

Effects of the high temperature plasma immersion ion implantation (PIII) of nitrogen in AISI H13 steel

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Received: 10 December 2007 / Accepted: 30 May 2008 / Published online: 13 August 2008
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Abstract In this paper we report the effect of high temperature PIII of nitrogen on the chemical and physical properties of AISI H13 steel. The implantation of H13 steels was carried out at different temperatures ranging between 300 °C and 720 °C. After the treatment, the surface morphology was drastically changed as observed by SEM analysis. Nitrogen penetration depth reaching up to 12 µm was achieved at 620 °C and 720 °C. The maximum hardness of about 592 HV was obtained for the sample treated at 470 °C that is 17% higher than for untreated specimen. There was a decrease of the hardness values for temperatures above 470 °C. The same hardness behavior with the temperature was confirmed by nanoindentation testing. Although an enriched nitrogen layer was obtained, no evidence of nitride compounds was detected by XRD analyses. On the other hand, improvements of the H13 steel tribological properties and corrosion resistance were obtained. The wear tests were conducted by pin-on-disk tribometer (rotating mode). The wear volume decreased by factor of 4.5 compared to the standard tempered and annealed H13 steel and 2.6 times reduction of the coefficient of friction was achieved. The electrochemical measurements were performed in 3.5% NaCl solution,

pH = 6. Open circuit potential curves showed that the potentials are nobler for the PIII treated samples than for untreated specimen. In addition, the corrosion current density of the samples treated at 620 °C and 720 °C diminished to 3×10^{-8} A/cm².

Introduction

In the last decades, there has been an increasing demand for surface treatments that can modify the surface properties of different materials through enhancing their physical and chemical characteristics such as hardness, corrosion resistance, wear, coefficient of friction, etc. Among the existent processes, the plasma immersion ion implantation has attracted special attention due to its advantages such as treating of irregularly shaped samples, batch processing, low hardware cost, and also the possibility of conducting treatments at different temperatures [1]. In general, the PIII processing has been carried out using low temperatures among 200 °C and 450 °C [2–5] and only few works studied the effect of high temperature plasma implantation in some materials such as Ti alloys [6, 7], Si [8], and Mo [9].

Zagonel et al. [10, 11] investigated nitrogen ions implantation in H13 steel by conventional nitriding process. They examined the influence of the working temperature on H13 steel treated by pulsed plasma nitriding [11]. The authors found that the increase of process temperature causes hardness increasing, starting from ~8 GPa for untreated sample up to around 13.5 GPa for the sample treated at 510 °C. The layer with increased hardness reaches a depth of about ~100 µm for all nitrided samples treated at temperatures higher than 330 °C. In [11] the authors inferred that the relatively high hardness values obtained at

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the surface suggested the presence of ε -phase (hcp, Fe_{2-3}N). In another work, Zagonel et al. [10] reported the effect of hydrogen on the structural properties of H13 steel in low partial pressure oxygen atmosphere. The samples were implanted by using a broadband ion beam source, capable of producing ion beam constituted of different ions in adjustable proportions. Therefore in this study the hydrogen and nitrogen flux proportion were varied and others parameters were kept constant. The samples characterization shows that the hydrogen improves nitrogen retention at the material surface and influences the formed crystalline structures, α and ε phases.

PIII treatment appears as alternative method for surface processing instead of conventional plasma or gas nitriding generally used in industry. In previous works [3, 12–14], enriched nitrogen layer in H13 shock resistant steel to depth greater than 1 μm have been obtained by PIII treatment at temperatures lower than 500 °C. Hutchings et al. [12] demonstrated that PIII processing can produce duplex layers in 5% chromium tool steel (H13) whereby the nonequilibrium implanted layer is supported by a substantial diffusion zone. In our previous studies using H13 steel for PIII processing [3, 14], nitrogen penetration depth of more than 20 μm was achieved at 450 °C and hardness as high as 1340 HV (18.8 GPa) was obtained for 9 h PIII treatment due to enhanced nitrogen diffusion in the steel. Since the H13 tool steel is subjected to drastic mechanic and thermal shocks it is very important to improve its hardness, wear, and corrosion resistance through some surface treatment. Thus, the idea of present work is by increasing the treatment temperature above 450 °C and decreasing the treatment time with respect to [3, 14] to produce H13 steel with better properties for several industrial applications.

The effects of PIII surface modification of H13 steel at different temperatures ranging between 300 °C and 720 °C were investigated. The characterization of as-processed samples is performed using the following analyses: scanning electron microscopy (SEM), micro and nanoindentation tests, X-ray diffraction (XRD), glow discharge optic spectroscopy (GDOS), tribological measurements, and corrosion tests.

