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Determination of Ni Release in NiTi SMA with Surface Modification by Nitrogen Plasma Immersion Ion Implantation

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NiTi SMA is a promising material in the biomedical area due to its mechanical properties and biocompatibility. However, the nickel in the alloy may cause allergic and toxic reactions and thus limiting its applications. It was evaluated the influence of surface modification in NiTi SMA by nitrogen plasma immersion ion implantation (varying temperatures, and exposure time as follows: <250 °C/2 h, 290 °C/2 h, and 560 °C/1 h) in the amount of nickel released using immersion test in simulated body fluid. The depth of the nitrogen implanted layer increased as the implantation temperature increased resulting in the decrease of nickel release. The sample implanted in high implantation temperature presented 35% of nickel release reduction compared to reference sample.

Keywords Ni release, NiTi SMA, N-PIII

1. Introduction

The NiTi alloy has excellent mechanical properties such as good resistance to fatigue and good resistance to corrosion; therefore, it can be applied in several areas (Ref 1, 2). The NiTi SMA has been produced by ITA Group using two processes: Vacuum induction melting (VIM) and electron beam melting (EBM). Details of the processes can be found in Ref 3-5. NiTi SMA is an interesting candidate in the biomedical area due to its shape memory and superelastic effects. Actually, this material has been used in a wide range of biomedical applications such as orthodontic arc wires, endodontic files, stents for the vascular, urological and gastroenterological fields, staples for the orthopedic field, etc. (Ref 6). For specific medical applications, e.g., permanent implants, it is necessary to eliminate or reduce the nickel ion release that may cause adverse reactions after its implantation such as allergic reactions and rejections. It is also believed that there is a possibility of carcinogen in case of long-term exposure (Ref 7, 8).

One possibility is the surface modification by the Nitrogen Plasma Immersion Ion Implantation technique (N-PIII), which has some advantages when compared to conventional plasma nitriding such as: implantation on three-dimensional complex shapes, a reduced operation time, no significant dimensional changes, and it is a clean process with no generation of toxic waste. Furthermore, the N-PIII is a diffusion process with no surface delamination which usually occurs in conventional deposited thin layer (Ref 9, 10).

The studies indicate that N-PIII technique increases the surface hardness, decreases the friction coefficient and decrease the nickel release and also improve the surface corrosion resistance and biocompatibility vary largely with the thickness, composition and morphology of the modified layer on the NiTi surface (Ref 10).

In this study, the NiTi SMA samples were subjected to N-PIII treatment varying the implantation temperature, voltage, and exposure time relating them to nickel release by immersion in simulated body fluid (SBF).

2. Experimental Procedures

The samples used in this study were from a 50 mm in diameter ingot that was hot rolled down to 15 mm in diameter bar, and then hot swaged to a final 9 mm in diameter bar, produced by ITA Group in vacuum induction melting. From a 9 mm bar, 2 mm thick samples were cut transversally using a low speed diamond saw. Then they were manually ground with 220, 400, 600, 800, 1000, and 1200 grit emery water paper and polished in 9 μm diamond paste and then in OP-S abrasive solution sequentially, followed by ultrasonic cleaning in

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Table 1 Chemical composition and transformation temperature of Ti-49.42 at.% Ni ingot

Ni, at.%	C, wt.%	0, wt.%	M_s, °C	M_f, °C	A_s, °C	A_f, °C
49.42	0.066	0.1113	62.5	38.0	65.3	91.0

Table 2 Experimental conditions for N-PIII

Sample	Frequency, Hz	Voltage, kV	Time, min	Temperature, °C
A	300	10	120	<250
B	400	11	120	290
c	400	5	60	560

Table 3 Ion concentration of simulated body fluids (SBF) and human blood plasma

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl	HCO_3	HPO_4^{2-}	SO_4^{2-}
Blood plasma	142	5.0	2.5	1.5	103.0	27.0	1.0	0.5
SBF	142	5.0	2.5	1.5	148.8	4.2	1.0	0.5

acetone bath. Table 1 shows the chemical composition and transformation temperature of starting material.

The N-PIII was undertaken at Plasma Associated Laboratory (LAP/INPE) and consisted of three experimental conditions, varying accelerating voltage, and exposure time and temperature as shown in Table 2. The pulse frequency was kept in 40 µs. Before plasma implantation, the samples were cleaned by sputtering with argon plasma for 15 min at 5 kV. The experiments were done in two heating conditions: either by ion bombardment (samples A and B) or by sample-holder heating (sample C). The sample-holder temperature was monitored by an infrared pyrometer (MIKRON, model M90-Q).

