

# Tribological Properties of Biomedical NiTi Shape Memory Alloy after Rf Plasma Nitriding

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**Abstract-** Nickel titanium (NiTi) alloys are potentially useful in biomedical applications due to their unique superelasticity behaviour and shape memory effects (SME). However, these alloys are vulnerable to surface corrosion and the most serious issue is out-diffusion of toxic Ni ions from the substrate into body tissues and fluids. Hence, it is necessary to produce a surface barrier to impede the out-diffusion of Ni ions from the alloys. The inductively coupled radio frequency plasma (ICRFP) is an efficient technique for modifying the surfaces of NiTi alloys. The results exhibit the enhancement of the corrosion resistance and tribological properties of the NiTi substrate, but also effectively suppress the Ni ions release from the substrate. All these improvements can be attributed to the formation of titanium nitride (TiN) on the surface of NiTi alloys.

**Keywords-** Nickel Titanium (NiTi); Superelasticity; Shape Memory Effect SME; Inductively Coupled Radio Frequency Plasma (ICRFP); Corrosion Resistance; Fraction Coefficient

## I. INTRODUCTION

Nickel titanium (NiTi) is an intermetallic compound that possesses attractive properties such as superelasticity and shape memory effect [1]. Coupled with a reasonably high corrosion resistance, NiTi is emerging as a popular material for biomedical applications [2]. However, the high nickel content (about 50 at. %) in NiTi has caused some concerns of its safe use in vivo because Ni is allergenic and toxic when its concentration in the human body exceeds a certain level [3]. In view of this, surface treatment of NiTi implants for improving corrosion resistance and hence reducing the amount of Ni released is usually employed. Various surface treatment methods have been devised in this respect, including chemical passivation, electropolishing, anodization, thermal oxidation [4-9], laser surface melting [10-12], sol-gel method [13], gas nitriding technique [14], alkaline treatment [15], and ion implantation [16]. Even though it was reported that TiNi alloys with B2 phase (austenite parent phase) exhibit excellent wear resistance (due to its rapid work hardening and pseudoelastic properties) [17-21], the poor wear resistance of B19' (martensite) and high coefficient of friction for both B2 and B19' phases made them difficult to be used in orthodontic applications. Ion implantation [22, 23], gas nitriding [24-26] and TiN coating [27, 28] have been employed to improve surface properties of bulk TiNi alloys. After the surface treatment, hardness, wear and/or corrosion resistances were all improved [29].

The aim of this work is to study the tribological properties and corrosion resistance of Nitinol shape memory alloy (TiNi) for its further safe use as a surgical implant material by investigating the formation of nitrided layer on Nitinol produced by inductively coupled radio frequency plasma (ICRFP).

## II. EXPERIMENTAL PROCEDURE

The material studied was Ti<sub>50</sub>Ni<sub>50</sub> shape memory alloy. Coupon-shaped specimens are 1 cm × 2 cm in diameter and 2 mm in thickness. The coupons were prepared by arc-melting pure metals with nominal purities of 99.99 wt.% in an induction furnace under argon atmosphere (99.9999% purity). Produced castings were heated at 900°C for two hours. The heated specimens were hot rolled with about 10% reduction each time at 800°C up to 2 mm in thickness. The nitriding treatment of TiNi shape memory samples was carried out using a radio frequency (Rf) inductively coupled glow discharge, with a continuous mode of operation at 13.56 MHz. This system consists of a quartz reactor tube with 500 mm in length and 41.5 mm in diameter evacuated by a two-stage rotary pump to a base pressure of 10<sup>-2</sup> mbar. TiNi samples were maintained on one stainless steel bar 15 mm in length and 20 mm in diameter. This assembly was supported on copper sample holder fitted, which was equipped with water-cooling pips. Nitrogen (N<sub>2</sub>) gas was introduced to establish a gas pressure of 8-8.4×10<sup>-2</sup> mbar, measured by a Pirani gauge. The distance between the sample holder surface and the Rf coil was 2.9 cm and the water cooling rate for samples was 1500 cm<sup>3</sup>/min. The discharge was generated by an induction copper coil energized by Rf power generator (type HFS 2.5 kW, 13.65 MHz) via a tunable matching network. The surface and cross section morphology of tested samples were examined before and after corrosion measurements using metallurgical microscope type (Inverted Metallurgical

Microscope Epiphot 300). This microscope was attached with video camera and a computer. The phase compositions of the surface region of the nitrided layer were studied by X-ray diffraction (XRD) using CuK $\alpha$  radiation in the  $\theta$ - $2\theta$  geometry. The microhardness was measured by using a Wetzlar microhardness tester with the load of 0.98 N (100 g). Friction measurement was performed at room temperature in laboratory ambient (25°C and relatively low humidity of 24%) using an oscillating ball-on-disk type tribometer wear tester without lubrication. The 6 mm ball of aluminium oxide was moved at a mean sliding speed of 3 mm/sec-with 2 N load. Corrosion-resistance performance was carried out in the Ringer's solution 6.00 g/l NaCl, 3.20 g/l sodium lactate, 0.27 g/l CaCl<sub>2</sub>, 0.4 g/l KCl.(pH=7.4) at the temperature of 37 $\pm$ 1°C. The test solution was used no more than twice due to possible breakdown of solution purity. The sample was pressed into a holder with a Teflon gasket, which ensured only the front 0.78 cm<sup>2</sup> part of the sample comes in contact with the electrolyte. The electrochemical testing process was carried out without aeration. The experimental setup consisted of a conventional three-electrode cell containing the working electrode, reference electrode (Ag/AgCl) and platinum as the counter electrode. The potentiodynamic experiment was carried out using a computer-controlled potentiostat (Gill AC, model 88). Polarization experiments were started after the specimen have been immersed in the experimental solution for an hour under open circuit conditions and performed at a rate of 100 mV/min. The electrochemical behavior of nitrided NiTi samples was compared with that of untreated NiTi.