Experimental

AISI H13 (DIN X40CrMoV51) steel rod ($\varphi = 1.5$ cm) from Villares Metals, which had been tempered and annealed at 550–600 °C, was sliced into 3 mm thick disk samples and then polished to mirror-like finish. The samples were fixed onto a sample holder for PIII processing. PIII treatment was performed using the experimental vessel with a glow discharge plasma source for three-dimensional ion implantation

described elsewhere [15]. The novel parts of this system are a locally heated sample support (SS), and an electrical system to drive a coiled tungsten filament inserted inside the SS, isolated from the high voltage pulse applied to the holder. As described in the previous paper, we used the commercial RUP-4 device to pulse the SS at high negative voltages (nominal of 30 kV, 100 μs , and 1.1 kHz maximum). The filament floats with the high voltage pulse while a 110 V, 5 A a.c. power supply used to heat the SS up to 720 °C is kept on during the PIII treatment. Nitrogen was used as source gas for the plasma. The implantation parameters were as follows: pressure of 6.5×10^{-3} mbar, pulse width of 40 μs , pulse repetition rate of 400 Hz, treatment time of 3 h, and implantation voltage of 5 kV. The implantation treatment of H13 steels was carried out at different temperatures ranging from 300 °C to 720 °C. The samples temperature during the implantation was monitored by Raytek infrared pyrometer. The typical errors in pyrometer temperature measurements are about 15%. Before being taken out the PIII processed samples were cooled in the vacuum chamber for about 4 h. In the temperature range from 720 °C to 200 °C the cooling rate was approximately 400 °C/h. Below 200 °C our pyrometer does not operate so we were not able to evaluate the cooling rate. The morphology and microstructure of the samples were analyzed using a scanning electron microscope LEO 440. To expose the microstructure, cross sections of the samples were etched for 5 s in approximately 3% Nital solution and immediately rinsed in water, analytical alcohol and dried. The hardness profile of the samples was obtained using a microindenter from Future-Tech FM 700 and triboindenter from HYSITRON Incorporated, respectively. The glow discharge optical spectroscopy (GDOS) analysis was carried out using a LECO-GDS 750A equipment. This technique was used for determining nitrogen profiles of implanted H13 samples. The tribological measurements were conducted by CSEM-instrument pin-on-disk tribometer (rotating mode) followed by an assessment of the wear damage with microscopy. A universal photomicroscope ultraphot zeiss microscope evaluated the degree of wear as well as the track width. The equipment was operated at load of 5.0 N in environment with relative humidity of about 60%. Tungsten carbide (WC) pin with fixed linear velocity of 10 cm/s and the pin ratio of 3.0 mm was used.

The corrosion behavior of the samples was studied by electrochemical methods. The open circuit measurements and potentiodynamic polarization curves were obtained by means of an EG&G PAR 283 potentiostat using a conventional three-electrode glass cell. AISI H13 steel slices (cross section ~ 0.07 cm²) were employed as the working electrode. Two different sets of working electrodes, untreated and treated by PIII processing, were tested. The counter electrode was a graphite rod and a Ag/AgCl electrode served as reference electrode. All experiments were

conducted at room temperature ($\sim 25\text{ }^{\circ}\text{C}$). Polarization curves were acquired in 3.5% NaCl solution, pH = 6 and recorded in electropositive direction at a sweep rate of 0.33 mVs^{-1} , starting from the corrosion potential. The electrochemical measurements were performed in naturally aerated solutions.

Results and discussions

SEM, XRD, GDOS, hardness, and wear analyses

Figure 1 shows the surface morphology of untreated (Fig. 1a) and treated AISI H13 steel samples (Fig. 1b–c). SEM examination revealed that the surface morphology of the samples was significantly altered after PIII processing. The surface modification is more pronounced for the sample treated at the highest temperature ($T = 720\text{ }^{\circ}\text{C}$). It contains ball-like structures forming small agglomerates over entire surface while the samples treated at lower temperature ($T = 300\text{ }^{\circ}\text{C}$) do not show this feature, but only scratches originated from the polishing. This picture is possibly due to the coalescence of precipitates in H13 steel when submitted to PIII treatments at temperatures higher than $470\text{ }^{\circ}\text{C}$. The ball-like structures are probably associated with formation of the iron carbide (Fe_3C). It is characterized by small spheroidal particles dispersed in the $\alpha\text{-Fe}$ matrix for the tempered and quenched steel submitted to elevated temperatures ($\sim 720\text{ }^{\circ}\text{C}$) as cited in [16]. This assumption is in agreement with the X-ray results (Fig. 5) that show an intense $\alpha\text{-Fe}$ peak at 44.67° . This peak also corresponds to one of the three strongest peaks (022) of orthorhombic iron carbide in the powder diffraction files (PDF). The coalescence of precipitates in the H13 steel when submitted to high temperature treatment produces a hardness reduction as can be seen from the indentation results and described in [16]. Figure 2 shows the cross-section micrographies in the backscattered electron signal mode. There are no evidence of iron nitride precipitation (white layer) as generally observed in conventional plasma nitriding [11]. The arrows in Fig. 2 pointed out the sample surface. The martensite structure observed for the untreated and samples treated at lower temperature ($<470\text{ }^{\circ}\text{C}$) (Fig. 2a–b) was transformed in tempered martensite structure for the samples treated at $720\text{ }^{\circ}\text{C}$ (Fig. 2c). The last structure is characterized by small spheroidal particles dispersed in the $\alpha\text{-Fe}$ matrix as observed by other authors [16]. Figure 3 depicts the surface morphology after electrochemical corrosion of the standard and treated steel samples. Corrosion attack of the samples was carried out in 3.5% NaCl solution by applying one potential step from -0.8 up to 0.1 V . It can be seen that as the treatment temperature increases, the samples surface

