Properties of Carbonitrided Layer Formed on TiNbSn Shape Memory Alloy

Moataz H. Ata[1], F. M. El-Hossary[2] and A. M. Abd El-Rahman[3]

***Abstract*—** The aim of this study to improve the mechanical and tribological properties of TiNbSn shape memory alloy (SMA) by rf plasma carbonitriding for using in in a bio-medical implementation. The treatment process was proceed at low working gas pressure of 0.075 mbar in the nitrogen-acetylene gaseous mixture to produce a superficial carbonitrided layer. The rf inductively coupled were used to treat samples at different plasma processing power from 300 to 500 W and for a fixed time 15 minutes. The microstructure and properties such as mechanical and tribo-logical of the untreated and treated TiNbSn samples were inspected. The surface hardness is improved by rf plasma carbonitriding to a maximum of 491 HV for plasma-processing power of 400W, and the friction coefficient decrease to 0.463 for the sample treated at 400 W.

***Keywords*—** Plasma Carbonitriding, TiNbSn, Wear, Hardness, SMA.

I. Introduction

Nowadays, titanium and its alloys are utilized for industrial, aerospace, and medical applications. Among them, near equiatomic NiTi alloy is one of the most interesting materials owing to their unparalleled shape memory and superelasticity demeanor, and good biocompatibility [1-3]. However, the Ni hypersensitivity and toxicity of Ni have been indicated in Ti-Ni alloys [4]. For this reason, it was necessary to develop the Ni-Ti shape memory alloys with small amount of Ni or Ni free Ti-based SMAs is robustly demand [5]. Ti–Nb based alloys are favourable candidates to substitute Nitinol, especially in biomedical applications [6]. Science the discovery of shape memory effect in Ti-Nb alloys in 1970s [7], a large scale of research is being proceed on these alloys for biomedical applications [8-11]. Ti–Nb based alloys are used for biomedical applications because of its outstanding biocompatibility, low elastic modulus [12, 13], and good shape memory effect [14]. In medical applications, the microstructure and surface properties of Ti-Nb play an important role [15, 16].

Different types of plasma surface treatment techniques are investigated to improve the mechanical performance and to increase the service life of these alloys in different applications [9]. Among these types, rf plasma carbonitriding with nitrogen/acetylene gaseous mixture has been used before for surface modification of AISI 321 grade [17-19]. It has been able to realize an anticorrosive and wear-resistant superficial top layer with low friction coefficient [17, 20].

The principle advantages of plasma carbonitriding method are decreased process period; the ability to treat complex shape parts; and the disposal of unfavorable effects upon the surface smoothness of the treated parts. Moreover, the layers fabricated by this method are more resistant to wear and fatigue and show better plasticity properties [21, 22].

This work is conducted to fabricate a carbonitrided layer into the top of Ti-Nb-Sn substrate using RF plasma treatment, So as to get better tribo-logical and mechanical realization to reduce the price of orthopedic implants. The properties and the characteristics of the TiNbSn treated samples are estimated using X-ray diffraction (XRD), optical microscopy, microhardness tester, surface profile, oscillating ball-on-disk tribometer

II. Experimental Work

A. Sample Treatment

Ti-Nb-Sn shape memory alloy substrates with dimensions of 10 mm × 5 mm × 3 mm were used in this study. The chemical composition of these SMA is (84.35 at.% Ti – 11.66 at.% Nb and 3.99 at.% Sn). The substrates were polished mechanically and then cleaned ultrasonically in acetone, them into the plasma reactor tube. The samples were carbo-nitrided using radio frequency (RF) plasma inductively coupled operated in continuous mode. Details of the system was used somewhere else [23, 24].

In summarize, the RF plasma method is included in a quartz reactor tube with 500 mm length and 41.5 mm diameter and it was evacuated to 1.0 × 10-2 mbar base pressure by a two-stage rotary pump. The Ti-Nb-Sn samples were centered in the RF coil on a supported bar which is fixed on a water-cooled copper sample holder. The carbo-nitrided process was performed using a gas mixture containing 90% N2 and 10% C2H2, and the gas flow rates were adjusted to establish a total gas pressure of 7.5 × 10-2 mbar, as measured by a capacitance manometer. The induction copper coil, energized by an RF power generator model HFS 2500 D at 13.65 MHz via a tunable matching network, generated the discharge. The

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samples were treated at a different plasma- processing power 300 W, 400 W and 500 W at processing time of 15 minutes. After the carbo-nitrided process, the samples were allowed to cool slowly in the evacuated reactor plasma tube.