### III. RESULTS AND DISCUSSION

#### A. Cross-Section Morphology

Optical microscope (OM) study served to determine the thickness of the nitrided cross-section layer (compound layer) of NiTi shape memory alloy samples. The typical cross section views of nitrided samples treated for 10 min using input plasma power of 525 W are shown in Fig. 1. It can be seen that the thickness of the compound layer is 28  $\mu$ m. This leads to the conclusion that the Rf plasma power has a remarkable effect on the thickness of compound layer. However, this conclusion agrees with that of [25]. It was reported that the cross section of Ti<sub>50</sub>Ni<sub>50</sub> shape memory gas-nitrided at 900°C consists of two distinguishable nitrided layers of TiN and new Ti<sub>2</sub>NiH<sub>0.5</sub> compounds. Meanwhile, the compound layer of 600°C gas-nitrided Ti<sub>50</sub>Ni<sub>50</sub> specimen consists of two distinct nitrided regions: one is a random mixture of TiN, Ti<sub>2</sub>NiH<sub>0.5</sub> and a nickel-rich phase; and the other consists of columnar-like structures of mixed TiN and nickel rich phase. The thicknesses of the two regions for 600°C and 900°C are approximately 30 and 40  $\mu$ m respectively. Gilad et al. proposed that nickel titanium (NiTi, nitinol) shape memory alloy was nitrided using a powder immersion reaction assisted coating (PIRAC) method to modify its surface properties [30]. After 1 h of PIRAC treatment at 1000°C, the thicknesses of the TiN and Ti<sub>2</sub>Ni layers are 0.4 and 0.8  $\mu$ m, respectively. Moreover, Cui et al. reported that cross-section measurements of laser gas nitriding of NiTi shows that a continuous thin TiN surface layer with thickness of 2  $\mu$ m was formed on the outmost surface of the sample [31]. Also, the cross-section microstructure of the laser gas nitriding of NiTi specimen indicated that a continuous thin surface layer with thickness of about 2  $\mu$ m formed on the outmost surface of the specimen [32].

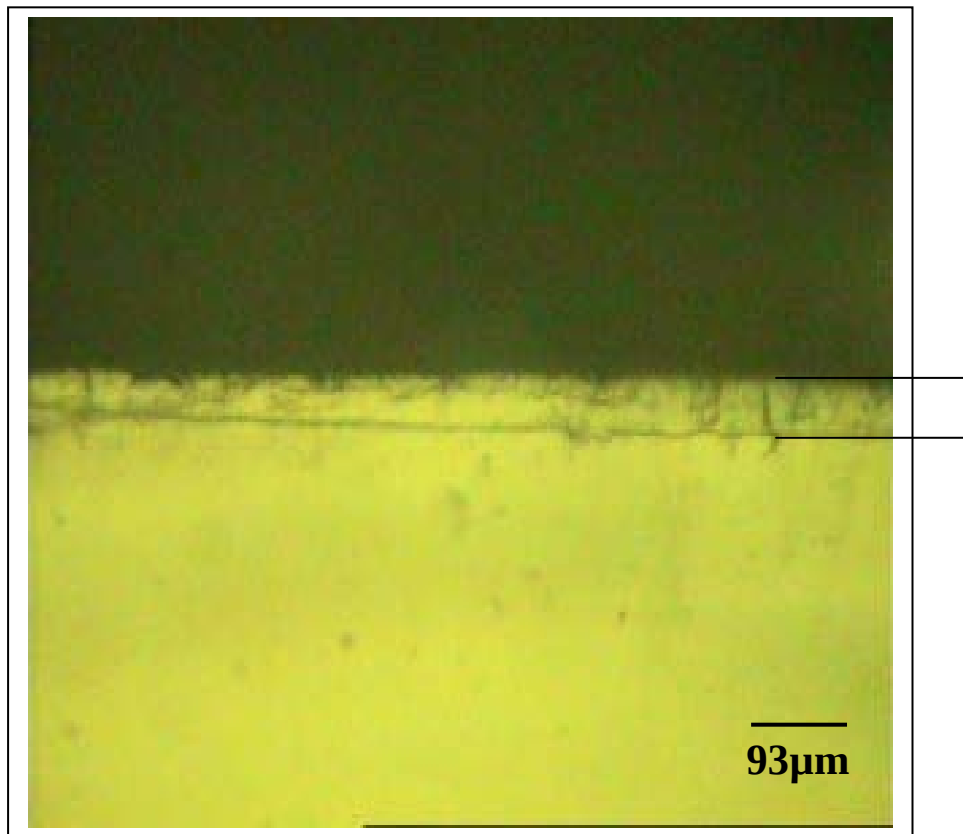


Fig.1 Optical micrographs of compound layer thickness of TiNi shape memory alloy treated by plasma processing power input at 525 W

### B. Surface Morphology

The typical OM micrograph of untreated TiNi shape memory alloy sample is shown in Fig. 2(a). Examination of structures reveals fine-grained structure composed of NiTi. Fig. 2(b) seems a different microstructure with respect to the untreated sample when plasma power input is set-up at 525W. Also, from this figure, a clear difference between the original and treated samples can be seen. The color of treated sample altered to golden yellow, demonstrating formation of TiN phase. Similar observation has been made by Starosvetsky et al. [33]. Through this method, Nickel-titanium (NiTi, nitinol) shape memory alloy was nitrided using an original powder immersion reaction assisted coating (PIRAC) method in order to modify its surface properties. From this method, PIRAC nitriding of NiTi alloy at 900-1000°C yielded a characteristic golden-colored TiN coating on the samples' surface. Also, Wu et al. reported that the gas-nitrided  $\text{Ti}_{50}\text{Ni}_{50}$  specimens showed homogeneous surface morphologies, with colors ranging from purple to golden yellow, and an increase in the nitriding temperature [25]. A smooth surface morphology appears in the 900°C nitrided specimens. From the above, it can be concluded that the change of surface morphology is correlated with input plasma power.

