WEAR PROPERTIES OF NiTi SHAPE MEMORY ALLOY AFTER NITROGEN-BASED PLASMA TREATMENTS

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Abstract.
The NiTi shape memory alloys (SMA) is a promising material with applications in several areas due its good mechanical properties, shape memory effect and superelasticity. The samples are produced by the SMA / ITA group by Electron Beam Melting (EBM) process. This work aims to improve the wear resistance of this alloy using Nitrogen Plasma Based Ion Implantation (PBII) technique. PBII at various temperatures (400°C to 770°C), for 120 to 360 minutes with 16kV high voltage pulses (repetition rate of 200Hz, pulse length of 30 to 40 µs). The wear behaviour of such surface layers are measured and compared to the untreated NiTi. Measurements of dry friction coefficient were accomplished in a Pin on disc test. The surfaces were analysed by White Light Interferometry (WLI). The average friction coefficient of the reference sample is around 0.9. The best results are obtained with the sample treated at 550°C, during 360 minutes and with the one treated at 770°C, during 120 minutes. Both present very small wear rate and volume loss close to zero. Their friction coefficients decreased 67% compared to initial value what means a great improvement in wear resistance.

Keywords*: NiTi, shape memory alloy, Nitrogen- Based Plasma Ion Implantation, wear behavior*

1. INTRODUCTION

The NiTi shape memory alloys (SMA) is a promising material that is widely used in several areas such as aerospace, nuclear, automotive, robotics and medical applications thanks to its mechanical properties, its shape memory effect and its superelasticity (Otubo et al, 1997). This material has specific mechanical properties such as shape recovery when deformed beyond its elastic limit, either by heating (shape memory effect) or by applied load release (pseudoelastic effect) (Otubo et al, 2003) and (Otubo et al, 2006).

Nitrogen Plasma Based Ion Implantation (PBII) is a usual method for surface modification to improve the surface mechanical properties (Fouquet et al. 2004), to reduce the friction coefficient and to increase the wear resistance of materials (Mändl et al, 2006), (Liu et al, 2007) and (Levintant-Zayonts and Kucharski, 2009). Ion implantation can induce large residual compressive stresses in the surface and this can protect against wear (Silva et al, 2005), (Silva et al, 2007), (Mello et al, 2007) and (Pichon et al, 2010). PBII is an advanced technique that allows three-dimensional ion implantation in complex shape work-pieces, with no dimensional change of treated components and no film formation, avoiding delamination (Conrad et al, 1987) and (Ueda et al, 2003). In this work, samples of NiTi SMA were treated at high temperatures (400°C to 770°C) with 16kV high voltage pulses aiming to evaluate the wear resistance of this alloy.

2. EXPERIMENTAL PROCEDURES

The NiTi alloys have been produced by the Otubo's Group from ITA using two processes: Vacuum Induction Melting (VIM) and Electron Beam Melting (EBM). The alloy used in this work has the composition Ti50.63at%Ni and was produced by EBM (Otubo et al, 2003), hot rolled down to 15 mm in diameter bars. From the 15 mm diameter bar they were taken 2mm thick samples cut in low speed diamond saw. Then they were automatically ground, polished and ultrasonically cleaned in acetone bath.

The contamination by carbon is completely eliminated since melting is done in a water-cooled copper crucible; the contamination by oxygen is minimized thanks to operation in high vacuum (Otubo and Antunes 2010). The carbon contamination was only 0.016wt% compared to usual 0.05wt% of VIM process and the oxygen contamination was 0.07wt%.

Nitrogen PBII experiments were performed in the TAPIIR set-up (Thermally Assisted Plasma Ion Implantation Reactor), whose scheme is shown in figure 1 and which was already described in details (Marot et al.2002; Pichon et al. 2010).

