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TECHNICAL NOTE

# Duplex Surface Treatment of AISI 1045 Steel via Plasma Nitriding of Titanized Layer

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*ABSTRACT*

In this study, surface of medium carbon steel (AISI 1045) was modified by titanizing followed by plasma nitriding. Titanizing was performed using pack cementation method, in a pack mixture of ferrotitanium, ammonium chloride and alumina, at 950 °C for 45 and 180 min. Plasma-nitriding was conducted at two temperatures of 530 and 550 °C for 5 h, in a gas mixture of $75N_2+25H_2$ (vol.%). The samples were characterized by scanning electron microscope (SEM), X-ray diffractometre (XRD), Vickers microhardness and pin-on-disk wear tests. The thickness of titanized layers was 8-10 µm, the thickness had no significant change after plasma nitriding. The duplex treated surface layers consisted of $Fe_4N$, TiN and TiCN phases. Lower titanizing time and higher plasma nitriding temperature provided superior wear resistance and hardness. The highest wear resistance and the lowest friction coefficient were achieved in the sample which was titanized for 45 min and then plasma nitrided at 550 °C , with 2130 HV microhardness.

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## 1. INTRODUCTION

Hard coating with nitride, carbide or carbonitride of transition metals is a common method of improving the wear resistance of ferrous materials [1]. In addition, carbonitrides and nitrides of transition metals, especially TiCN and TiN, have drown significant attentions [2, 3], because of their unique combination of properties such as high melting temperature, excellent hardness and wear resistance, high electrical and thermal conductivities, excellent biocompatibility, high hardness and good chemical stability [2-5], and are widely used in industrial applications such as moving mechanical components, cutting tools, and dies [2, 6, 7].

Although these coatings are commonly applied by physical vapor deposition (PVD) [5, 6, 8] and chemical vapor deposition (CVD) methods [7, 8], some surface treatment techniques can be combined or performed sequentially in industry to reduce fabrication expenses.There are several studies about duplex surface treatment, which involve successive metal diffusion and nitriding treatments [1, 9-12]. The techniques promote a hard superficial layer consisting of various nitrides and carbonitrides with high load bearing capacity [10].

Duplex titanizing treatment followed by nitriding is expected to form TiCN on the surface of medium carbon steel, since the duplex treatment provides the required titanium and nitrogen, furthermore the steel contributes to supply the necessary carbon. In the present study, medium carbon steel was treated by duplex treatment, which involved pack titanizing at 950 °C for different diffusion times of 45 and 180 min, followed by plasma nitriding at two nitriding temperatures of 530 and 550°C for 5 h. A carbon steel was selected, in order to avoid any interaction of alloying elements in the steel with titanizing and plasma nitriding treatments. Medium carbon content balances ductility and strength, and it is heat treatable; used for large parts, forging and automotive components. Microstructure, microhardness, friction coefficient and wear rate were evaluated and the results were discussed.

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## 2. MATERIALS METHOD

Cylindrical samples from medium carbon steel (AISI 1045) were cut to dimensions of 20 mm in diameter and 8 mm in height, and ground up to 2500 grid emery paper, polished, and cleaned in ethanol. The samples were titanized at 950°C for two diffusion times of 45 (Ti45) and 180 (Ti180) min, in a pack mixture of 40 wt.% ferrotitanium, 40 wt.% $Al_2O_3$ as inert filler, 15 wt.% $NH_4Cl$ as activator and 5 wt.% naphthalene as deoxidizing agent [13]. The titanized samples were then placed in a pulsed plasma chamber and primarily cleaned by hydrogen sputtering for 30 min at 3 mbar pressure. Plasma nitriding was performed in a gas mixture of $75N_2$+25 $H_2$ (%vol.) at 530 (PN530) and 550 °C (PN550) for 5 h at 4 mbar pressure.

The duplex treated samples were cross-sectioned, prepared, and etched in 3% nital for metallographic observations. The microstructures were studied using SEM equipped with energy dispersive X-ray spectroscope (EDS). Phase analyses of the surface layers were carried out by XRD (Bruker D8 advanced) with Cu kα (λ=1.54 Å, step = 0.05 and step time = 1s). Vickers microhardness test for each sample with MMT-7 buehler digital micro hardness was utilized using 0.1 kgf load. Three hardness tests were performed and the average values of them were reported.