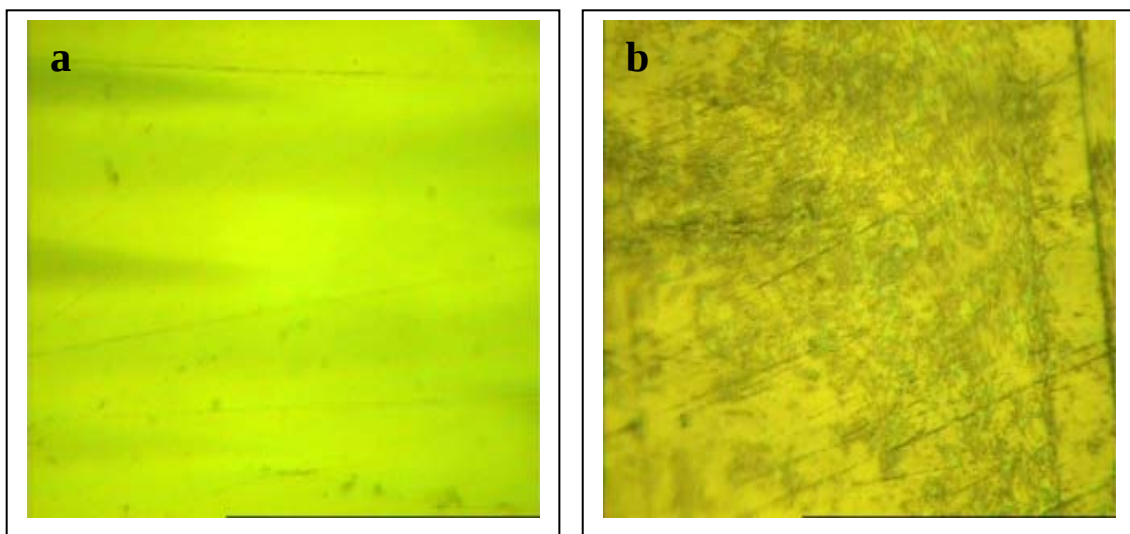


Fig.2 (a-b) Optical micrographs of the surface morphology of TiNi shape memory alloy samples treated for plasma processing power input (a) 0.0W (b) 525 W

### C. X-ray Diffraction Analysis

The information about the structure of the layers, formed on NiTi alloy, was obtained from analysis of the X-ray diffraction patterns. The X-ray diffraction peaks produced by  $\text{CuK}\alpha$  radiation were investigated for the native and nitrided TiNi shape memory alloy samples using Rf plasma processing power of 525 W. Fig. 3(a) shows the diffraction peaks of the as-received (untreated) sample of TiNi shape memory alloy. The as-received specimen shows a highly intense peak at  $45.1^\circ$ , which is typical for the B19' martensite (NiTi phase) [25]. The diffractogram does not identify the oxide phase observed on the surface, as it is quite small in thickness. This observation well agrees with Neelakantan et al. 2009 [34]. Fig. 3(b) shows the diffraction peaks of the treated TiNi shape memory alloy at 525 W, it can be seen that the XRD spectrum is composed of TiN and  $\text{Ti}_2\text{Ni}$  phases. This formation of structure is due to the fact that the Ti atoms react more easily with N than Ni [34]. No diffraction peaks attributable to B19' martensite (NiTi phase) were detected. In addition, peaks of a nickel-rich phase were not observed, due to that the nickel atoms diffused into the TiNi matrix because both the diffusion rate and the saturated quantity of dissolved nickel atoms in the TiNi matrix were much higher at  $800^\circ\text{C}$ . Meanwhile, peaks of NiN phase are absent because the heat of formation of TiN is  $-305.6 \text{ kJ mole}^{-1}$  [35], while nickel nitrides such as  $\text{Ni}_3\text{N}$  are unstable compared with TiN [36]. On the other hand, the  $\text{Ni}_3\text{Ti}$  intermediate layer, which decreased the quality of the nitriding process, cannot be detected [37]. From the above, it can be concluded that the disappearance of NiTi intermediate layer enhanced the quality of the nitriding process.

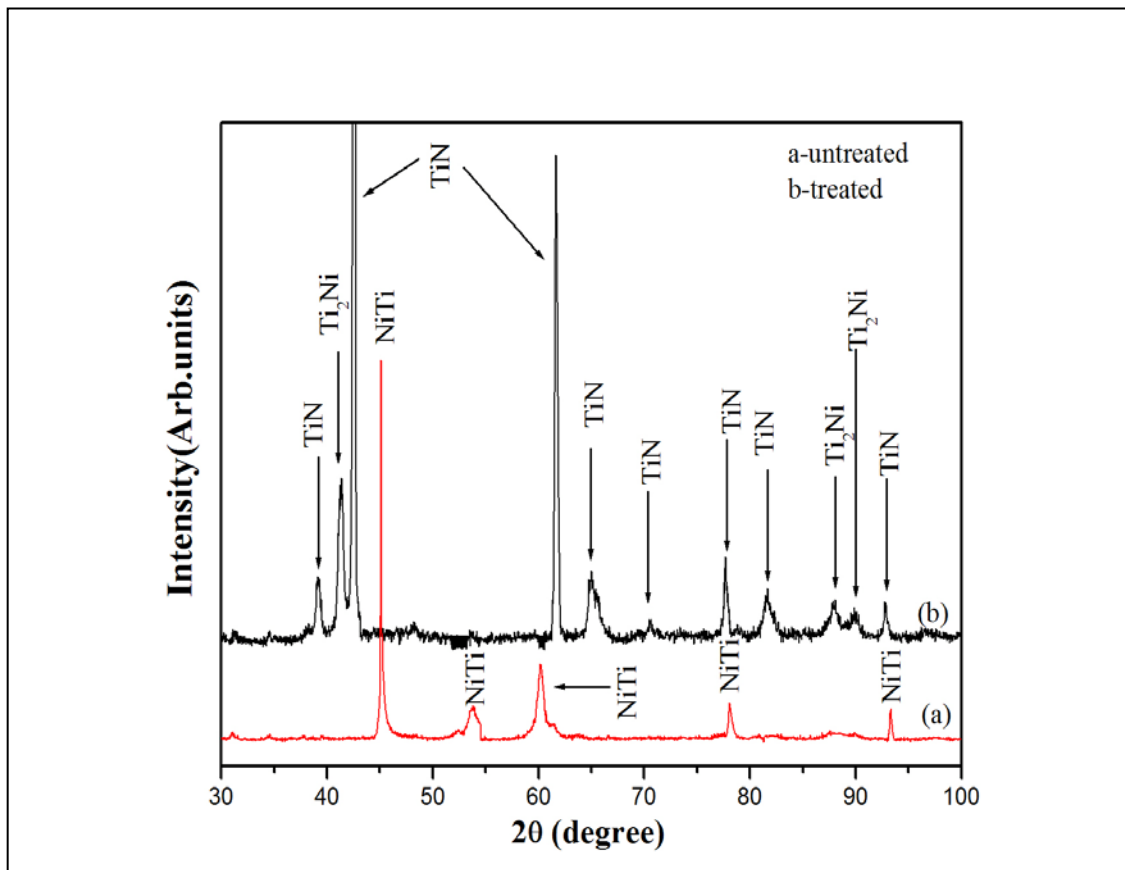


Fig.3 (a-b) X-ray diffraction patterns for TiNi shape memory alloys (a) untreated (b) treated by plasma processing power at 525 W