The nitrogen implanted layer were analyzed by Auger Electron Spectroscopy (AES, Fisons Instruments Surface Science, model Microlab 310-F) for samples A and B and by glow discharge optical emission (GDOES, Jobin-Yvon GD-Profiler) for sample C which was supposed to present thicker implanted layer.

The liquid extracts of NiTi were prepared according to ISO 10993-12. NiTi alloys (63.61 mm^2) were supplied sterile by 24 h with UV radiation, and incubated with 30 mL Minimum Essential Medium (MEM) cell culture. The samples were incubated in darker environment for 7 days in MEM with pH 7.0 at 37 °C, using a shaker CT-712R Cientec (75 rpm). After incubation, 1.0% HNO_3 was added to prevent loss of ions by the hydrolysis and oxidative process. Prior to analysis, the solutions were preserved at 4 °C. The study was performed in sterile conditions, under a laminar flux, using sterile materials. No antibiotic/antimycotic substance was added.

Table 3 shows that the SBF presented values nearly equal to those of human blood plasma.

The concentrations of released metal ions from the NiTi samples into SBF were evaluated by inductive coupled plasma optical emission spectrometry (ICP-OES), in an axially viewed configuration (Vista AX, Varian, Melbourne, Australia). A Sturman-Masters nebulization chamber and a V-groove nebulizer were used. The matrix-matched calibration curves were established by employing SBF solution. The concentrations used were: 0.025, 0.05, 0.1, 0.2, 0.4, and 1.0 mg/L obtained from the dilution of 1000 mg/L stock solutions of each element (Ni). Deionized distilled water was used in the preparation. The ICP-OES operating conditions are given in Table 4. The mass of NiTi samples was weighed and the values of metal ions released were normalized for 1 mg/L.

Table 4 Operating conditions: ICP-OES with axially viewed configuration

Radio-frequency generator, MHz	40
Plasma power, kW	1.1
Plasma gas flow, l/min	15.0
Auxiliary gas flow, l/min	1.5
Nebulization gas flow, l/min	0.9
Injector tube diameter, mm	2.4
Spectral lines, nm	Ni: 231.604

3. Results and Discussion

Figure 1 shows the results of implanted nitrogen concentration profile as a function of depth varying the implantation conditions. Also it is shown the profiles of others elements such as oxygen, carbon, titanium, and nickel. The samples A and B were analyzed by AES technique and sample C by GDOES technique which is supposed to have thicker nitrogen layer. For sample A, as shown in Fig. 1(a), implanted temperature is lower than 250 °C, the maximum nitrogen concentration is about 38 at.% at a depth of 20 nm and then decreases to zero at around 50 nm. The same figure shows that there are some increase in oxygen and carbon content near the surface. The thickness of the carbon layer on the sample is about 10 nm, while for the oxygen layer is 5 nm. The appearance of carbon and oxygen should be due to the contamination inside the chamber during the N-PIII process.

For sample B, as seen in Fig. 1(b), the nitrogen concentration is around 30 at.% up to a depth of 55 nm then decreases rapidly to a residual level at around 80 nm. The carbon concentration profile as a function of depth is similar to sample A, about 10 nm while that of the oxygen concentration decreases slower than that of sample A up to 60 nm depth.