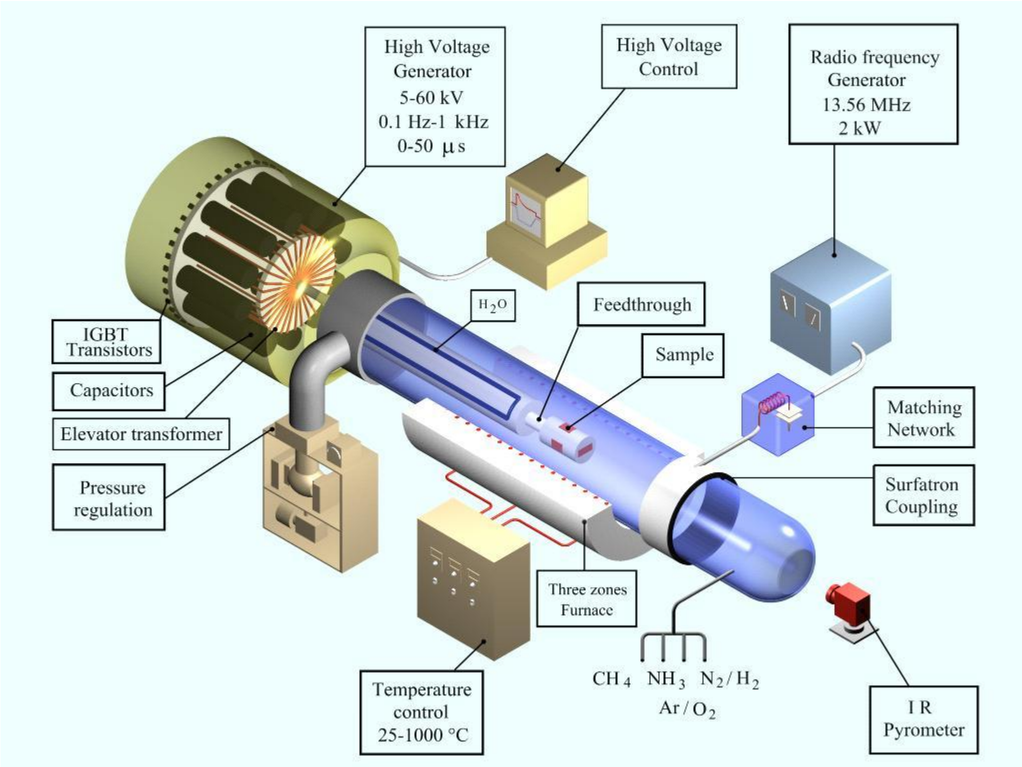


Figure 1. Schematic diagram of TAPIIR reactor

The specimens were treated at 16 kV and samples temperature varying from 400°C to 770°C, during 120 or 360 minutes as presented in Table 1. An additional heating under vacuum (base pressure about 10^{-4} Pa) was performed for 60 minutes with the external furnace surrounding the quartz tube reactor. The working temperature is reached with the additional energy brought by the plasma excitation and, most of all, by the ions implantation. It becomes stable after less than 20 min of PBII operating and is monitored by a thermocouple attached just below the samples. The PBII high voltage pulses frequency and length were adjusted to maintain the desired operating temperature. The atomic nitrogen dose implanted in the sample was calculated from the total current measurement, by taking into account only N_2^+ ions and a secondary electronic emission coefficient of 4. After the treatment, the samples are allowed to cool under vacuum down to room temperature.

Table 1. Experimental conditions for nitrogen PBII treatments of NiTi SMA.

Sample	Frequency (Hz)	Pulse (µs)	Temperature (°C)	Time (min)	Estimated dose (N /cm²)
1	100	32	400 ± 20	120	6.40E17
2	500	32 - 39	550 ± 15	120	1.70E18
3	500	32 - 39	550 ± 20	360	5.00E18
4	500	35	770 ± 5	120	7.19E17

