

## Article

# Nanocrystallized Surface Effect on the Tribocorrosion Behavior of AISI 420

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**ABSTRACT:** Nanopeening treatment was applied to the AISI 420 steel to decrease its sensitivity to the tribocorrosion damage. Microstructural investigation highlighted that the Nanopeening treatment led to a high plastic deformation and nanostructured surface layer with 110  $\mu\text{m}$  depth. In order to study the combined effect of corrosion and mechanical wear, tribocorrosion tests were performed on non-treated and nanopeened samples in boric acid and lithium hydroxide solution, considering both continuous and intermittent sliding. It was found that the AISI 420 steel is sensitive to the synergism between mechanical friction and electrochemical corrosion with a domination of abrasive wear. Adhesive wear was also detected in the wear track. Indeed, the mechanical wear was pronounced under intermittent sliding because of hard wear debris generation from the repassivated layer during rotating time. The Nanopeening treatment led to enhance mechanical performance and corrosion properties. Such improvement could be explained by the high plastic deformation resulting in the nano-structuration of grains and increasing hardness of AISI 420 steel.

**KEYWORDS:** Microstructure; Grain size; Hardness; Tribology; Corrosion; Passivation

## List of symbols

C <sub>dl</sub>	Double layer capacitance
Cr	Chromium
EBSD	Electron Back Scattered Diffraction
EIS	Electrochemical Impedance Measurements
ECD	Equivalent Circular Diameter
Fe	Iron
IPF	Inverse Pole Figure
Mo	Molybdenum
Ni	Nickel
NT	Non-Treated
NP	NanoPeened
OCP	Open Circuit Potential
PAG	Prior Austenite Grain
RCCA	Rod Cluster Control Assemblies
EC	Equivalent circuit
R <sub>p</sub>	Polarization Resistance ( $\Omega$ )
R <sub>s</sub>	Solution Resistance ( $\Omega$ )
SEM	Scanning Electronic Microscopy
t <sub>lat</sub>	Latency time (s)
t <sub>rot</sub>	Rotation time (s)
t <sub>stop</sub>	Stop time (s)
W <sub>tr</sub>	Total wear ( $\text{cm}^3/\text{cycle}$ )
W <sub>act</sub> <sup>c</sup>	Material loss due to corrosion of active material in the wear track ( $\text{cm}^3/\text{cycle}$ )
W <sub>m<sup>act</sup></sub>	Material loss due to mechanical wear of the active material in the wear track ( $\text{cm}^3/\text{cycle}$ )
W <sub>repass</sub>	Material loss due to corrosion of repassivated material in the wear track ( $\text{cm}^3/\text{cycle}$ )

$W_{\text{repass}}$  Material loss due to the mechanical wear of repassivated material in the wear track (cm<sup>3</sup>/cycle)

$Z_{\text{im}}$  Imaginary part of the impedance (Ω.cm<sup>2</sup>)

$Z_{\text{re}}$  Real part of the impedance (Ω.cm<sup>2</sup>)

## 1. INTRODUCTION

Over the past seventy years, many researches were conducted in order to develop advanced materials and to improve system performance of nuclear reactor. In the reactor pressure vessel, some components are sensitive to wear damage and degradation, which affect the efficient operation and safety of nuclear power plant. Materials degradation in fuel assemblies results from a complex process which is affected by various factors such as contacting materials, environmental conditions and wear phenomena [1-2]. Heat is generated by the energy released by the fission products, taken place in the fuel held and transferred to the primary coolant. The heat generation needs adjustment during the operational process which is performed by the relative motions of Rod Cluster Control Assemblies (RCCA) [3-7]. RCCA translation is conducted by control rod guidance assemblies and monitored by the control rod drive mechanism. In fact, stellite-covered latch arms allow the displacement of control rod drive shafts in latch housings [6-7]. The gripper latch arms (AISI 304L stainless steel) interact with the drive rod (AISI 410 martensitic stainless steel) in the reactor during each step of processes. The contact area between the gripper latch arms is protected by a cobalt-based hard facing alloy (stellite grade 6). The repeated interactions between components are subject to a particular environment of reactor containing boric acid and lithium hydroxide at high temperature and pressure [3, 6]. Those operational conditions lead to a singular wear phenomenon which is critical for the lifetime of martensitic stainless steel. Four basic types of wear are identified in the contact between solids: abrasive [8,11], fatigue [12-14], adhesive [15-16] and corrosion [17, 18]. Previous studies were mostly focused on the wear and corrosion behaviors acting separately on martensitic stainless steels [13-26]. The corrosion resistance of martensitic stainless steels depended on the oxide film. The oxide film was composed of iron (Fe), chromium (Cr) and nickel (Ni) oxides. It spontaneously covered the stainless steel surface in presence of oxygen [27-28]. Chromium oxide (Cr<sub>2</sub>O<sub>3</sub>) shows a very low corrosion rate of the metal in the surface. Nickel serves to improve the stability of the oxide film. Corrosion studies indicated that pitting was the main corrosion type of the martensitic stainless steels. Their susceptibility to pitting corrosion was related to the amount of precipitated carbides and the Cr depleted regions [28-37]. Wear studies demonstrated that the most typical wear phenomena of martensitic stainless steels were abrasion and adhesion. Indeed, the presence of carbides promoted the generation of hard debris and abrasive wear [30].