B. Sample Characterization and Testing

Crystal structure of the Ti-Nb-Sn SMA samples after and before carbo-nitried was analyzed by X-ray diffraction using (Philips-PW1710 diffractometer) with Cu Kα radiation of λ = 1.541838 Å. The scans were obtained with a 0.02° step size in a range from 20° to 100°. The morphology of substrates surface after and before carbo-nitried was obtained by Olympus BX51 optical microscope. Vickers microhardness measurement was measured by a Leitz Durimet microhardness tester equipped with 25 mf static loads. The friction coefficient was utilized at 10 mm/s as a mean sliding speed with 1N normal load. A 3 mm tungsten carbide (WC) ball was used as counterpart material without lubrication at room temperature in air atmosphere with humidity of 35% - 40%. Wear measurements were conducted depending on ASTM G133-10 standard test method. Wear track were measured by Form Talysurf 50. The K = V/SF equation were used to obtain the rate of wear, where V is the wear volume in mm3, S is the total sliding distance in m and F is the applied load in N.

III. RESULTS AND DISCUSSION

A. X-Ray Analysis

The chemical composition of the TiNbSn SMA sample before carbo-nitride treatment has been identified with EDX elemental analysis and is observed to be Ti84Nb12Sn4. Crystal structure of the Ti-Nb-Sn SMA samples after and before carbo-nitried at different plasma-processing powers; 300, 400 and 500 W are presented in Fig. 1.

The patterns indicate that the main phases observed after acarbo-nitrided of the samples are five spectral lines appear at different angles □□□□ follow; 38.92o, 41.76o, 48.84o, 72.92o and 88.08o corresponded to NbTi4 (111), (Nb0.03Ti0.97)Sn3 (202), Ti6Sn5 (214), NbTi4 (220) and Ti3Sn (204) respectively. For the treated sample at plasma power of 300 W, the spectral line at angle of 38.92o is minimized and the rest four spectral lines found and appeared at the same angles as in the untreated blank sample. The XRD scanning of the treated sample at plasma power 300 W shows very small spectral lines for many phases such as; Sn3N4 (331) appeared at angle of 44.48o, NbN (311) at 70.12o and Nb2N3 (311) at 70.92o. These peaks may be attributed to that the carbo-nitriding process at the plasma power of 300 W is initiated and not as well at these conditions.

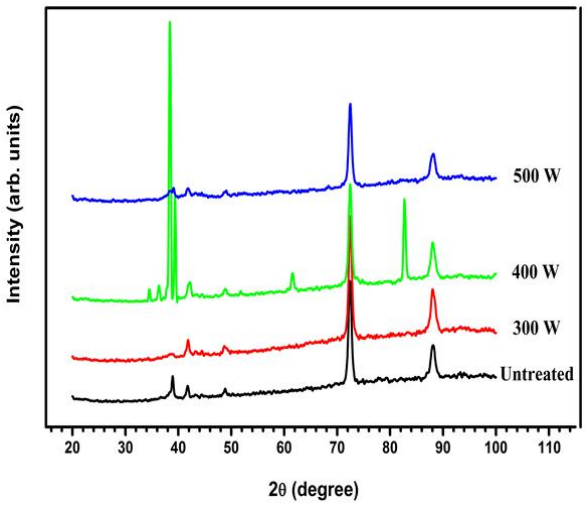

Fig. 1: The XRD patterns of the carbonitrided Ti84Nb12Sn4 at different plasma-processing power

The XRD pattern of the treated sample at plasma power of 400 W has spectral lines as in the untreated one except the spectral line at 38.42o is maximized compared with that of the untreated sample. In addition there are new phases appear at different angles such as at 34.52o is corresponding to NbN (111) phase, 36.34o corresponding to the phase of TiN (111), 40.04o to Nb4N3 (200) phase, 61.56o to Sn3N4 (531) and 82.73o to the phase of Nb4N3 (314). These new phases are attributed to that the nitriding process at the plasma power of 400 W is achieved as well at these conditions.

The XRD pattern of the treated sample at plasma power of 500 W much like the XRD pattern of the untreated sample. Very small peak is observed at 68.32o corresponding to the phase of Sn3N4 (533). This indicates that the nitriding process at the plasma power of 500 W is achieved but not well as in the case of 400 W at these conditions. The formation of NbN (111) and TiN (111) hard phases at a plasma power of 400 W are the reason for the superior mechanical and tribological properties of Ti84Nb12Sn4 carbo-nitrided [25]. According to Debye Scherrer, the mean crystallite size of the samples after carbo-nitrided treated can be determined from the X-ray diffraction patterns at different plasma power [26].