The wear tests were performed on samples untreated and treated by nitrogen PBII, using a rotating pin-on-disc Tribotester TB Tribotechnic, with applied load of 2.0 N, 30 mm/s of linear speed, 3.0 mm of wear track radius, ~2,000 revolutions (40 m), at room temperature, in air and with a ruby ball of 6 mm of diameter as counterpart. The wear scares and the warn profiles were observed by White Light Interferometry (WLI) with a Talysurf CCI 6000 3D optical profiler, operating with Mireau interference objectives and white light source. The investigated areas were 900X900 µm^2 (with X20 objective), with lateral resolution lower than 1 µm and expected vertical resolution of about

0.1 nm. Registered and stitched images were numerically processed using Talymap software V4.1 thus providing 3D profiles of large areas. Disk volume loss V_p and wear rate K were calculated according to equations (1) and (2) respectively (ASTM G-99 standard):

$$V_p = 2\pi R\left[r^2 \sin^{-1}\left(\frac{d}{2r}\right) - \left(\frac{d}{4}\right)\left(4r^2 - d^2\right)^{1/2}\right] \quad (1)$$

Where: *R* is the wear track radius, *d* is the wear track width and *r* is the pin radius.

$$K = \frac{V_p}{PL} \quad (2)$$

Where: *P* is the distance in meters and *L* is the applied load.

3. RESULTS AND DISCUSSIONS

The evolutions of the friction coefficient during the wear tests are shown in figure 2. The average friction coefficient of the reference sample lies around 0.9 (figure 2(a)). With the sample treated at 400°C during 120 minutes, the coefficient is around 0.2 in the beginning of the test, increasing gradually within the first 100 cycles, as shown in figure 2(b). Then it suddenly increases to 0.8, probably when the modified layer is getting worn. In the figures 2(c), concerning the sample treated at 550°C during 120 minutes, the friction coefficient has a similar behavior: it is around 0.25 - 0.3 in the first 450 cycles and it then quickly reaches a value of about 0.8, increasing slightly until 1,000 cycles up to 0.9. However the evolution of the friction coefficient is noisier compared to the reference and 400°C treated samples.

When treated during 360 minutes at 550°C, the coefficient is stable around 0.25 until 750 cycles and then slowly increasing to reach the reference value of about 0.9. The noise is increasing too. The sample treated at higher temperature (770°C) exhibits a similar behavior, maybe with a lower noise level. The low friction coefficient value, kept for a large number of cycles, means a significant improvement in the wear properties for these samples treated for a longer time or at a higher temperature.

From the above results, it can clearly seen that the higher the implantation temperature or longer the implantation time, higher is the number of low friction cycle. Those results can be corroborated with 3D wear track images and materials loss as shown below.