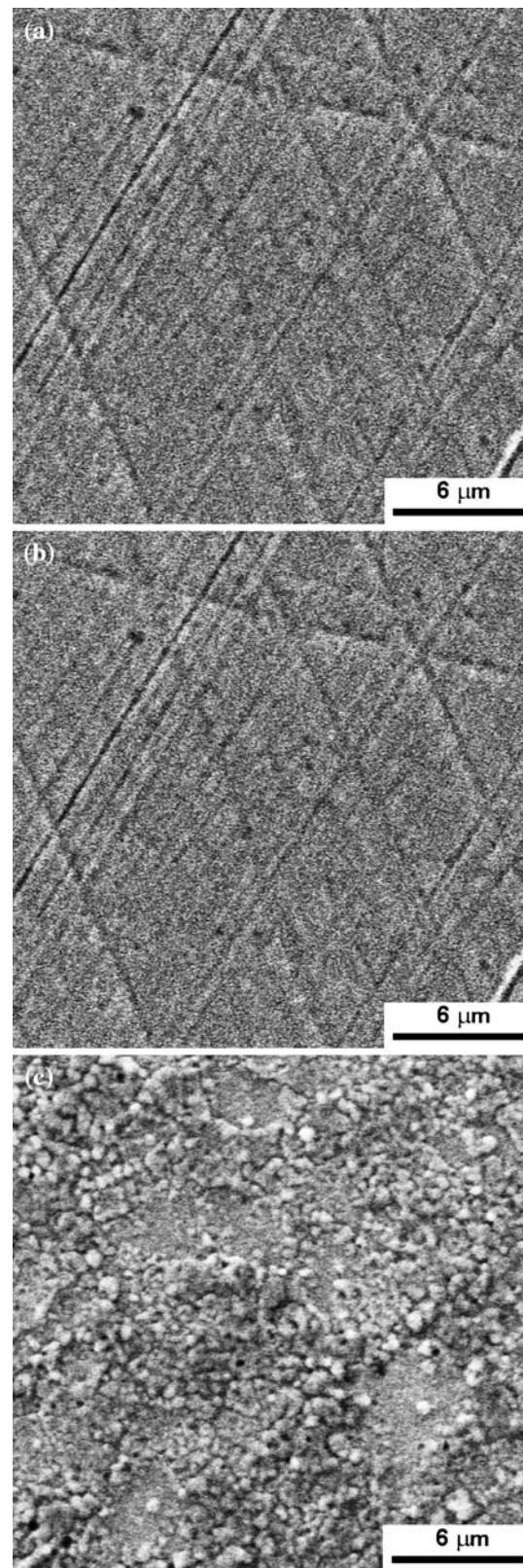


Fig. 1 SEM images of the AISI H13 steel: (a) untreated sample, Nitrogen PIII processed sample. (b) at $300\text{ }^{\circ}\text{C}$, (c) at $720\text{ }^{\circ}\text{C}$. Magnification: $5000\times$