### D. Microhardness Measurements

To study the influence of plasma processing power on the mechanical properties of nitrided TiNi shape memory alloy samples, the surface microhardness of untreated and treated samples versus the input Rf plasma were measured using 100 g load. From these measurements, the microhardness values are 350 and 383 HV for untreated and treated samples, respectively. The little increase in microhardness is due to the presence of TiN layers, which is produced by Rf plasma nitriding. This result agrees well with Starosvetsky et al. (2001) [38], who reported that the increment of knoop microhardness of nitrided NiTi samples is owing to small thickness of the hard TiN layer. Also, Cui et al. 2003 [31] concluded that the hardness enhancement of the laser gas nitriding (LGN) NiTi was attributed to the high hardness of TiN was distributed in the modified layer and on the top surface layer. Meanwhile, the study proposed by Yeung et al. [39] revealed that the layers of TiN could form on the

surface of NiTi alloy after nitrogen plasma treatment. These layers can actually enhance the surface mechanical properties in terms of corrosion resistance and hardness as compared with the untreated samples. On the other hand, in potential medical applications, the investigation done by Man et al. [32] concluded that the large increase in hardness of laser nitriding NiTi was due to the presence of TiN and the change in hardness was consistent with the graded distribution of the hard TiN phase in the matrix. From the above, it can be decided that TiN layer produced by Rf plasma nitriding contributes to the improved microhardness.

#### *E. Friction Coefficient Measurements*

The wear resistance and the friction coefficient of the untreated and nitrided TiNi shape memory alloy at plasma-processing power of 525 W were assessed using a ball-on disk tribometer type under dry sliding conditions. Alumina balls with a diameter of 6 mm were used as the counter face materials under normal loads of 2 N. The tests were conducted in laboratory ambient 25°C and humidity of 24% for 200, 400 and 2000 tracks at a sliding speed of 3 cm/s. Fig. 4(a-c) shows the typical optical micrograph of the wear (scratch) tracks for the untreated sample at different track numbers. It can be seen that the scratch channel expansion increased rapidly with increasing number of tracks. The scratch channel values record 67.2, 74 and 102  $\mu\text{m}$  at a track number of 300, 400 and 500, respectively. Fig. 5(a-d) shows the typical optical micrograph of the wear tracks for the treated sample. From this figure, it can be seen that the scratch channel expansion increased slowly with increasing number of tracks. The scratch channel values record 7, 10, 14 and 21  $\mu\text{m}$  at a track number 300, 400, 500 and 2000, respectively. This cracking form failure indicates that the TiN coating adheres to the substrate strongly under this condition [40].

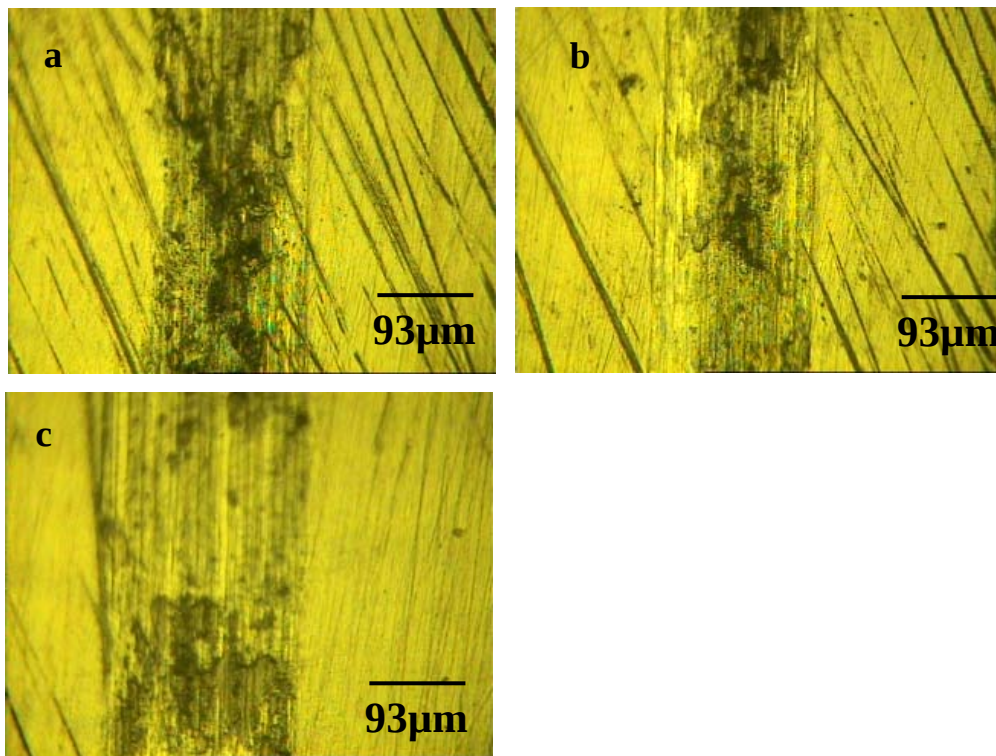


Fig.4 (a-c) Scratch tracks for untreated sample for 300, (b) 400 and (c) 500 tracks