Figure 2 demonstrates the crystallite size of the untreated and treated samples compound at different plasma-processing power. One can observe from the figure that, the mean grain size increases from nearly 50 nm for the sample that was carbo-nitrided at plasma power of 300 W to approximately 90 nm for the sample that was carbo-nitrided at plasma-processing power of 500 W.

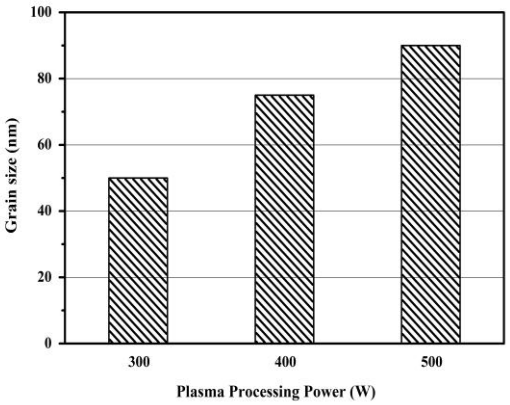

Fig. 2: Mean grain size of the carbonitrided Ti84Nb12Sn4 as a function of plasma-processing power

B. Layer Thickness

Figure 3 presents the carbo-nitrided layer thickness at different plasma-processing power. One can observe from the figure that, the layer thickness increases with increasing plasma power. The layer thickness increases from nearly 4 μm for the sample that was carbo-nitrided at a processing power of 300 W to approximately 8 μm for the sample that was carbo-nitrided at a processing power of 500 W.

C. Microhardness

Figure 4 presents the variation of the microhardness for the untreated and carbonitrided treated samples at different plasma power. One can notice from the figure that, the microhardness increases up to 491.3 HV as the plasma-processing power increases up to 400 W. This value represents 2.5-folds increase in microhardness in comparison with the untreated sample. The increase in microhardness is ascribed to the formation of NbN, TiN hard phases, and the high intensity of NbTi4 phase. Bendavid et al. [25] have achieved a significant improvement in the surface hardness due to the presence of NbN and TiN hard phases. The low hardness for the sample that was treated at a plasma-processing power of 500 W is ascribed to the low intensity of NbTi4, NbN and TiN phases. The expansion of nitride and carbide phases might block the formed microcracks in the treated layer. Therefore, the rate of nitrogen and carbon penetration decreases through these microcracks. Consequently, the concentration of nitrogen and carbon in the far depth region of the compound layer decreases and then reducing of microhardness will occur to reach the lower values [27].

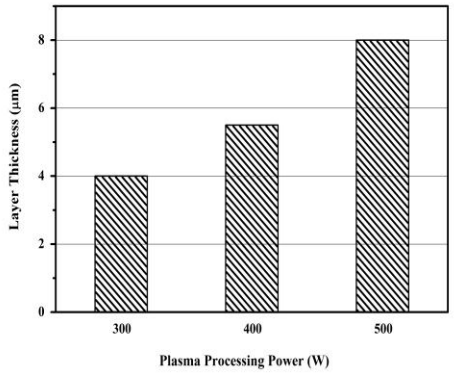

Fig. 3: Carbonitriding layer thickness at different plasma-processing power.

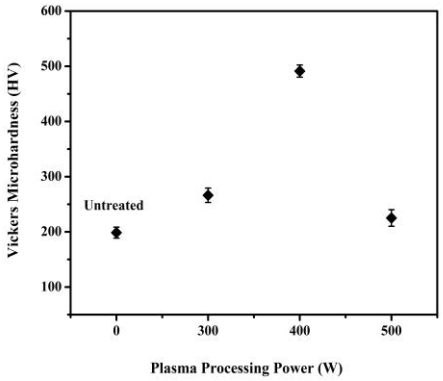

Fig. 4: Surface microhardness of the the carbonitrided Ti84Nb12Sn4 versus plasma processing power

D. Wear and Friction Measurements

Figure 5 shows the friction coefficient of the untreated and carbonitrided TiNbSn samples at different plasma power. From this figure one can monitor that, the friction coefficient for the carbonitrided samples decreases from nearly 0.557 for the untreated sample to nearly 0.463 for samples treated at 400 W, representing a reduction of 17%.