Despite these numerous studies, the tribocorrosion was not well studied although it pronounced action on stainless steel alteration. It is a form of solid surface degradation that involves both corrosion and mechanical wear. The resulting material degradation process was completely different to that obtained when the corrosion and the mechanical wear mechanisms acting separately [31-33]. Stachowiak and Zwierycki [34] studied the tribocorrosion behavior of the AISI 420 martensitic stainless steel in sulfuric acid using pin-on-plate tribometer. They founded that the tribocorrosion response and the wear behavior depended on the steel properties such as the hardness and the pace of repassivation. Esfandiari and Dong [35] studied the tribocorrosion response of plasma nitrided 17-4PH stainless steel in a 3.5 wt% NaCl solution under sliding conditions. This treatment improved the tribocorrosion behavior by increasing corrosion-wear resistance and surface hardness. Lin *et al.* [36] investigated that the chromizing coating on the P110 steel had lower mass losses due to the higher surface hardness than the bulk steel under

tribocorrosion conditions. However, the tribocorrosion behavior of martensitic stainless steels, which used for nuclear reactor components, was not studied in previous researches.

This work aims at studying the tribocorrosion of AISI 420 and the effect of the nanopeening surface treatment on the corrosion-wear behavior. Electron Backscatter Diffraction (EBSD) was used to characterize the microstructure of nanopeened layer and bulk material. Tribocorrosion experiments were performed in boric acid and lithium hydroxide solution with pin-on-disc tribometer. *In situ* techniques as open circuit potential measurements and electrochemical impedance spectroscopy were performed. Tribocorrosion wear was qualitatively studied by means of Scanning Electron Microscope (SEM) and white light interferometer, in order to characterize the wear track. Quantitative analysis was also carried out to determine the material loss.

## 2. EXPERIMENTAL PROCEDURES

### 2.1. Nanopeening treatment

Cylindrical samples of 10 mm in height and 30 mm in diameter were prepared from AISI 420 stainless steel bars. Samples were then mechanically polished to get a suitable surface for the nanopeening treatment performed by Winoa Company [37].

The nanopeening treatment is a severe plastic deformation technique. It leads to a mechanically-induced nanometric grains in the surface layer by a blasting shot peening. It consists of shot projection for few minutes under carefully selected operating conditions (shot diameter [0.1 mm-2 mm], projected speed [40 m.s<sup>-1</sup>-100 m.s<sup>-1</sup>], incidence angle [10°-45°] and recovery rate [1000%-2000%] [38]).