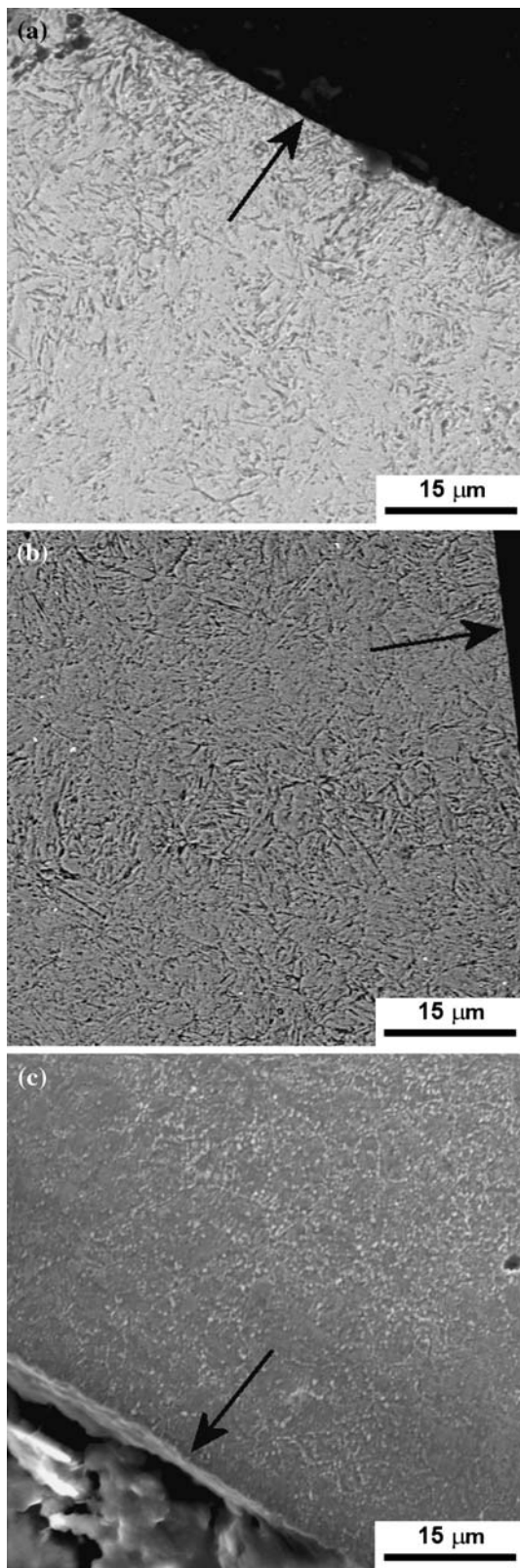


Fig. 2 SEM Cross-section images of the AISI H13 steel after PIII (a) at 300 °C, (b) at 470 °C, (c) at 720 °C. Magnification: 2000×

becomes less susceptible to corrosion attack. Figure 3a shows corrosion products over whole surface of the sample treated at 470 °C while the sample treated at 620 °C shows small attacked regions and still contains smooth regions without corrosion damage (Fig. 3b). The H13 sample treated at 720 °C presented the best corrosion resistance due to the low porosity of its surface (Fig. 3c). This observation is in agreement with the thick nitrogen enriched layer ($\sim 12 \mu\text{m}$) that serves as protection against corrosion as can be seen from GDOS measurements (Fig. 4). Further corrosion results will confirm this fact. Figure 4 presents nitrogen depth profiles for implanted H13 samples under different treatment temperatures. The GDOS nitrogen depth profiles were fitted with simple exponential decay (300 °C and 470 °C) and double exponential decay at high temperature treatments (620 °C and 720 °C). Threefold time relaxation constant of the exponential decay fittings was adopted as N depth profiles cut-off point. For lower temperatures an increment of the nitrogen penetration depth was observed in the H13 steel from approximately 1.2 μm up to 8.0 μm as the treatment temperature increases from 300 °C to 470 °C. In these conditions, the nitrogen surface concentration varied from around 15 up to 21 at. %, respectively. An error up to approximately 50% of nitrogen concentration must be considered because GDOS technique is not accurate below the surface.

Generally, the PIII processing at higher temperatures favors the nitrogen diffusion into the samples. As can be seen in Fig. 4 at higher temperatures (620 °C and 720 °C) the nitrogen profile exhibits longer tail reaching penetration depth of about 12.0 μm . However the PIII process with temperature of 720 °C resulted in lower nitrogen concentration on the surface ($\sim 20\%$) than the one treated at 620 °C ($\sim 40\%$). This finding is probably due to the higher sputtering in the sample surface during the 3IP treatment at higher temperature (720 °C). When the sample surface is subjected to an intense sputtering, the nitrogen concentration on the surface is reduced. Although the higher temperature of sample benefits the diffusion process, the reduced nitrogen content on the surface does not allow obtaining deeper nitrogen penetration.

These results are different from the ones obtained in our previous study of H13 steel [3, 14] because in these works thicker nitrogen enriched layer of 20 μm was attained for sample treated at 450 °C. This discrepancy can be attributed to the different experimental conditions applied during PIII processing in [3, 14] such as higher implantation voltage (11 kV), higher frequency (1.5 kHz), and longer treatment time (9 h).

Although a thick nitrogen enriched layer was obtained, no evidence of iron nitride compounds was observed by