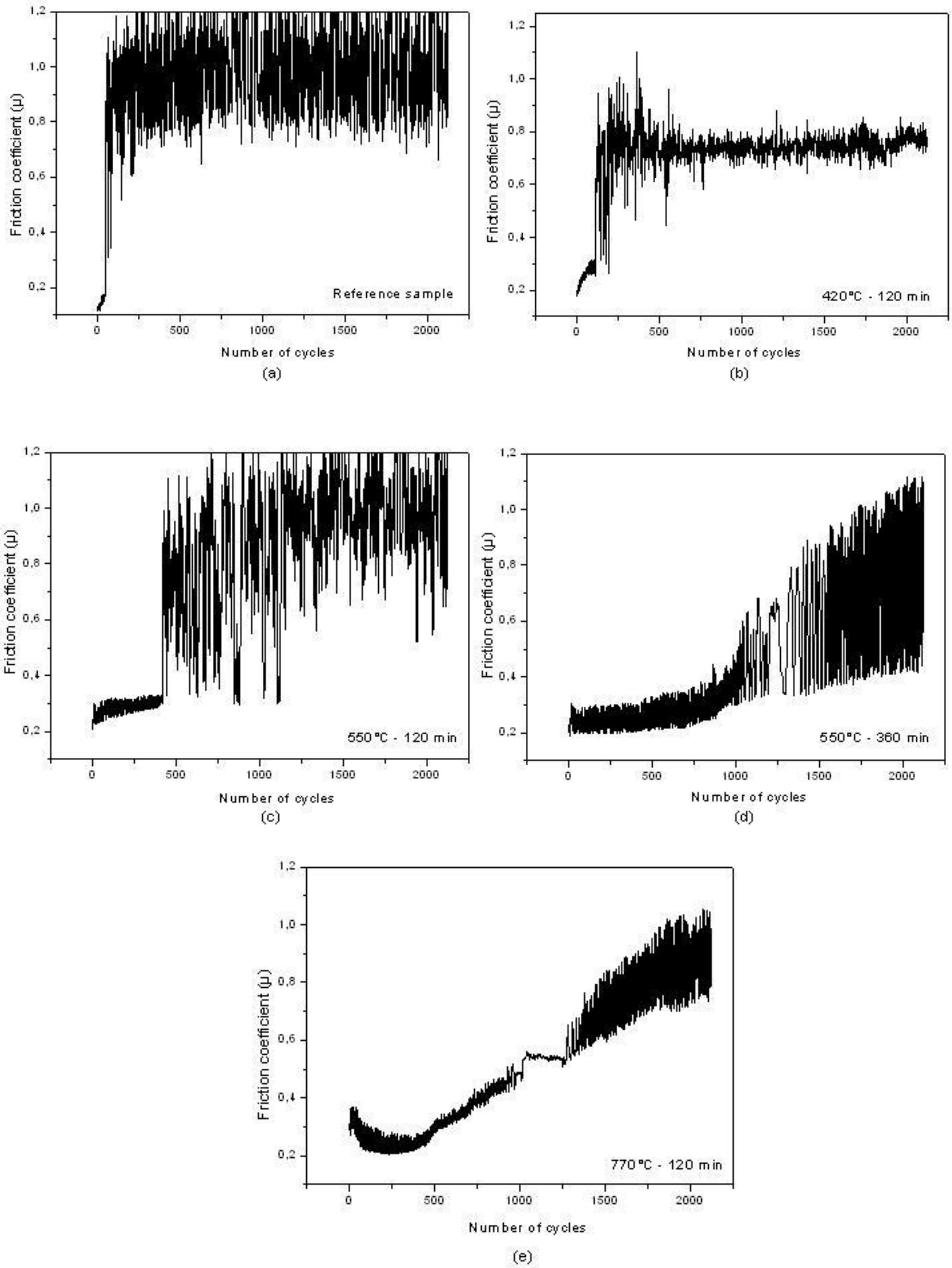


Figure 2. Friction coefficient of NiTi samples: (a) untreated (reference sample); treated by nitrogen PBII (b) 400°C, 120min; (c) 550°C, 120min; (d) 550°C, 360min; (e) 770°C, 120min.

The 3D images of wear tracks are shown in figure 3. The samples untreated, treated at 420°C, 120min, and treated at 550°C, 120min (figures 3(a), (b) and (c) respectively) present an important and similar wear. The material has low wear resistance, according to the conditions adopted in the wear test. As suggested by the noise level in the friction coefficients evolution during the test, presence of debris and scratches in the wear track can be observed. It is an indication of a very thin hard layer, either obtained by natural oxide passivation or by the PBII treatment. This layer, with a low friction coefficient, can protect the material only for few hundreds of cycles but it is finally destroyed likely because of its too low thickness. The created hard material debris are then involved in a 3 bodies wear mechanism, detrimental to the wear rate, and they may be responsible of the high noise observed in the friction coefficient evolution. However the hard material debris are small enough (i.e. the nitrided layer is thin enough) to not induce a worse wear than with the untreated sample.

In the figure 3(d) and 3(e) obtained with the samples treated with a longer duration (550°C-360 min) or a higher temperature (770°C – 120 min), the scars width and depth are about 10 times smaller. The combination of high temperature and/or long time makes the treatment more efficient, increasing the thickness of the surface nitrided layer with a lower friction coefficient and consequently improving the wear resistance for a longer time.