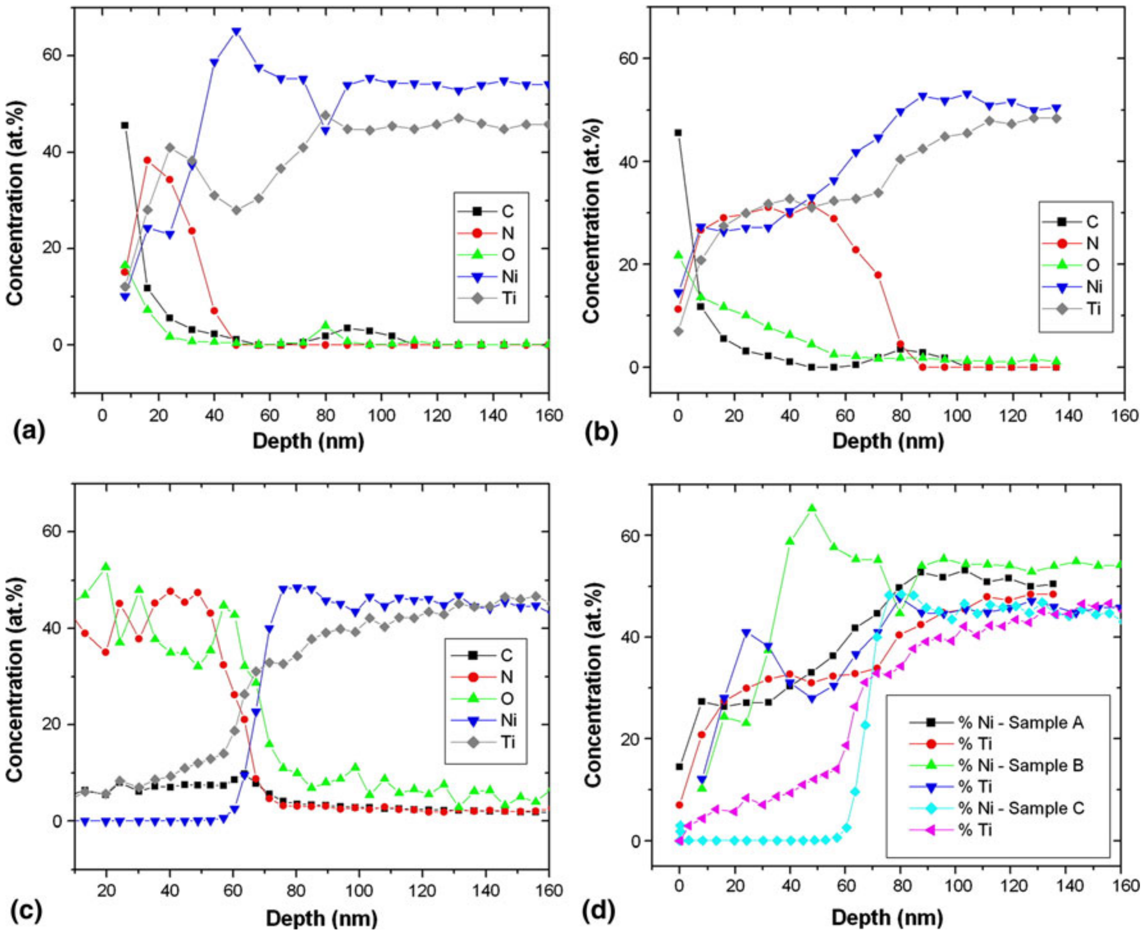

Fig. 1 Atomic concentration profiles of the elements as a function of depth of N-PIII samples. (a) sample A (AES), temperature: <250 °C, voltage: 10 kV, time: 120 min, (b) sample B (AES), temperature: 290 °C, voltage: 11 kV, time: 120 min, (c) sample C (GDOES), temperature: 560 °C, voltage: 5 kV, time: 60 min, and (d) comparison between Ti and Ni in different N-PIII experimental conditions versus depth

Figure 1(c) shows the results of sample C, implanted at highest temperature (560 °C). The nitrogen concentration as a function of depth is, in average, around 45 at.% up to a depth of about 50 nm, that is, the highest value when compared to samples A and B implanted at lower temperature, <250 and 290 °C, respectively. The oxygen concentration profile followed the nitrogen profile very closely as shown in Fig. 1(c). Theirs values were very high, around 40 at.% up to a depth of 50 nm. The carbon profile was very similar to samples A and B with initial values of 45 at.% at surface and then decreasing to residual level. Inversely to nitrogen profile, there was clear nickel depletion up to a depth of 55 nm then increasing rapidly to a nominal level. Underneath the implanted layer (50 nm) and up to 100 nm depths, the material is enriched in nickel compared to titanium, whereas the nitrogen, oxygen, and carbon concentrations rapidly decrease.

Figure 2 shows the amount of nickel released into SBF after immersion for 7 days. As expected, the worst result was presented by an untreated sample with nickel ion release of 0.0261 ppm. The N-PIII samples presented decreasing nickel ion release as the treatment temperature increased as follows: 0.0211, 0.0174, 0.0169 ppm, respectively, for samples A (<250 °C), B (290 °C), and C (560 °C).