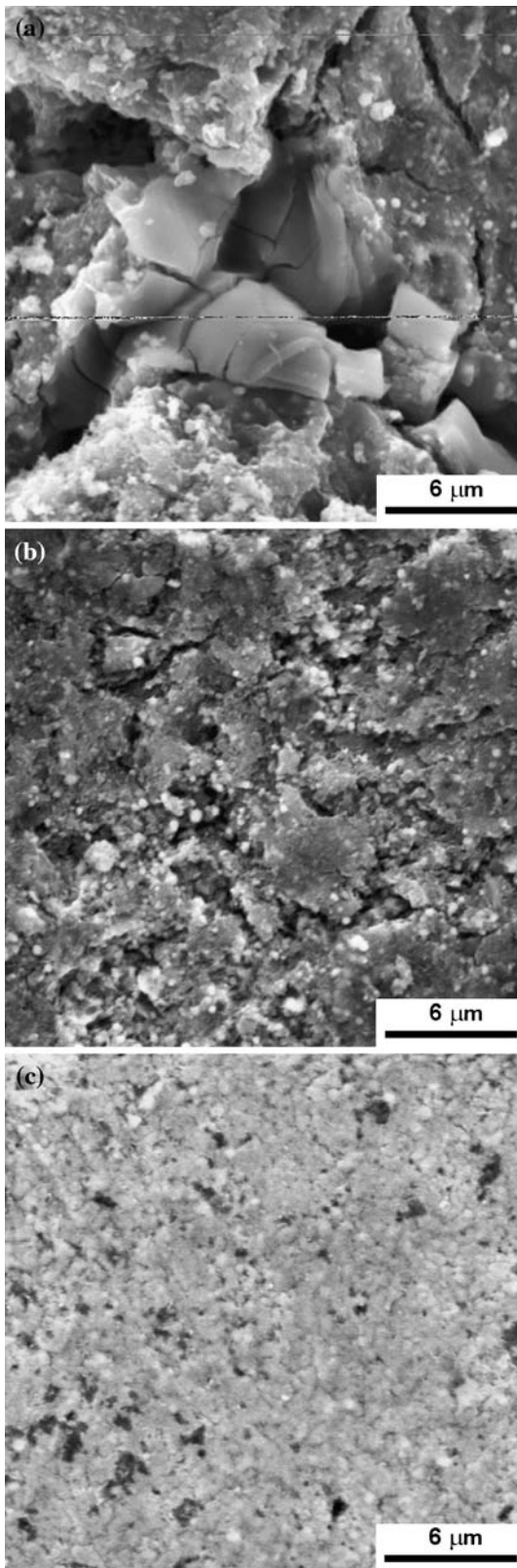


Fig. 3 SEM images of the AISI H13 steel after electrochemical corrosion in 3.5% NaCl by applying one potential step from -0.8 up to 0.1 . The samples were PIII treated at: V (a) 470 °C, (b) 620 °C, (c) 720 °C. Magnification: $5000\times$

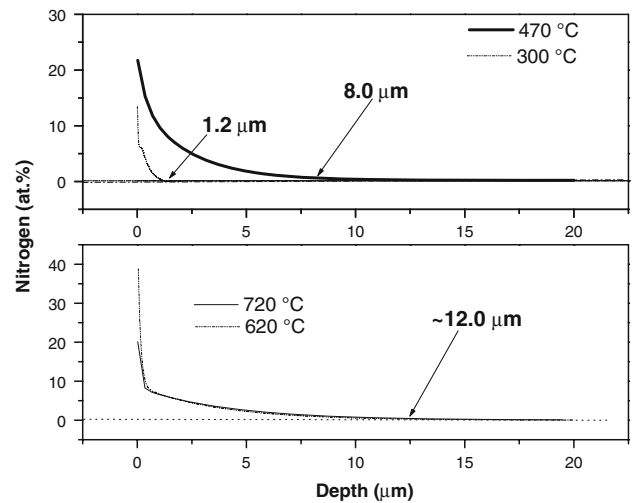


Fig. 4 Profiles of nitrogen atomic concentration of H13 steel implanted by PIII for different treatment temperatures, as a function of depth

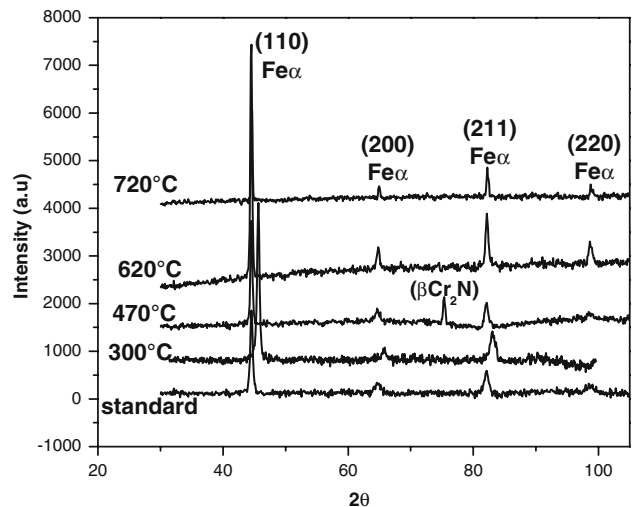
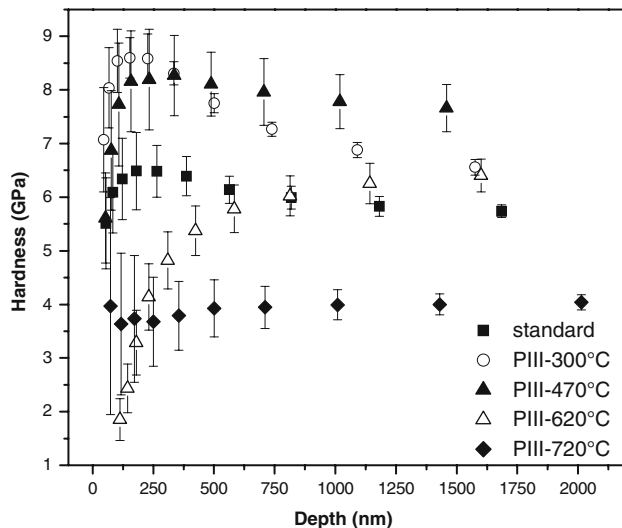


Fig. 5 X-ray diffraction of H13 steel standard and treated samples at different treatment temperatures