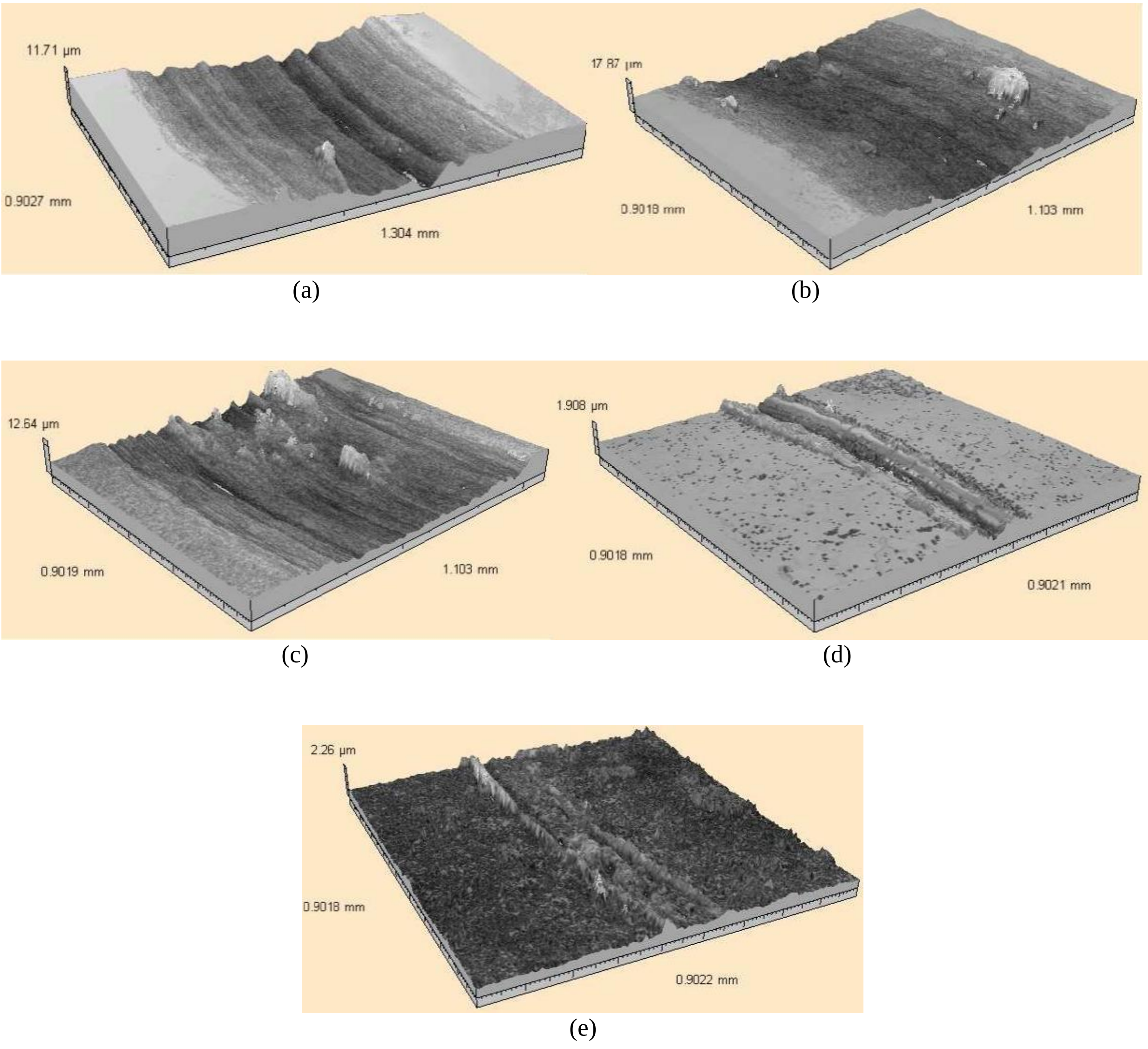
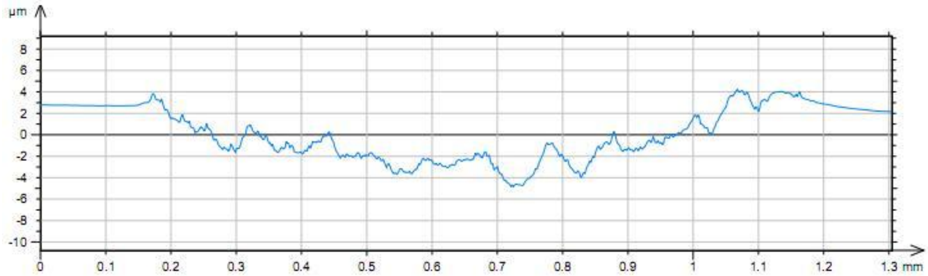
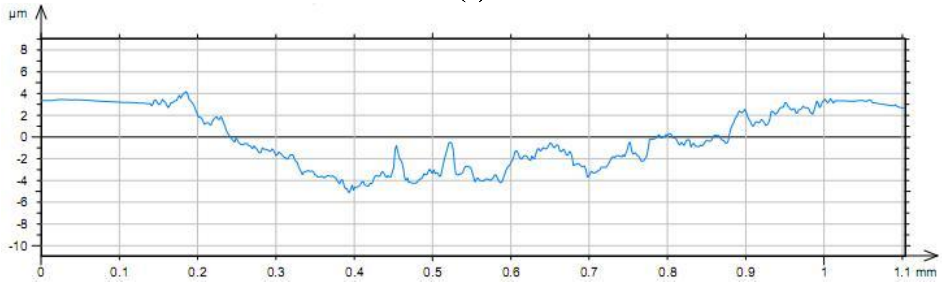