Rocher et al. (Ref 11) showed that in commercial NiTi alloys the nickel ion release values were 6.6 ppm (or 15.4 ppm in 7 days) and 11.4 ppm (or 13.3 ppm in 7 days) after 3 and 6 days culture, respectively. Liu et al. (Ref 8) showed that samples N-PIII treated in high implanted voltage, in 30 kV, the best nickel release value was near to 0.05 ppm after 5 week (0.01 ppm for 7 days) culture in simulated body fluid. Yeung et al. (Ref 12) comparing the amount of the ions leached from the nitrogen and oxygen PIII samples after 8 days were 0.106 ppm (or 0.093 ppm in 7 days) and 0.109 ppm (or 0.095 ppm in 7 days), respectively, demonstrating that nitrogen plasma implantation seems to be better than the oxygen plasma implantation. Xu et al. performed a comparison of nickel ions release between NiTi chemically polished and anodized (Ref 13). For the immersion times of 5 weeks, the amounts of nickel leached from the anodized NiTi was 0.30 ppm (0.06 ppm in 7 days). These results were less than 5% of those leached from the chemically polished one, 0.715 ppm after 5 weeks immersion (or 0.143 in 7 days). The results of this work are comparable to the result presented by Li et al. but superior when compared to the literature shown above as summarized in Fig. 2.

Esenwein et al. (Ref 14) evaluated the potential release of Ni ions in different treatment conditions and incubation times. Nickel release from etched NiTi, coated NiTi (hydroxyapatite films), and NiTi was analyzed in phosphate-buffered saline (pH 7.4) over a period from 3 to 56 days. Etched NiTi samples showed a much higher release of nickel ions than coated NiTi samples or non-treated NiTi samples. The amount of nickel

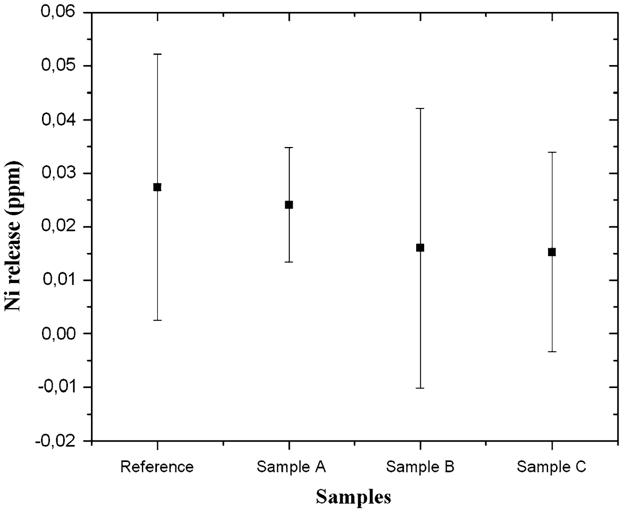

Fig. 2 Nickel ion released after 7 days immersion in SBF

ions released (after ppm data conversion) from etched NiTi ranged from 11.68 ppm (day 3) up to 21.63 ppm (day 21) and from coated NiTi from 2.98 ppm (day 3) up to 7.21 ppm (day 56). Compared to this, in untreated NiTi, the ion Ni release between 0.09 ppm (day 7) and 0.14 ppm (day 49) was measured. Compared to the best nickel release obtained by Esenwein et al. with our results shows clearly a very lower Ni release (Fig. 2). The ions Ni release values obtained here were between 0.0169 (the implantation in high temperature) and 0.0261 ppm (untreated sample).

The immersion test demonstrated that the nickel release reduction occurs in all samples treated by N-PIII. After 7 days in immersion it is possible to say that the amount of Ni released decreases with the increase of the implanted layer thickness. For sample A, which has a lower implanted layer (50 nm) showed a 19% reduction in the nickel release, while samples B and C that have greater implanted layer thicknesses (80 and 150 nm) reduced from 33 and 35%, respectively. Further work should be done taking into account the biocompatibility and some others aspects should be important as a biomaterial.

4. Conclusion

Nitrogen plasma immersion ion implantation is efficient to reduce the nickel ion release from the NiTi SMA surface. The higher N-PIII temperature, the higher is nitrogen implanted layer and lower is the nickel ion release for 7 days immersion time in SBF.

For a highest N-PIII temperature it is seen a clear nickel depletion on the modified layer that could contribute to lower nickel release.

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