XRD analyses. Figure 5 demonstrates XRD diagrams from $2\theta = 20 - 100$ for untreated and samples treated at different temperatures. The same characteristics phase reflections of α -iron were detected for all treated samples as indicated at each peak in the Fig. 5. The only exception is the sample treated at 470 °C which exhibits a peak at around 75 that is attributed to the β - Cr_2N phase. This finding contradicts the iron nitride phases observed by others authors [11, 17] in H13 steel surface treatments using temperatures up to about 510 °C. This discrepancy is probably due to the fact that in the present work the nitrogen ions are in a solid solution in the H13 steels treated at higher temperatures. The iron nitride compounds obtained in [11] were produced by conventional nitriding process. The implantation

Table 1 Microindentation results

Treatment temperature (°C)	300	470	620	720
Hardness (HV)	505	592	482	311

**Fig. 6** Hardness profiles of untreated and nitrogen PIII processed samples of H13 steel

voltage of 45 kV used in the PIII processing in [17] was nine times higher than that one (5 kV) used in our experiment.

Indentation analysis was carried out on the samples treated at different PIII temperatures. Both microindentation and nanoindentation measurements, showed a decrease of the hardness with the increase of processing temperatures (up to 720 °C). Hardness values obtained from micro- and nanoindentation are shown in the Table 1 and Fig. 6, respectively. The maximum hardness of 592 HV was reached for the sample treated at 470 °C. The hardness value (Table 1) obtained for the sample treated at $T = 470$ °C is about 17% higher in comparison with the untreated sample (~ 500 HV). This hardness enhancement is due to the chromium nitride presented in this sample as can be seen in XRD results (Fig. 5). When the temperature rose up to $T = 720$ °C the hardness value decreased. The nanohardness measurements showed about the same maximum hardness (~ 8.5 GPa) on the surface of both samples treated at 300 °C and 470 °C. However in the deeper layers the sample processed at 470 °C exhibits bigger hardness value than the one at 300 °C. For the sample treated at 720 °C the hardness value remains approximately 4.0 GPa for the whole measurement range. In general (see Fig. 6) the maximum hardness value occurs just below the surface and gradually decreases as the indentation depth increases until becoming constant in the bulk of the sample. However, for the sample treated at 620 °C, the opposite

behavior was observed (Fig. 6). The nanohardness results are consistent with the microindentation ones but the maximum hardness value obtained for the sample treated at $T = 470$ °C is about 26% higher in comparison with the untreated sample. The decrease of the hardness can be explained by the degradation of steel martensitic phases, which was obtained through the thermal treatments (quenching and tempering) prior to the PIII process. This characteristic was observed in the SEM cross-section image and was already discussed in this paper. On the other hand, in the literature [17], the maximum temperature for PIII processing of H13 steel was 500 °C. The achieved maximum steel hardness (1300 HV for 50 g load) is attributed to the sample treated at 400 °C. This hardness value is superior to the value attained in this work. But we must consider that the implantation voltage of 45 kV used in the PIII processing in [17] was nine times higher than the one (5 kV) used in our experiment. Additionally, the H13 steel utilized in [17] possesses alloy elements' composition different from that used by us.

The elastic modulus was also obtained from the nanoindenter measurements. Figure 7 shows the elastic modulus as a function of the depth. The elastic modulus value is minimal below the surface and gradually increased as the indentation depth increased up to turn constant in the bulk of the sample. On the surface, a slight decrease of elastic modulus was observed with the increase of the processing temperatures ($T = 300$ – 720 °C). However the lowest value of the elastic modulus was reached for the sample treated at 620 °C. This behavior suggests that the PIII treatments at higher temperatures modify the H13 surface (see Fig. 3) in such way that when the steel is submitted to small stresses, permanent deformation can be achieved.

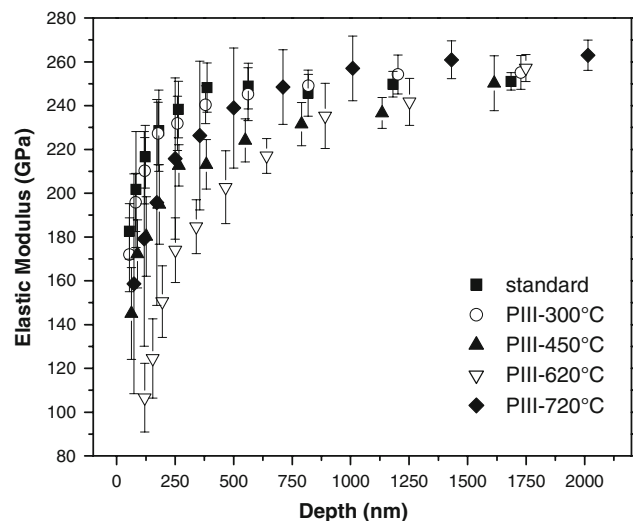
**Fig. 7** Elastic modulus profiles of untreated and nitrogen PIII processed samples of H13 steel

Table 2 Wear measurements results

Treatment temperature (°C)	Standard	300	470	620	720
Wear volume (mm ³)	566	254.0	131.0	187.0	120.0
Wear rate (mm ³ /N m)	0.57	0.25	0.13	0.19	0.12