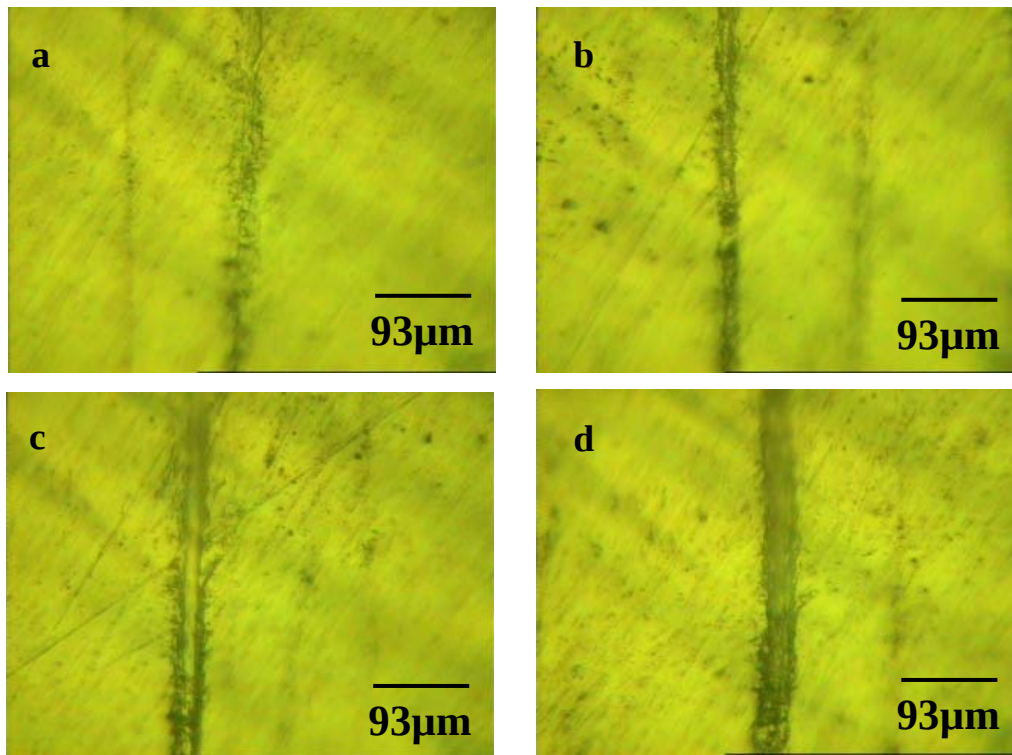


Fig.5 (a-d) Scratch tracks for treated sample for 300, (b) 400, (c) 500 and 2000 tracks

The friction coefficient of the untreated and treated TiNi samples at 100 and 200 tracks under a low load of 2 N are shown in Figs. 6 (a, b). In these figures, for the treated sample, the friction coefficient exhibits the same tendency; it first increases smoothly for up to 17 sec and then reaches a stable low value (0.08 and 0.06 respectively). For the untreated sample, the friction coefficient remains a stable value (0.13 and 0.15). In contrast, the variations of friction coefficient at 300 and 500 tracks are shown in Figs. 6 (c and d) respectively. For the treated samples, the friction coefficient seems stable (0.04-0.05). For the untreated sample, at the initial stage (0-21 sec) the friction coefficient seems stable with a value ranging between 0.05 and 0.25; this result agrees with [29]. After that, it increases sharply at the final stage (21-200 sec) and reaches a relatively high value around 0.88. This high value can be attributed to the removal of the thin oxide layer ( $\text{TiO}_2$ ). Also, the high value of friction coefficient of untreated sample may be attributed to the poor wear resistance and high fraction of B19' (martensite) phase. However, this observation agrees with the XRD analysis. The behaviour of friction coefficient of treated TiN samples at 2000 tracks is displayed in Fig. 6(e). This figure can be divided into two parts; the first part is from 0 to 674 s, when the friction coefficient seems relatively low (0.02-0.09). The second part is from 674 to 1259 s, when the friction coefficient is relatively high (0.6-0.77). This relatively high value may be attributed to the removal of nitride layer (TiN) after 674 s. Also, this hard layer which is produced by Rf plasma nitriding at 525 W can serve as a protective layer for improving load bearing capacity, effectively reducing the friction coefficient thus providing good tribological behaviour. Generally, from the above, the excellent tribological properties of nitrided (TiNi) shape memory may be attributed to two reasons: Firstly, the compound hard layer of TiN possesses very high hardness, and can serve as a protective layer for improving load bearing capacity. The second reason is that the Rf plasma nitriding effect improves the adhesion strength between the compound layer and substrate refraining from the compound layer elimination during the process.

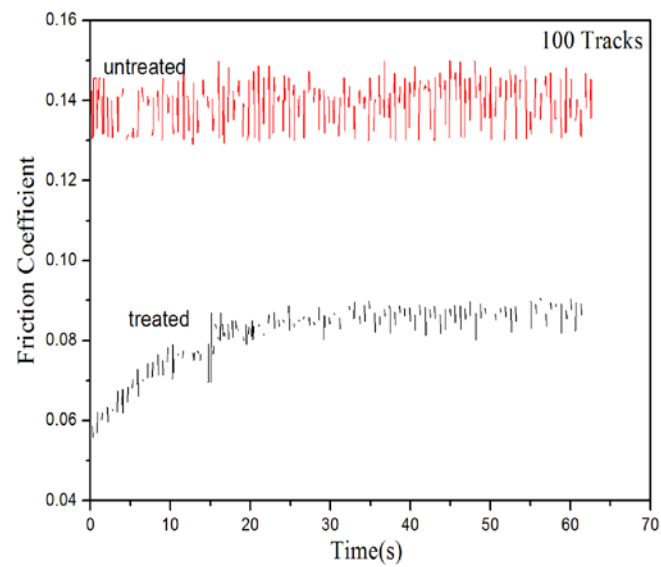


Fig.6.(a) Friction coefficient at 100 tracks of untreated TiNi shape memory alloy and treated by plasma processing power at 525 W

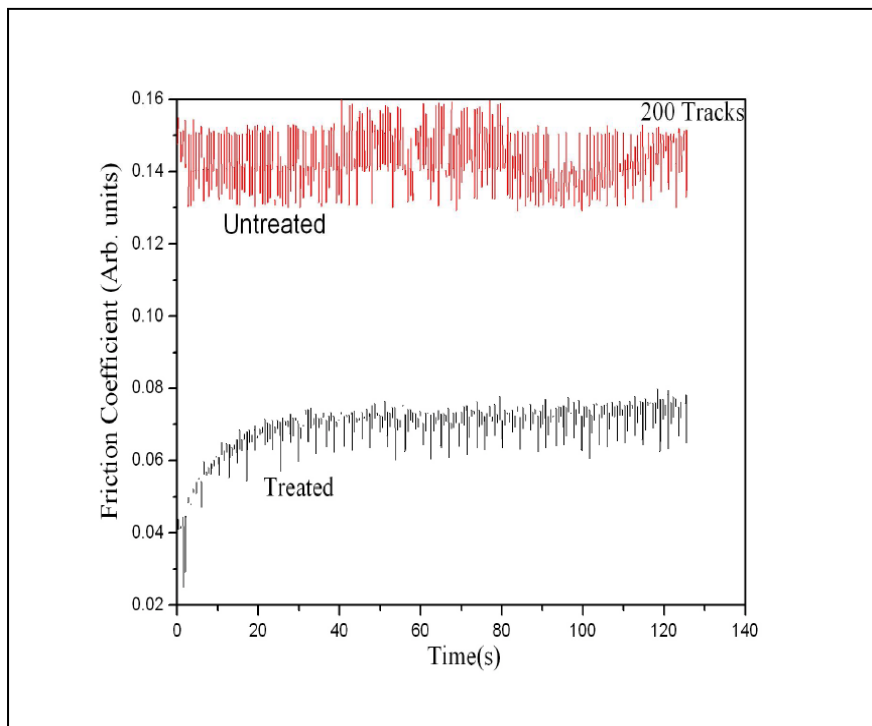


Fig.6.(b) Friction coefficient at 200 tracks of untreated TiNi shape memory alloy and treated by plasma processing power at 525 W