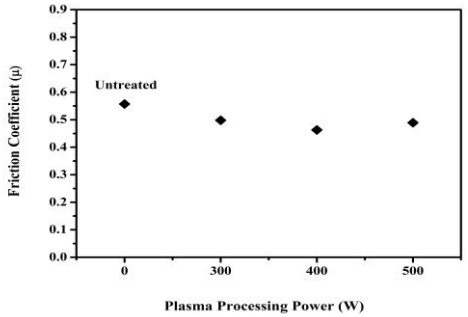

Fig. 5: Friction coefficient variation with plasma-processing power of untreated and carbonitrided SMA samples

The subsistence of a large volume fraction of nitrogen and carbon modulates the composition of the surface that accompanied by a lowering in coefficient of friction and rising in wear resistance.

Figure 6 and Figure 7 shows the optical micrographs and the wear track width of the untreated and carbonitrided samples at

different plasma-processing power. Generally, it has been noticed that the track width of carbonitrided samples is narrower than that of the untreated sample, demonstrating the augmentation in wear resistance for the carbonitrided samples. The high hardness of treated sample at 400 W due to the high intensity of $NbTi_4$ phase leads to decrease the wear track width and increase the wear resistance as shown in Fig. 6 and Fig. 7.

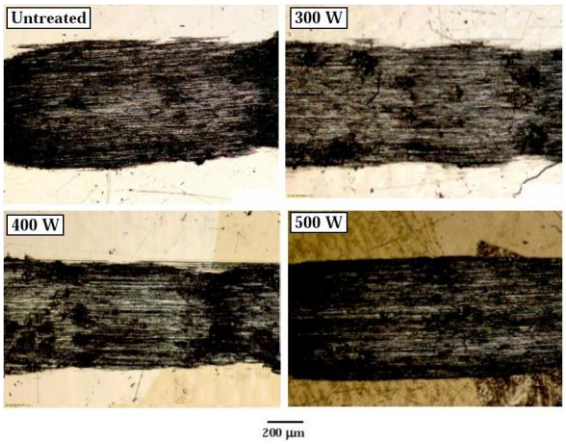

Fig. 6: Optical micrograph of wear tracks for the untreated and carbonitrided SMA samples at different plasma processing-power

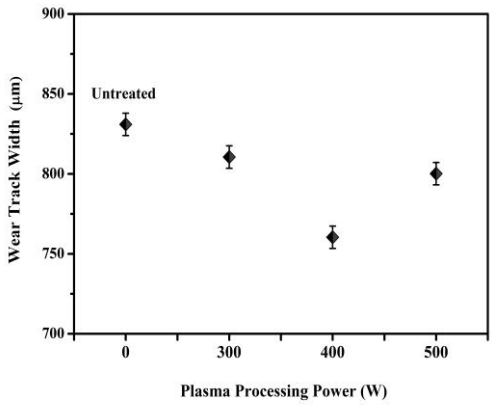

Fig. 7: Wear track width for the untreated and carbonitrided SMA samples at different plasma processing-power

Figure 8 displays the wear rate of the investigated TiNbSn samples at different plasma-processing power, where the wear rate is calculated as the wear area × track length/total sliding distance. One can expose from the figure that, the rate of wear decreases as the plasma power increases. The decrease in the wear rate is ascribed to the surface strengthening resulting from the formation of hard phases of NbTi4, NbN and TiN precipitates in the near-surface region of TiNbSn.

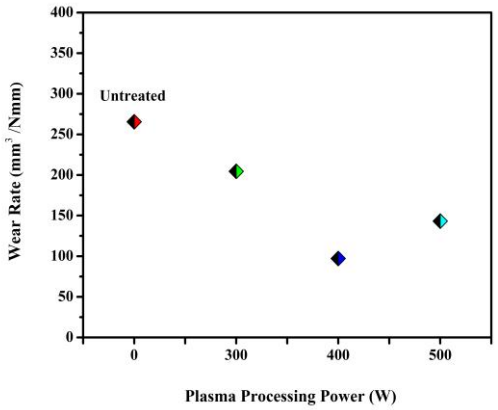

Fig. 8: The wear rate of the investigated carbonitrided SMA samples as a function of plasma-processing power

IV. CONCLUSION

Carbonitriding by RF plasma achieved a modified surface layer into TiNbSn SMA substrate with a layer thickness varied from 4 µm up to 8 µm. It has been found that the nitrogen/carbon solid solutions improve the surface hardness of the treated layer by more than 2.5 times compared to the untreated one. Moreover, the values of wear resistance for TiNbSn carbonitrided are improved compared to those for TiNbSn. The friction coefficient decreases from nearly 0.557 for the untreated sample to nearly 0.463 for Carbonitrided TiNbSn SMA sample.

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