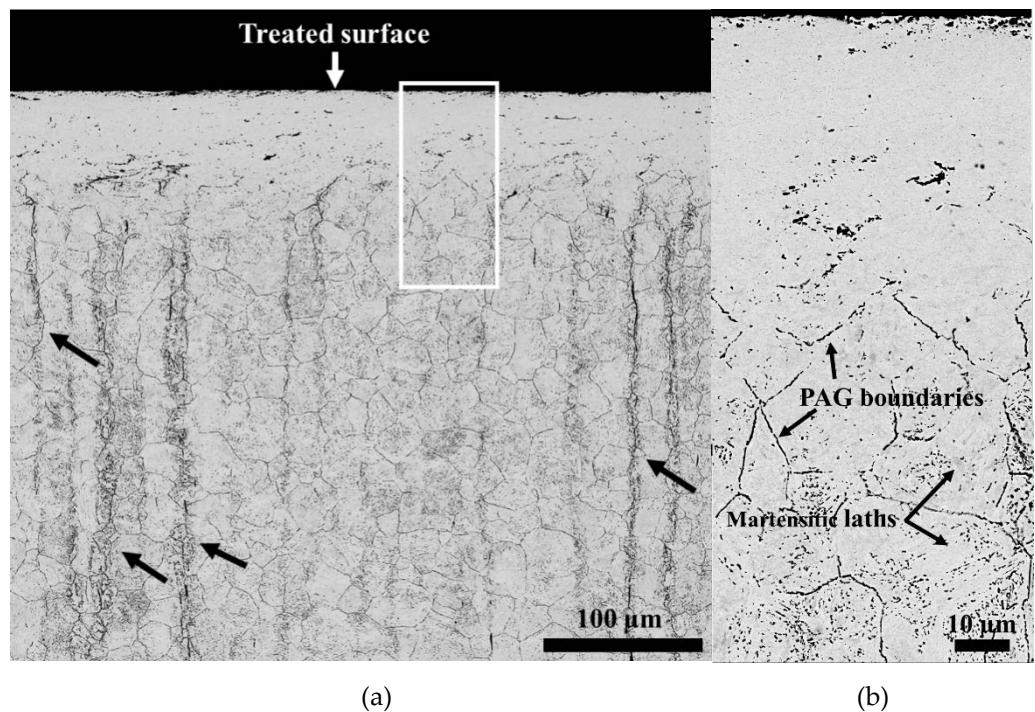
The surface chemical composition of AISI 420 steel was obtained by optical emission spectroscopy and is summarized in Table 1. Two measurements on the non-treated and on the nanopeened samples were performed. Thereafter, the Non-Treated sample and the NanoPeened sample are named respectively NT sample and NP sample.

**Table 1** surface chemical composition (wt. %) of the AISI 420 NT and NP samples.

Elements	C	Si	Mn	P	S	Cr	Ni	Mo
NT sample	0.3	0.36	0.64	0.02	0.02	13	0.22	0.04
NP sample	0.02	0.37	1.6	0.03	0.04	16.5	10.14	2.2

### 2.2. Samples characterization

For microstructure characterization, a longitudinal cut was achieved in the central part of NP sample. To get a suitable surface quality for SEM examinations and EBSD measurements, the cross section was prepared using the JEOL cross section polisher with an argon ion beam (the voltage and the current of ion beam were respectively of 4 kV and 60  $\mu$ A). The cross section polisher preparation can accentuate the channeling contrast among the different grains. It facilitates an easy and straightforward EBSD pattern acquisition due to the minimal surface strain and distortion [39].



**Fig. 1** (a) SEM micrograph in secondary electron mode of cross-sectional microstructure of NP sample at large scale.(b) Zoom of the square region in (a).

EBSD map was also performed on the cross-section of the NP sample in order to characterize in detail the microstructural changes under the nanopeening treatment, from the top treated surface to the untreated core of the same sample. The EBSD map was carried on with an accelerating voltage of 15 kV at a working distance of 15 mm in a JEOL SEM equipped with AZTEC EBSD system from Oxford Instruments. The acquisition step size was 0.3  $\mu$ m and the map size was of 550 x 850  $\mu$ m. The mean martensite grain size was quantified from the EBSD maps. The grain detection procedure proceeds in two steps and defines an upper and lower threshold angle [40]. The upper value was set here to 5° to identify a first network of grain boundaries. The lower angle was set to 1° in order to close the open lines by tracking path between neighboring pixels considering disorientation angles down to the lower bound. The average grain size measured by this method is given in Equivalent Circular Diameter (ECD)<sup>(1)</sup>.

For tribocorrosion and micro-hardness tests, NT and NP samples were mechanically polished until obtaining a final surface roughness of about 0.11  $\mu$ m. After sliding, the wear was quantified by profilometry measurements in four areas regularly spaced along the sliding track [37]. The wear track volume was determined by multiplying the area of the profiles by the wear track perimeter. SEM micrographs were also acquired in four areas of each sample to describe the type of wear tracks.