Figure 3. 3D representation of wear tracks of NiTi samples: (a) untreated (reference sample); treated by nitrogen PBII (b) 400°C, 120min; (c) 550°C, 120min; (d) 550°C, 360min; (e) 770°C, 120min.

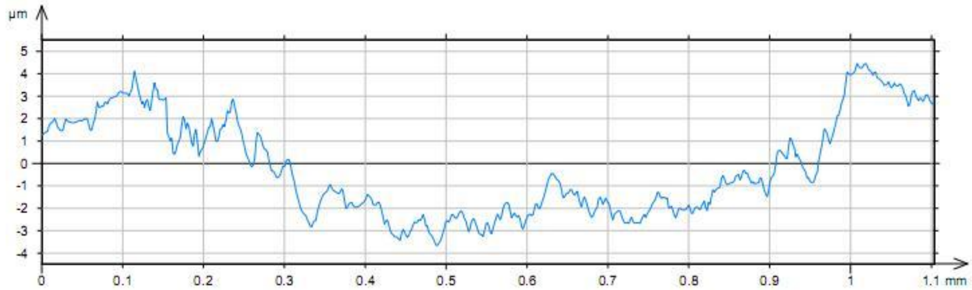
The analyses of tracks profiles (figure 4) show the decrease of depth and width of the wear tracks with the increase of treatment time and the increase of temperature. The volume loss and wear rate are obtained through the equations (1) and (2) and they are depicted in Table 2. The widths and heights shown in figures 4(a), 4(b) and 4(c) are similar, then, their volume loss and wear rates are in similar range of value. A significant decrease of worm volume was observed with the samples treated for longer time (550°C, 360min) and at higher temperature (770°C, 120min). This is clearly visible in their wear tracks presented in figures 4(d) and 4(e), respectively.