Pin-on-disk wear test was conducted at normal load (F) of 7 N, sliding distance (S) of 500 m, sliding speed of 0.08 m/min, and using a tungsten carbide pin with tip diameter of 5 mm. The volume wear of samples (V, $mm^3$) was calculated according to ASTM G 99-05(2010) standard.

$$V = \frac{\pi\,(WearTrackRadius,\ mm)(TrackWidth,\ mm)^3}{6\,(PinSphereRadius,\ mm)} \quad (1)$$

The wear rate (W, $mm^3$/Nm) was obtained as:

$$W = {}^{V}/_{SF} \quad (2)$$

## 3. RESULTS AND DISCUSSION

Figure 1 shows the effect of titanizing time on the thickness of surface layer at 950°C treating temperature. The thickness of surface layer grows logarithmically by titanizing time. This means that the rate of titanium diffusion decreases by diffusion time, suggesting that the titanized layer acts as barrier for further titanium diffusion in the surface.

Figure 2 demonstrates SEM micrographs of the titanized layers before and after plasma nitriding. The superficial layer becomes slightly thicker by titanizing time, while post-plasma nitriding treatment has no significant effect on the layer thickening (see Table 1).

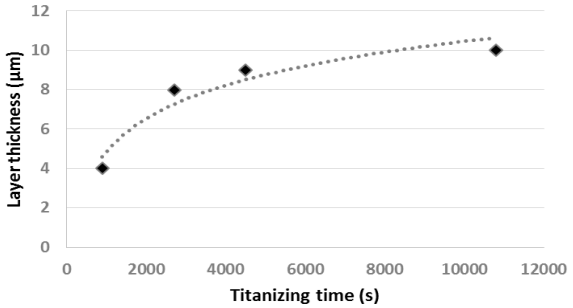


**Figure 1.** Layer thickness formed on steel as a function of treatment time at 950 °C .

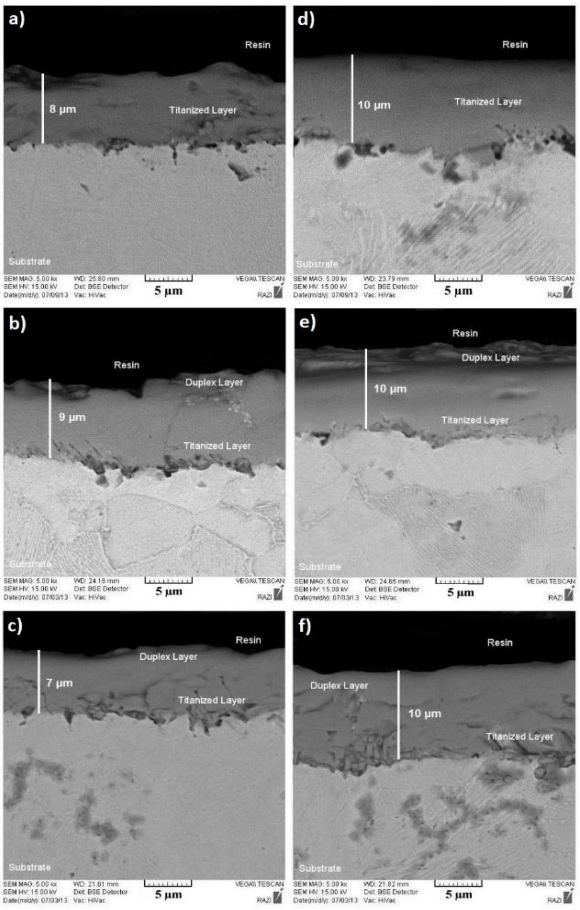


**Figure 2.** SEM micrographs of treated samples; (a) Ti45, (b) Ti45-PN530, (c) Ti45-PN550 (d) Ti180, (e) Ti180-PN530 and (f) Ti180-PN550.

The thickness even decreases in some cases, which was ascribed to sputtering effect of the high energy ions in plasma nitriding chamber [14]. Higher nitriding temperature increases sputtering rate instead of nitride precipitation [15]. This phenomenon provides a coarse surface and also partially removes the superficial layer [14].