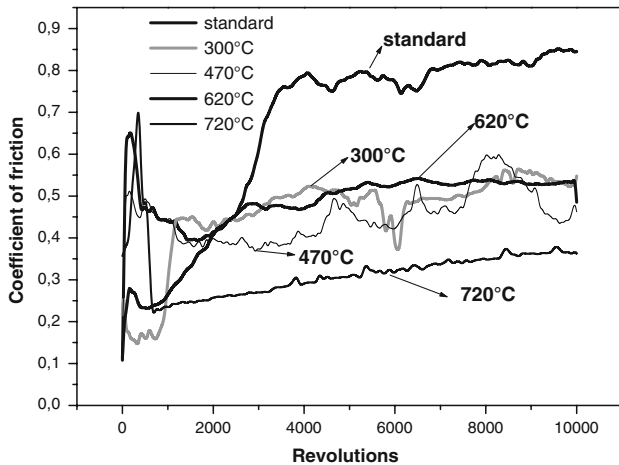


Fig. 8 Friction as a function of the number of wear cycles for H13 steel standard and treated samples at different treatment temperatures

Despite the unfavorable hardness behavior with increase of the temperature the results from wear and friction measurements (Table 2 and Fig. 8) showed an improvement of the tribological properties of the samples at high temperatures. The mean friction coefficient was reduced from 0.87 ± 0.07 up to 0.32 ± 0.06 when the temperature rose from 300 °C to 720 °C. The friction coefficient for the untreated sample was 2.6 times higher than that of the specimen treated at 720 °C.

The wear volume is obtained through the equation from standard test method for wear testing with a pin-on disk apparatus (ASTM G99) and is depicted in Table 2. A decrease of the wear volume was observed from approximately 254 mm³ up to 120.0 mm³ with increasing temperature (300–720 °C). The wear rate, calculated by the volume of material removed per wear cycle, was 4.5 times higher for the unimplanted sample (0.57 mm³/N.m) in comparison to the sample treated at 720 °C (Table 2). The enhancement of the tribological properties of H13 steel is due to the effects of nitrogen implantation. The depth of the wear tracks varied from 1.0 μm up to 0.25 μm as the temperature increases from 300 °C up to 720 °C, respectively. Thus the increase of the wear resistance is due to the influence of the deeper nitrogen enriched layers formed at higher temperature treatments since the N depth reached about 12 μm at higher temperature (720 °C). On the other hand, at higher temperatures disperse Fe₃C precipitates were formed in α-Fe matrix. The coalescence of these

precipitates in the H13 steel can also promote an increase of the wear resistance.

Anders [18] inferred that the introduction of a large volume fraction of the implanted species in PIII results in decreasing of the coefficient of friction, which in turn leads to an improvement of the wear resistance of the surface. The improvement of the tribological properties also was noted by Hutchings and coworkers [17] where the coefficient of friction varied from 0.2 for untreated sample down to 0.08 for PIII treated tool steels. Although these values are quite different from those obtained in our work because of the different experimental conditions and steels used, in both cases there was 2.6 times reduction of the friction coefficient.

Corrosion analyses

The corrosion behavior of the samples was analyzed by open circuit potential measurements and potentiodynamic polarization curves. Results of open circuit potential variation as a function of the time are shown in Fig. 9. Similar behavior is observed for all samples, that is, the potential decreases gradually in time until a saturation value is reached. This feature is own to materials with low corrosion resistance like steels. On the other hand, the potentials of the PIII treated samples are nobler than the one of untreated specimen. The potential rose from -622 mV for untreated sample up to -580 mV for the sample treated at 720 °C. This result suggests that after PIII processing the sample surface became less susceptible to corrosion attack and the analysis of next figure will confirm this tendency.

The anodic branches of the polarization curves are presented in Fig. 10. It can be clearly seen that the corrosion potential is almost the same for all treated and untreated

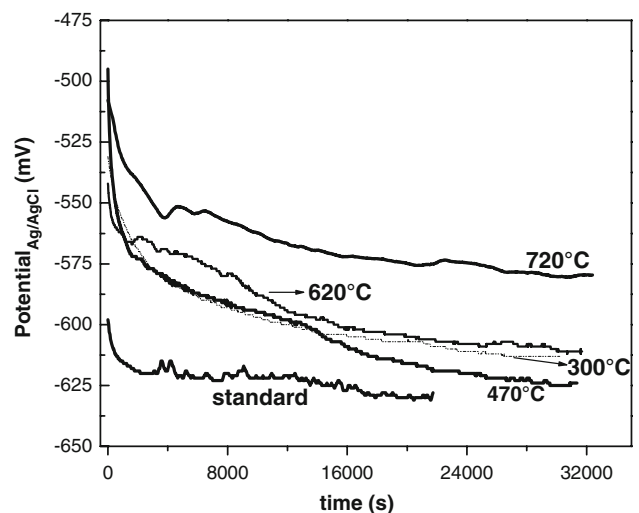


Fig. 9 Open circuit potential curves of the AISI H13 steel for untreated and nitrogen PIII processed samples at different temperatures