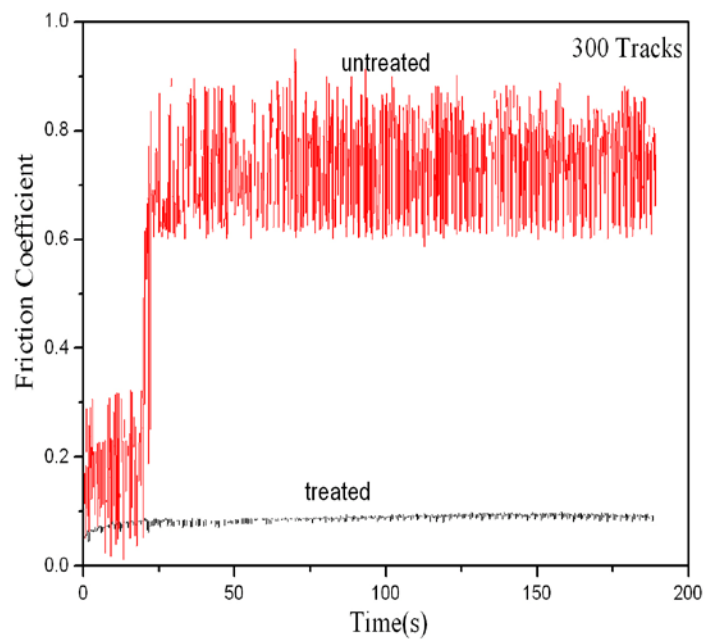


Fig.6.(c) Friction coefficient at 300 tracks of untreated TiNi shape memory alloy and treated by plasma processing power at 525 W

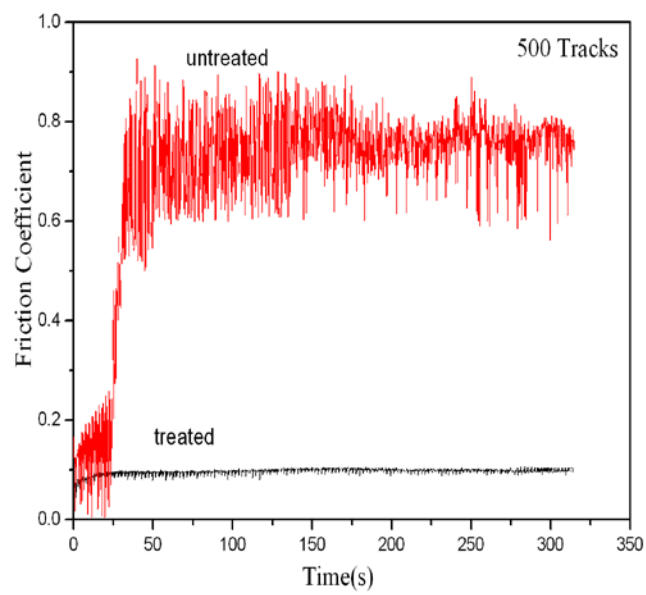


Fig.6.(d) Friction coefficient at 500 tracks of untreated TiNi shape memory alloy and treated by plasma processing power at 525 W

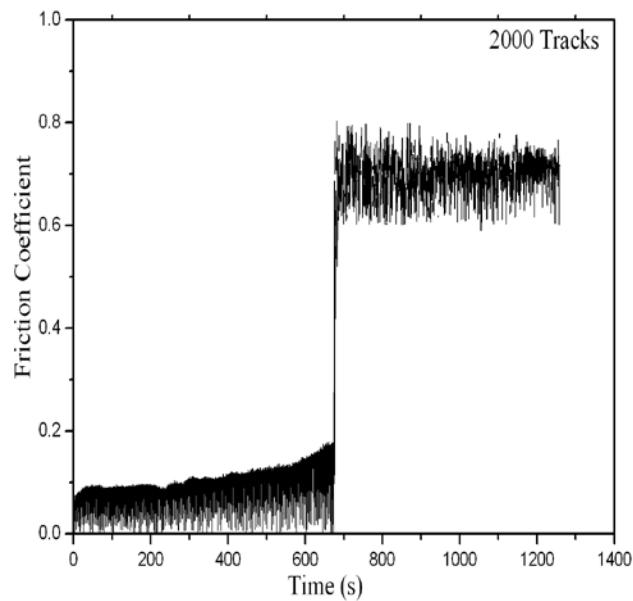


Fig.6.(e) Friction coefficient at 2000 tracks of treated TiNi shape memory alloy by plasma processing power at 525w

#### F. Corrosion Measurements

In this part, the general analysis of the corrosion measurements of the untreated and treated TiNi shape memory alloys samples is presented.