**TABLE 1.** Thickness and surface microhardness of superficially treated samples

| Modifying type | Thickness (μm) | Micro hardness ($HV_{0.1}$) |
|---|---|---|
| Ti45 | 8 | 1520 |
| Ti180 | 10 | 1310 |
| Ti45-PN530 | 9 | 1980 |
| Ti45-PN550 | 7 | 2130 |
| Ti180-PN530 | 10 | 1410 |
| Ti180-PN550 | 10 | 1540 |

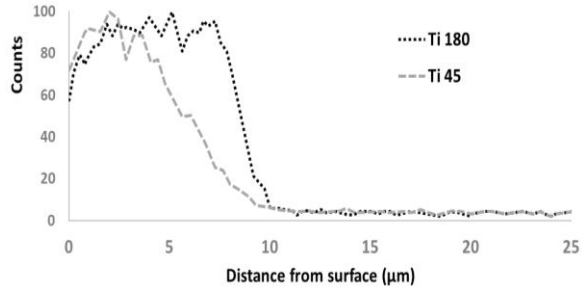


**Figure 3.** Titanium elemental line scans of cross-sectioned titanized samples for 45 and 180 min.

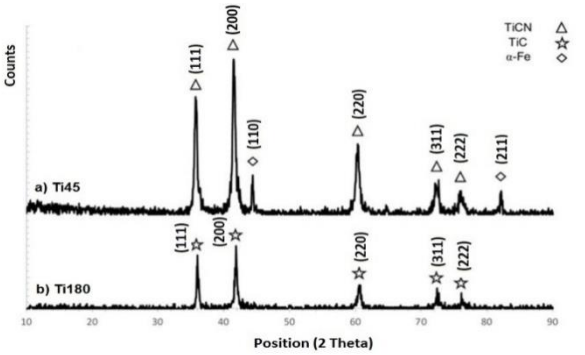


**Figure 4.** XRD patterns of titanized samples for (a) 45 and (b) 180 min.

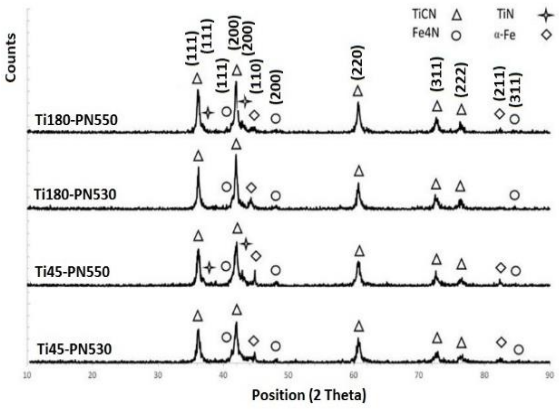


**Figure 5.** XRD patterns of duplex treated samples.

Titanium line scans for titanized samples (Ti45 and Ti180) are shown in Figure 3. The graphs demonstrate that the titanium content of Ti45 and Ti180 superficial layers remains nearly constant up to a maximum of 4 and 7.5 microns, respectively, and then they decline to about zero; diffusive layers of ~4 and ~2.5 micron thick present beneath the Ti-rich zone, respectively.

The surface layer in the Ti45 sample consists of $TiC_{0.7}N_{0.3}$ (TiCN) and α-Fe phases (Figure 4a). XRD patterns of titanized sample showed dependence of layer phases on processing time, as TiCN-like structure (Figure 4a) transforms to TiC-like structure (Figure 4b) by increasing titnizing time from 45 to 180 min. Similar results have been reported by Ustel et al. [13]. Source of the nitrogen component in the cementation environment is decomposition of the activator (ammonium chloride in this work), where the produced atomic nitrogen diffuses into the surface [13, 16, 17]. Content of nitrogen in the pack environment decreases by treating time, while carbon is continuously provided by substrate. Therefore nitrogen to carbon ratio decreases by the treating time, and in the long term, TiC-like structure replaces the TiCN-like structure.

XRD pattern of TiCN phase is close to that of TiN ($TiC_{0.3}N_{0.7}$) [13], it appears that $TiC_{0.3}N_{0.7}$ initially forms in the layer while it transforms to $TiC_{0.7}N_{0.3}$ at higher titanizing time; the $TiC_{0.7}N_{0.3}$ phase is stochiometrically closer to TiC [13]. As they have very close lattice constant values, the diffraction peaks of them at low angle such as (111) plane appears to be very close, so that it is not easy to be exactly distinguished. But at higher diffraction angles, the diffraction peaks can be clearly separated, e.g. (220) or (200) planes for TiN, TiCN and TiC phases [13, 18].

The replacement of TiC-like phase for nitride phase in the Ti180 sample makes a 200HV drop in the surface hardness (Table 1), in comparison to the hardness of the Ti45 sample, this is in accordance with other investigations [12, 19].