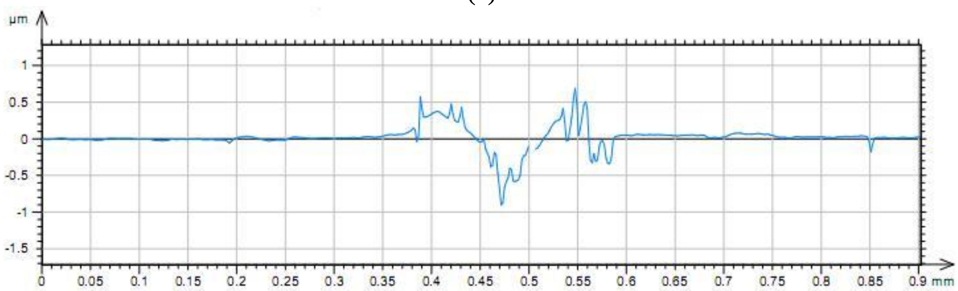
(a)



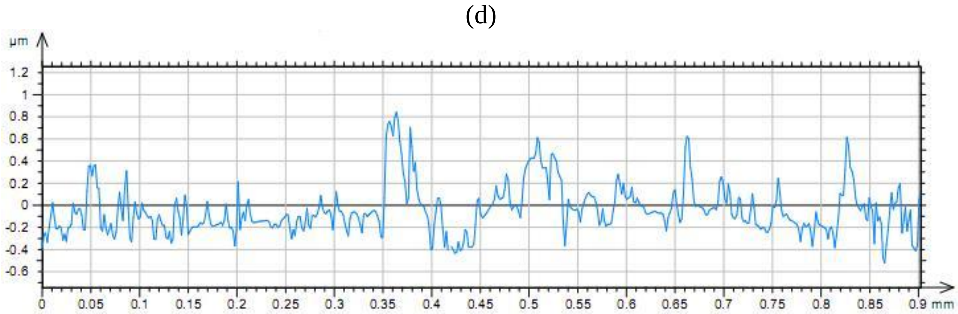
(b)



(c)



(d)



(e)

Figure 4. Profiles of wear scare of NiTi samples (a) untreated (reference sample); treated by nitrogen PBII (b) 420°C, 120min; (c) 550°C, 120min; (d) 550°C, 320min; (e) 770°C, 120min. Please note the different scales.

The surface roughness was measured by WLI (Table 2). It is found to increase with the treatment duration and temperature, likely because of plastic mechanisms induced by the TiN growth and because of the ion sputtering. It can be seen in the figure 4(e) that the low wear rate and the higher roughness makes the wear track almost invisible on the sample treated at 770°C-120min.

Table 2. Roughness, volume loss and wear rates of NiTi SMA of untreated and treated samples, by nitrogen PBII.

Treatment conditions	Rms roughness (nm)	Volume loss (mm^3)	Wear rate (10^{-3} mm^3 /N.m)
Reference sample	17	0.53	6.63
440°C, 120 min	55	0.38	4.75
550°C, 120 min	44	0.48	6.00
550°C, 320 min	50	$2.50X10^{-3}$	0.03
770°C, 120 min	83	$1.89X10^{-3}$	0.02

Summarizing, the above results of friction coefficient, 3 D images and volume loss/wear rate clearly show the efficiency of nitrogen PBII process to improve the tribological properties of NiTi shape memory alloys. We can't compare these results of those obtained by (Mändl et al, 2006) and (Liu et al, 2007), because they used different treatments conditions. Mändl et al implanted oxygen and Liu et al treated the alloy in different temperatures conditions.

4. CONCLUSION

PBII is an attractive surface modification method for the improvement of wear resistance of NiTi alloys, extending their use to tribological applications. Through the Pin-on-disc wear test it is possible to confirm the decrease of friction coefficient of nitrogen implanted NiTi compared to the untreated one, as well as the decrease of wear rate. Both decrease with the time and temperature of treatment. With PBII treatment, the effect of implantation is added to the diffusion, making the process more efficient in shorter time. The increase of wear resistance is related to the thickness of the titanium nitride formed at the surface. The major improvements are obtained with the sample treated at 770°C during 120 minutes, which had its friction coefficient reduced from 0.9 to 0.3 and a large decrease of volume loss, that is, very close to zero.

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