Fig. 7 shows the relationship between the corrosion rate and immersion time. As shown, the corrosion rate increases continually with the increasing time for both untreated and treated samples. The percentage of the increase of corrosion rate is 28:500 for the treated and untreated respectively. On the other hand, Fig. 8 depicts the relationship between current density versus immersion time. As a result, the current density increases with the increase of the time for the untreated sample. However, no change is observed for the treated. So, the percentage of current density increases is 61:45294 for treated and untreated respectively. In addition, the relationship between the open circuit potential and immersion time can be seen in Fig. 9, where the treated sample experiences a slow decrease in the potential while a sharp decline occurs for the untreated. Additionally, the percentage of potential decreases is 0.2: 0.5 for the treated and untreated respectively. Besides, the relationship between the linear polarization resistance and immersion time can be seen in Fig. 10, which that the linear resistance of both samples decreases. The percentage of resistance decreases is 27: 514 for treated and untreated respectively. More to the point, the relationship between the corrosion current density and immersion time can be seen in Fig. 11: the corrosion current density increases for the two kinds of samples; the percentage of corrosion current density increases is 30: 454 for treated and untreated respectively. This result reflected the high corrosion resistance for the treated sample with respect to the untreated. Furthermore, it is known that nitrogen may be involved chemically in establishing the passive layer. If nitrogen becomes oxidized, it may enhance the passivation in several ways [41]: (i) the oxidized nitrogen species can become an intimate chemical part of the bonding in the passivation layer by producing an oxide film of a lower ion conductivity reported by Akolzin et al. [42]; (ii) it may act catalytically to produce a special chemical state of the oxide, such as a higher concentration of the stable  $Ti^{4+}$  ion. The resulting enhanced corrosion resistance is then due to the formation and maintenance of a more passive oxide layer. This enhanced production of  $Ti^{4+}$  with the nitrogen content in the combined layer is responsible for the improved corrosion passivation of plasma-nitrided TiNi shape memory alloy in Ringer's solution, which can be attributed to the fact that the formation of a stable and insoluble oxide layer has reduced ions diffusion. These results show that Rf plasma nitriding is a promising method to improve the corrosion resistance of TiNi shape memory alloy in Ringer's solution.

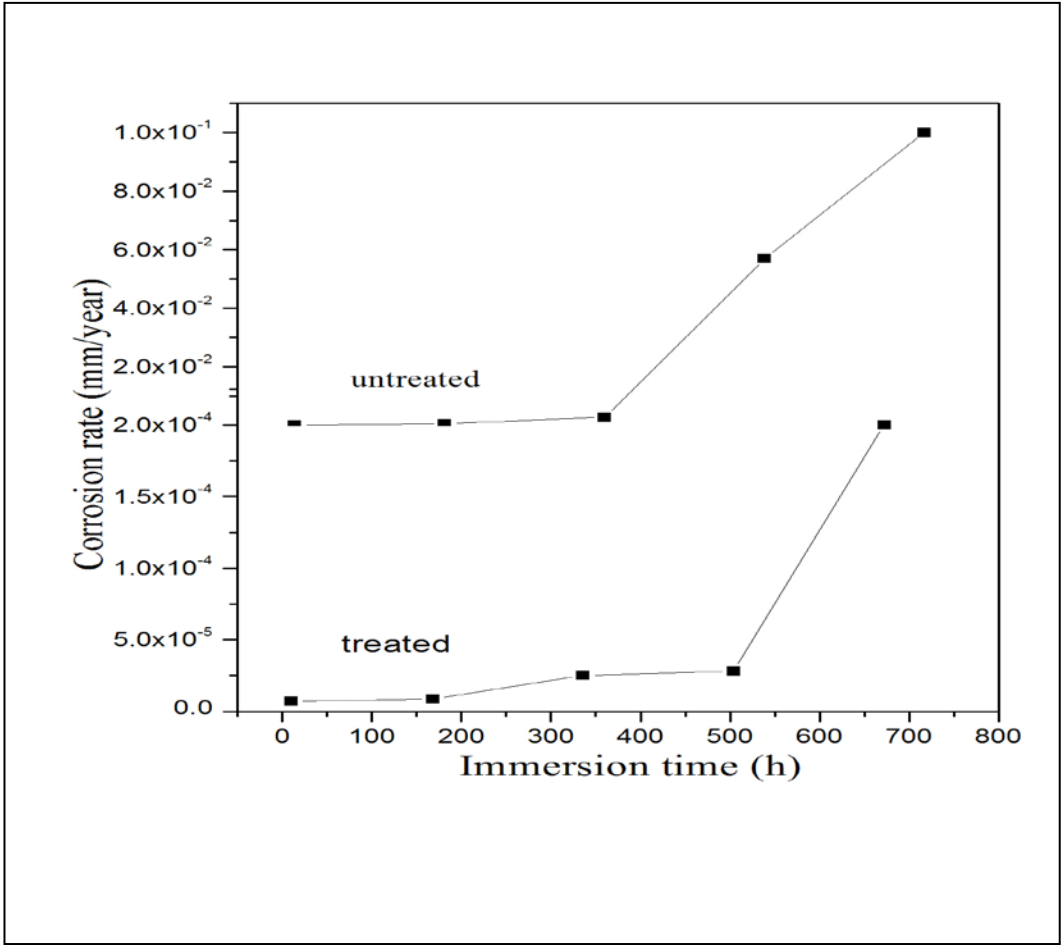


Fig.7 The relationship between the corrosion rate and immersion time for treated and untreated TiNi shape memory alloys

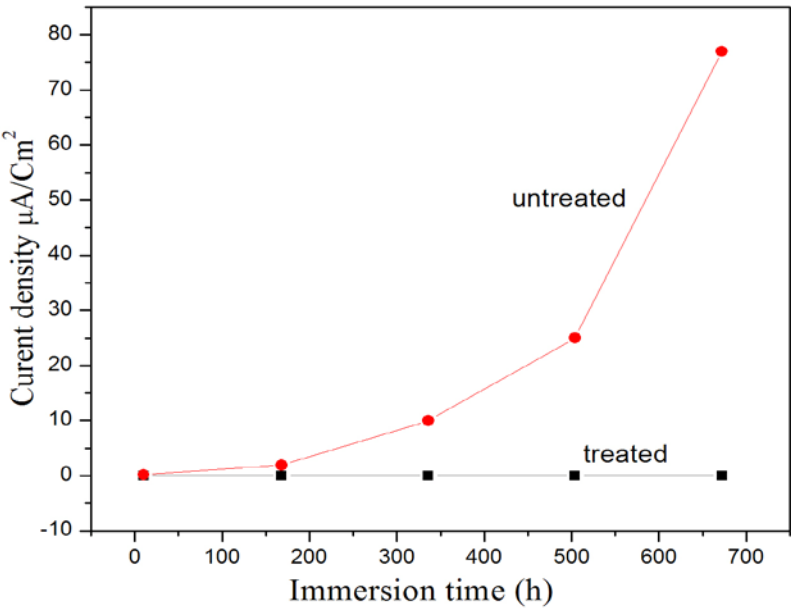


Fig.8 The relationship between the current density and immersion time for treated and untreated TiNi shape memory alloys