Plasma nitriding of titanized layer in the Ti45 sample leads to precipitation of $Fe_4N$ phase, while TiCN phase remains unchanged in the microstructure, as shown in the XRD pattern of Ti45-PN530 sample (Figure 5). Plasma nitriding of the Ti180 sample (Ti180-PN530) results in elimination of TiC phase and promotes formation of TiCN phase, beside some $Fe_4N$. TiN phase also appears in the XRD patterns at higher plasma nitriding of 550°C , as it is observable in both Ti45-PN550 and Ti180-PN550 samples. The results reveal that TiC becomes less stable upon plasma nitriding of the titanized layer.

Since TiN and TiC are isomorphous, a TiCN coating can have a variety of compositions, from carbon rich to nitrogen rich. Hence, its properties are very different during deposition [20]. The surface hardness measurements (Table 1) indicate that plasma nitriding

of the titanized layers increases the surface hardness, the increase in hardness is more significant when titanizing time is 45 min. Post-plasma nitriding of the Ti45 sample hardens the surface by 500-600 HV (as in Ti45-PN530 and Ti45-PN550 samples), which could be related to precipitation of some $Fe_4N$ and TiN phases and changes in TiCN composition [20] after plasma nitriding (Figures 4 and 5). The corresponding hardness increment after plasma nitriding of the Ti180 sample is about 100-200 HV, as in Ti180-PN530 and Ti180-PN550 samples (Table 1). It is also evident that the surface hardness becomes higher as nitriding temperature increases from 530 to 550 °C, which is probably due to increasing of the contents of nitrogen in the films and coarsened of the TiCN coating [21]. It should be noted that during microhardness measurements, the load must be high enough to produce an indentation easy to measure using an optical microscope. Usually this requirement extends the plastic deformation zone into the substrate, thus the microhardness result of thin layers could be a combination of surface layer and substrate microhardness [22].

The microhardness profiles of titanized and Ti-PN samples are illustrated in Figure 6, indicating that the highest level of microhardness profile relates to the Ti45-PN550 sample. Its hardness remains almost constatnt within ~3 micron of the superficial layer, while it drops rapidly to the substrate hardness. Microhardnss profiles of the other samples shows lower level of microhardnss profile, and their hardness profile reduces more gently to the substrate hardness.

Variations in wear rates correspond to the results of microhardness measurements (Table 1) and friction coefficients (Figure 7). Wear rate of the sample declines by increasing of its microharnesses. The highest wear resistance and the lowest friction coefficient belong to the Ti45-PN550 sample with the highest surface microhardness of 2130 HV (Table 1).

It is evident that at a given titanizing time, wear rate decreases by increasing plasma nitriding temperature. Therefore, lower titanizing time and higher plasma nitriding temperature provide superior wear resistance in the duplex treated samples. Similar discussions are applicable for the friction coefficients, as the wear rates and the friction coefficients demonstrate similar variations in this study. Diagram of the friction coefficient against wear distance for duplex treatment is illustrated in Figure 8.

SEM micrographs of the wear tracks on the duplex treated samples (Figure 9) are in good agreement with the wear rate results, whereas the Ti45-PN550 sample has the narrowest wear track of 770 µm, and the widest one is 937 µm relating to the Ti180-PN530 sample with the lowest wear resistance (Figure 7).