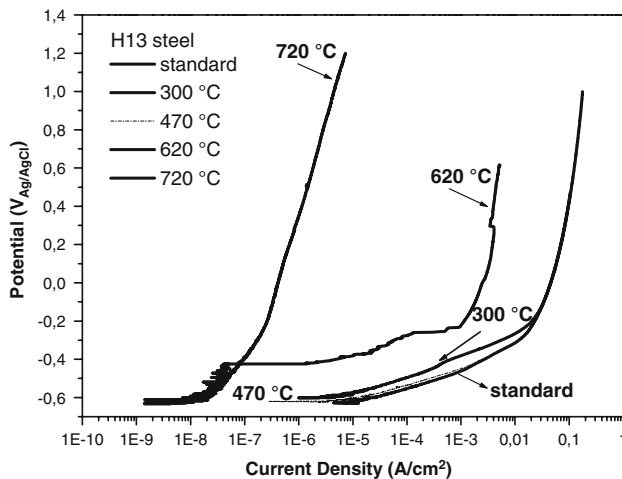


Fig. 10 Potentiodynamic polarization curves of the AISI H13 steel for untreated and nitrogen PIII processed samples at different temperatures

samples. When the potential increases, the current density also increases which corresponds to degradation of the H13 steel sample. There was a decrease of the current density to 3×10^{-8} A/cm² for the samples treated at 620 °C and 720 °C. Current densities for the samples treated at 300 °C and 470 °C were practically unaltered in comparison to the unimplanted specimen. At 1.0 V, their values were four orders of magnitude bigger than that of sample treated at higher temperature ($T = 720$ °C).

For the sample treated at 620 °C, the breakdown of passive film was observed at -0.42 V. The potential increasing above this value provokes a considerable elevation of the current density up to become constant at 4×10^{-3} A/cm². This current density is two orders of magnitude lower than that of samples treated at lower temperatures ($T = 300$ e 450 °C) and the unimplanted specimen. Thus for H13 steel treated at elevated temperature ($T \geq 620$ °C), an enhancement of the corrosion resistance was achieved. This fact is due to the deeper modified layers that form at high temperature. This finding can be linked to the smooth surface attained after corrosion attack of the sample treated at 720 °C (Fig. 3c). This observation suggests the formation of better protective layer against corrosion than that for the samples treated at lower temperatures considering that in these experimental conditions the degradation of H13 samples begins in the heterogeneities. Similar features were also observed for Ti–6Al–4V alloy treated by PIII processing at elevated temperatures [7].

There have been few studies of the corrosion behavior of H13 steel treated by PIII. Our previous study [3], also demonstrated the formation of protective film on the H13 samples PIII treated at 450 °C. The current density of about 3.5×10^{-6} A/cm² is close to the value obtained in the present study for the sample treated at the same temperature.

On the other hand, Kariofillis et al. [19] examined the corrosion behavior of H13 hot work steel in specific acid solutions. They carried out pack cementation in the steel samples to form FeB and Fe₂B borides. For short exposure time the boride coatings improve corrosion resistance of H13 steel mainly in H₂SO₄ and H₃PO₄ solutions when compared to H13 standard steel. The corrosion current density obtained by these authors is approximately 10^{-4} A/cm². However this value cannot be compared with the current densities obtained in this work because of the very different surface treatments and solutions used for corrosion tests.

Conclusions

AISI H13 steel samples were subjected to nitrogen PIII treatment at different temperatures ranging between 300 °C and 720 °C. After the processing the surface morphology was drastically changed as revealed by SEM analysis. The surface modification was more apparent for the samples treated at the highest temperature ($T = 720$ °C).

Nitrogen penetration depth of about 12 μm was obtained at temperature above 620 °C. Although a thick enriched nitrogen layer was formed no evidence of nitride compounds was observed by XRD analyses. The maximum hardness was achieved for sample treated at 470 °C. There was a decrease of the hardness values for temperatures higher than 620 °C and the elastic modulus also slightly decreased as the temperature was increased. In spite of this hardness reduction at high temperatures improvements of the wear and corrosion resistance were observed. There was a decrease of the wear volume by factor of 4.5 compared to the standard tempered and annealed H13 steel. The coefficient of friction was also reduced by factor of 2.6. Open circuit potential curves showed that the potentials are nobler for the PIII treated samples than for untreated specimen. In addition, the corrosion current densities of the samples treated at 300 °C and 470 °C were practically unaltered in comparison to the unimplanted sample. These current density values were significantly higher than the ones of the samples treated at higher temperatures ($T \geq 620$ °C).

Regardless of the H13 steel hardness decrease obtained at high temperatures, the PIII treatment at elevated temperature can be considered as successful because it promotes significant improvement of the wear and corrosion resistance. This fact is very important for H13 industrial applications since this steel is submitted to severe wear processes during its operation.

Acknowledgement This work was supported by CNPq (process: 382838/2004-1), FAPESP and MCT.

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