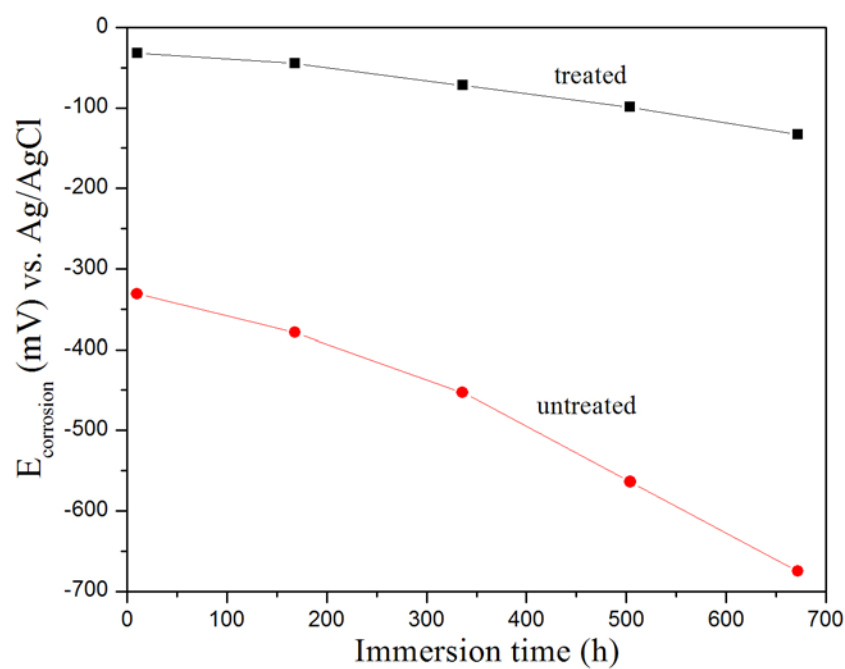


Fig.9 The relationship between the open circuit potential and immersion time for treated and untreated TiNi shape memory alloys

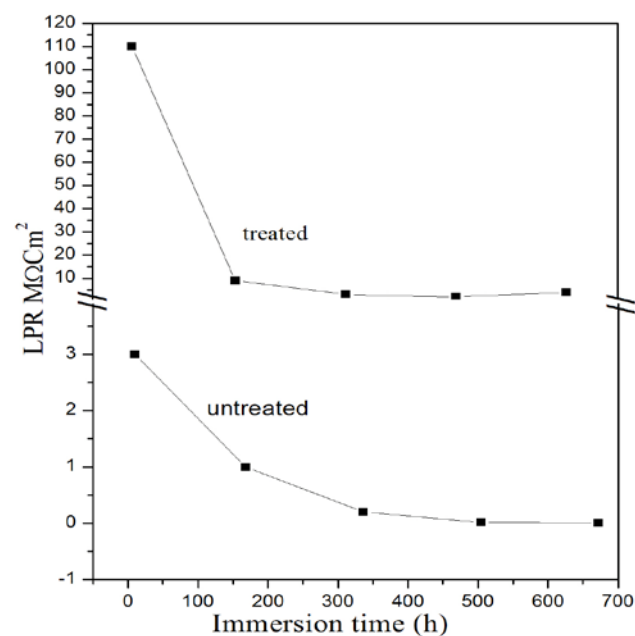


Fig.10 The relationship between linear polarization resistance and immersion time for treated and untreated TiNi shape memory alloys

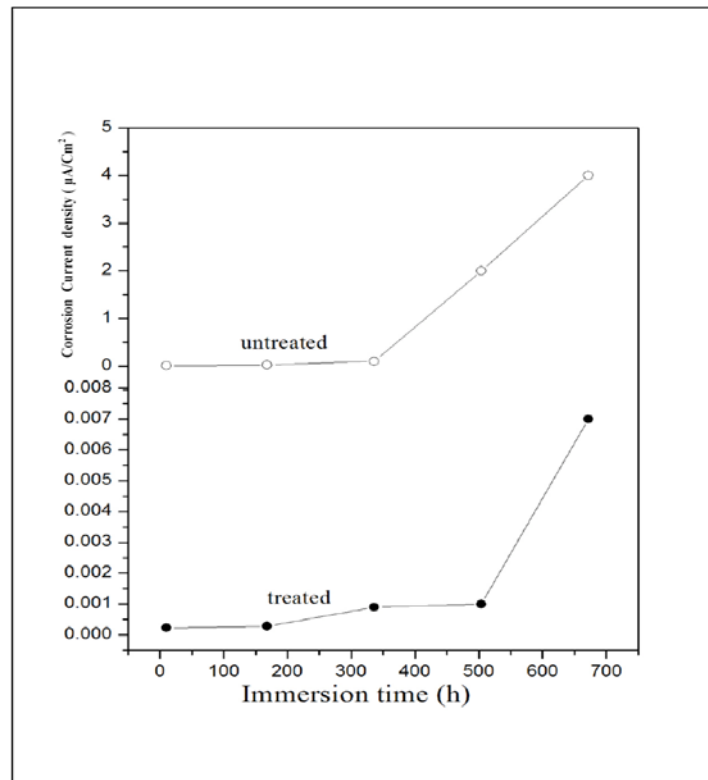


Fig.11 The relationship between the corrosion current density and immersion time for treated and untreated TiNi shape memory alloys

#### IV. CONCLUSIONS

Based on the obtained results, the following conclusions can be derived:

1. OM micrograph reveals that the color of nitrided NiTi shape memory alloy alters to golden yellow, demonstrating the formation of TiN phase.
2. Examination of structures reveals that the nitrided equiatomic NiTi shape memory alloy has excellent resistance to pitting and crevice corrosion.
3. X-ray diffractions of nitrided NiTi shape memory alloy demonstrates the predominance of new phases TiN and Ti<sub>2</sub>Ni phases and disappearance of the phase of B19' martensite (NiTi).
4. A little increase in microhardness using ICRFP is observed, which may be attributed to the small thickness of the hard TiN layer.
5. The enhanced corrosion resistance of nitrided samples is due to the formation of TiN layer.
6. The beneficial effect of nitrogen in improving the corrosion resistance of nitrided samples is due to the formation of a stable and insoluble oxide layer that has reduced ions diffusion.
7. The produced hard TiN layer can serve as a protective layer for improving load bearing capacity; effectively reducing the coefficient of friction; and thus providing good tribological behavior.
8. The excellent tribological property of nitrided TiNi shape memory alloy may be attributed to smooth surface.
9. Generally, the obtained results indicate that Rf plasma nitriding is a promising method to improve the tribological properties of TiNi shape memory alloy.

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