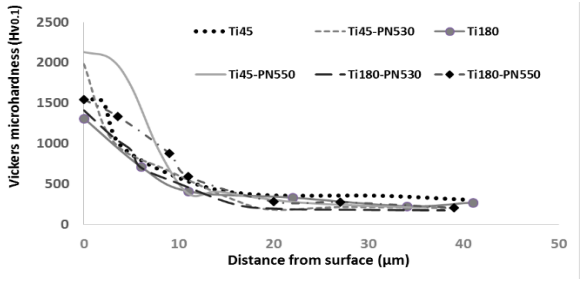


**Figure 6.** Depth profile of Vickers microhardness for different samples.

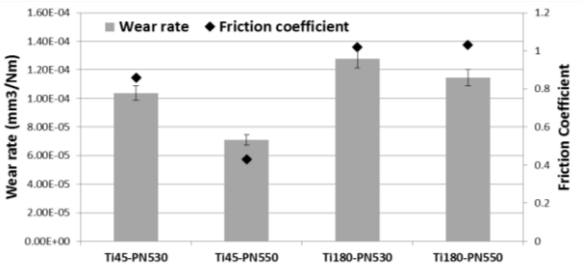


**Figure 7.** Wear rates and friction coefficients of duplex treated samples.

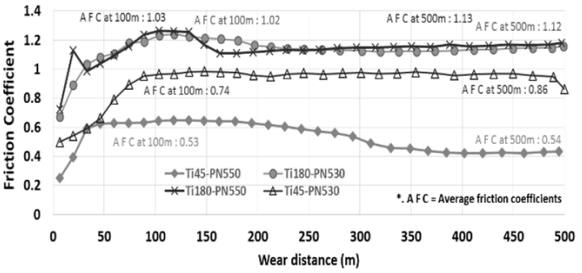


**Figure 8.** Diagram of the friction coefficient against wear distance.

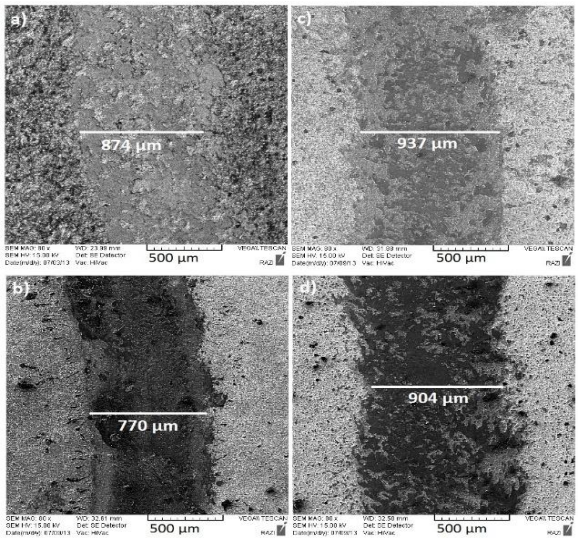


**Figure 9.** SEM micrographs of wear tracks on duplex treated samples; (a) Ti45-PN530, (b) Ti45-PN550, (c) Ti180-PN530 and (d) Ti180-PN550.

## 4. CONCLUSIONS

The stochastic duplex surface treatment was performed via post-plasma nitriding of titanized medium carbon steel (AISI 1045), the followings were concluded:

The thickness of surface layer varied logarithmically by titanizing time at titanizng temperature of 950°C .

Short titanizing time resulted in TiCN precipitation, while longer titanizing time provided TiC-like precipitation.

Plasma nitriding of titanized layer conducted to Fe4N precipitation beside TiCN, while TiC was eliminated from the superficial layer. Higher plasma nitriding temperature at 550°C promoted formation of TiN, in addition to the other phases.

Plasma nitriding of titanized steel hardened the surface layer in comparison to the titanized steel.

Lower titanizing time and higher plasma nitriding temperature provided superior surface microhardness, higher wear resistant and lower friction coefficient.

The optimum condition for duplex treatment in this study was achieved via titanizing at 950 °C for 45 min and post-plasma nitriding at 550 °C for 5 h, having the highest surface hardness of 2130 HV and the lowest wear rate and friction coefficient.

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# Duplex Surface Treatment of AISI 1045 Steel via Plasma Nitriding of Titanized Layer

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**چکیده**

در این تحقیق سطح فولاد کربن متوسط (AISI 1045) توسط فرایندهای تیتانیم دهی و به دنبال آن نیتروژن دهی پلاسمایی بهینه سازی شد. تیتانیم دهی با استفاده از روش سمنتاسیون جعبه ای با ترکیبی از فروتیتانیم، کلراید آمونیم و آلومینا در 950 درجه سانتی‌گراد برای مدت زمان 45 و 180 دقیقه انجام گرفت. نیتروژن دهی پلاسمایی نیز در دو دمای 530 و 550 درجه سانتی‌گراد برای 5 ساعت در ترکیب گازی 75 درصد نیتروژن و 25 درصد حجمی هیدروژن صورت پذیرفت. نمونه ها توسط میکروسکوپ الکترونی روبشی، پراش پرتوی ایکس، میکروسختی سنجی ویکرز و آزمایش سایش پین بروی دیسک مشخصه یابی شدند. ضخامت لایه های تیتانیم، 8–10 میکرون اندازه گیری شد، و پس از نیتروژن دهی پلاسمایی نیز تغییرات قابل توجهی حاصل نشد. لایه‌های سطحی تحت عملیات دومرحله ای شامل فازهای$Fe_4N$، TiNو TiCNبودند. زمان تیتانیم دهی کمتر و دمای نیتروژن دهی پلاسمایی بالاتر مقاومت به سایش و سختی بالاتری را فراهم آورد. بالاترین مقاومت به سایش و کمترین ضریب اصطکاک مربوط به نمونه ای با سختی 2130 میکروویکرز بود که برای 45 دقیقه تیتانیم دهی و سپس در 550 درجه سانتیگراد نیتروژن دهی پلاسمایی شده بود.

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