in artificial saliva at 37°C for 15 day. Result is shown graphically.

Nickel ion release number of the untreated sample was (0.9057 ppm), the lowest corresponding number of laser treated sample is (0.2919 ppm). This mean that an improvement of (310%) is introduce by laser treatment. However it appears that a further of improvement was obtained by the increase of laser power higher laser power lower of Nickel ion release number. Therefore the increase of power from (0.4 KW to 0.6KW) causes a decreases of (0.7261 to 0.2919 ppm), i.e. An improvement of (248%) was obtained Figure 6. Decrease of Ni/ti ratio also shown figure 7.

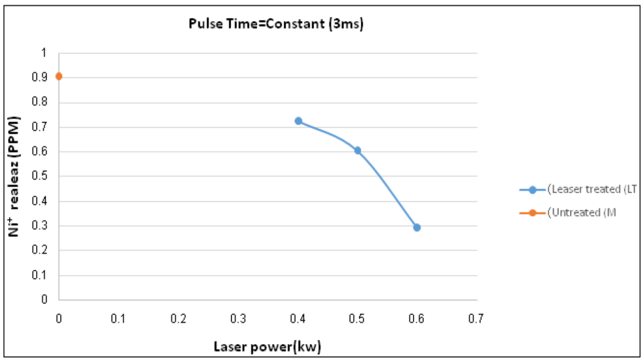
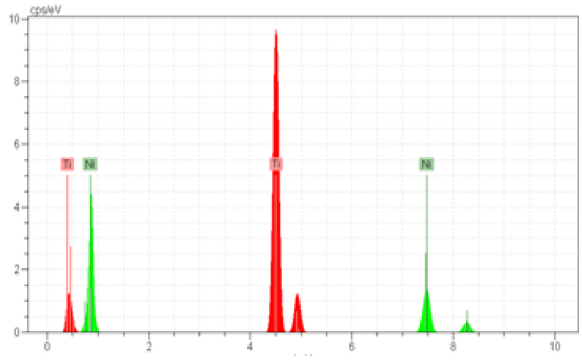
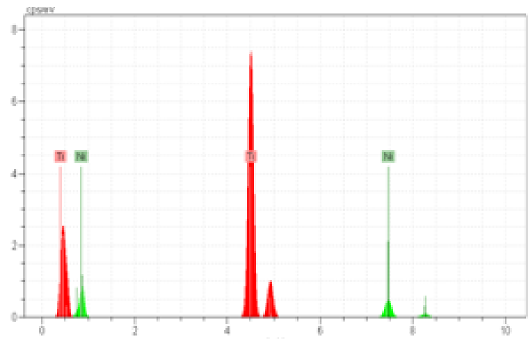


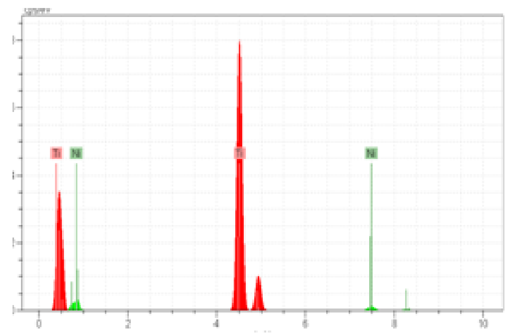
Figure 6: Nickel Ion Realize Values for the Master Sample and the Laser Treated Sample with Various Laser Power at the Same Pulsed Time (3ms)



(a)



(b)



(c)

Figure 7: (a), (b), (c) An EDS Spectrum for Laser Treated Sample of Laser Power (0.4, 0.5 0.6) KW, Respectively and Pulse Time 3ms

DISCUSSIONS

Corrosion behavior can be attributed to the formation a well-adherent corrosion resistant Layer of titanium oxide TiO_2. Since Ti is the less noble than Ni [6]. Hence the oxide is expected to be mainly of titanium oxide. The oxidation state of Ti changes from Ti^{4+} (corresponding to TiO_2) in the top layer of the laser treated oxide film to lower oxidation states Ti^{3+} and Ti^{2+} (corresponding to Ti_2O_3 and TiO). For bare NiTi, oxygen is almost absent in the substrate below the native film. However, nearly 10 at. % of oxygen is present in the substrate below the surface oxide film [1, 7]. When the surface of the substrate was irradiated by laser, then the reaction between ambient oxygen and metallic ions is accelerated by the high temperature reached at the surface. The film thickness rapidly increased. The elevated temperature in the HAZ below the film also promoted the diffusion of oxygen into the zone. Oxygen dissolved in the substrate below the film and remained in solid solution as the sample rapidly cooled down after the passage of the laser spot [1].

In the Laser treatment process, the absorbed energy is instantaneously transferred to the lattice and melt the near surface regions quickly. When the laser is removed, the metallic subsurface quenches quickly the melted layers. This provides a refinement in the surface microstructure, chemical homogenization of the surface, removal of inclusions, and reduced porosities. Hardness behavior may be attributed to the Narrow beams with high power density which allows extremely rapid processing, with minimum or no changes in the bulk material. Rapid rates of processing produce refined and novel microstructures in the surface region. Reasonable increase in hardness can be achieved by the extreme refinement of the grain structure, in comparison with the untreated sample.

A fine-grained material (one that has small grains) is harder and stronger than one that is coarse grained, since the former has a greater total grain boundary area to impede dislocation motion. Such as laser treated layer has shown a very high yield strength and hardness, while maintaining a high degree of ductility. Laser shock processing, also known as laser shot peening, involves a ve1y short, high-energy pulse. Because of the short duration of the energy pulse, the amount of surface hardening is limited. Laser induced shock introduces slightly residual compressive stress in the peened specimen. The ultrahigh-strain-rate plastic deformation by LSP results in dislocation substructure and amorphization underneath the surface which are responsible for the hardness increase [9]. Ni ion release behavior can be attributed to the effect of laser treatment resulting in decreases Ni/Ti ratio probably due to preferentially titanium oxides layer formation on the surface.

The reduced Ni/Ti ratio is similar to that reported by [8,9,10] and has been attributed to increased outward growth of Ti oxide at high oxidation temperatures. Smaller grain size and high density of grain boundaries provided a higher number of nucleation sites to quickly form a protectively passive layer from titanium oxide so titanium less noble than nickel and have high affinity to oxygen. Ti-rich surface layer and a lower Ni/Ti ratio can be expected after laser surface melting because the formation of titanium oxide. the existence of Ti_2Ni also demonstrate this since Ti_2Ni is normally formed in Ti-rich NiTi alloy. This redistribution of Ti near the surface will contributed to the improvement in corrosion resistance and reduce nickel release[11].

CONCLUSIONS

- Laser surface treatment improved corrosion resistance by a factor (1549%) compare with the corresponding reference untreated sample.
- A reduction of (310%) of toxic Ni-ion release was obtained in laser treated sample. Ni-ion may cause allergic.
- An increase in hardness of (368%) results in the laser surface treated sample.
- An increase in laser power produced fine grain size so farther enhancing in corrosion and hardness will produce.

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