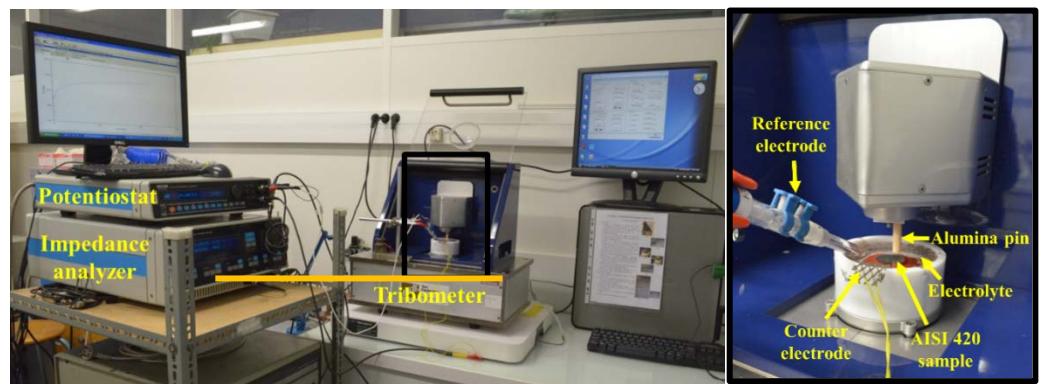
Vickers micro-hardness tests were performed on the NT and NP samples using the LEICA M400-H1 micro-hardness instrument. The tests were conducted by applying 50 g for 10 s by a square-based pyramid indenter on the surface of the polished samples. On each sample, about 15 measurements were performed. For microstructure characterization, a longitudinal cut was achieved in the central part of NP sample. To get a suitable surface quality for SEM examinations and EBSD measurements, the cross section was prepared using the JEOL cross section polisher with an argon ion beam (the voltage and the

<sup>(1)</sup> The Equivalent Circular Diameter (ECD) of an object represents the diameter of a disc that occupies the same area as that object.

current of ion beam were respectively of 4 kV and 60  $\mu$ A). The cross section polisher preparation can accentuate the channeling contrast among the different grains. It facilitates an easy and straightforward EBSD pattern acquisition due to the minimal surface strain and distortion [39].

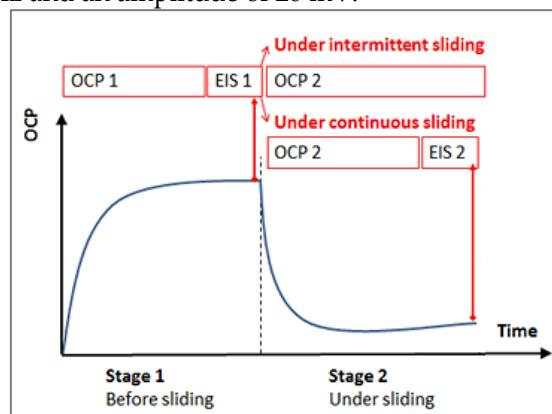
### 2.3. Tribocorrosion test

The samples were subjected to tribocorrosion experiments, which were carried out using a pin-on-disc tribometer (FALEX TRIBOLOGY) equipped with an electrochemical cell (Fig.2). For the electrochemical and tribocorrosion experiments, the electrolyte was an aqueous solution of boric acid and lithium hydroxide containing 1000 ppm of boron and 130 ppm of lithium with 8.3 pH. The average pH value of the prepared solution was about 8.3. This solution composition was similar to that of the primary environment of nuclear power plant. All experimental tests were carried out at ambient pressure and temperature.



**Fig. 2** Tribocorrosion set-up.

For corrosion test, three electrodes cell was used in this study. The cell was connected to a potentiostat (solartron 1287) and a frequency response analyzer (solartron 1250). The working electrode corresponded to NT or NP AISI 420 samples, which was coated with resin to get a working area of 4.52 cm<sup>2</sup>. A platinum titanium grid electrode was used as the counter electrode and placed against the internal side wall of the cell. The reference electrode was of silver/silver chloride with 3 M KCl solution (Ag/AgCl/KCl<sub>3M</sub>), which was characterized by  $E_{Ag-AgCl} = +0.200$  V/Standard Hydrogen Electrode. The corrosion test corresponded to the stage 1 (i.e. before sliding) of tribocorrosion protocol as shown in Fig. 3. During this stage, the samples were immersed in the solution and the Open Circuit Potential (OCP1) as a time function was measured for 3 h in order to reach a stable potential. Next, the Electrochemical Impedance Measurements (EIS1) were performed to characterize the corrosion behavior without sliding. The EIS1 was measured with a frequency range from 1 mHz to 10 KHz and an amplitude of 20 mV.



**Fig. 3** Tribocorrosion test protocol.

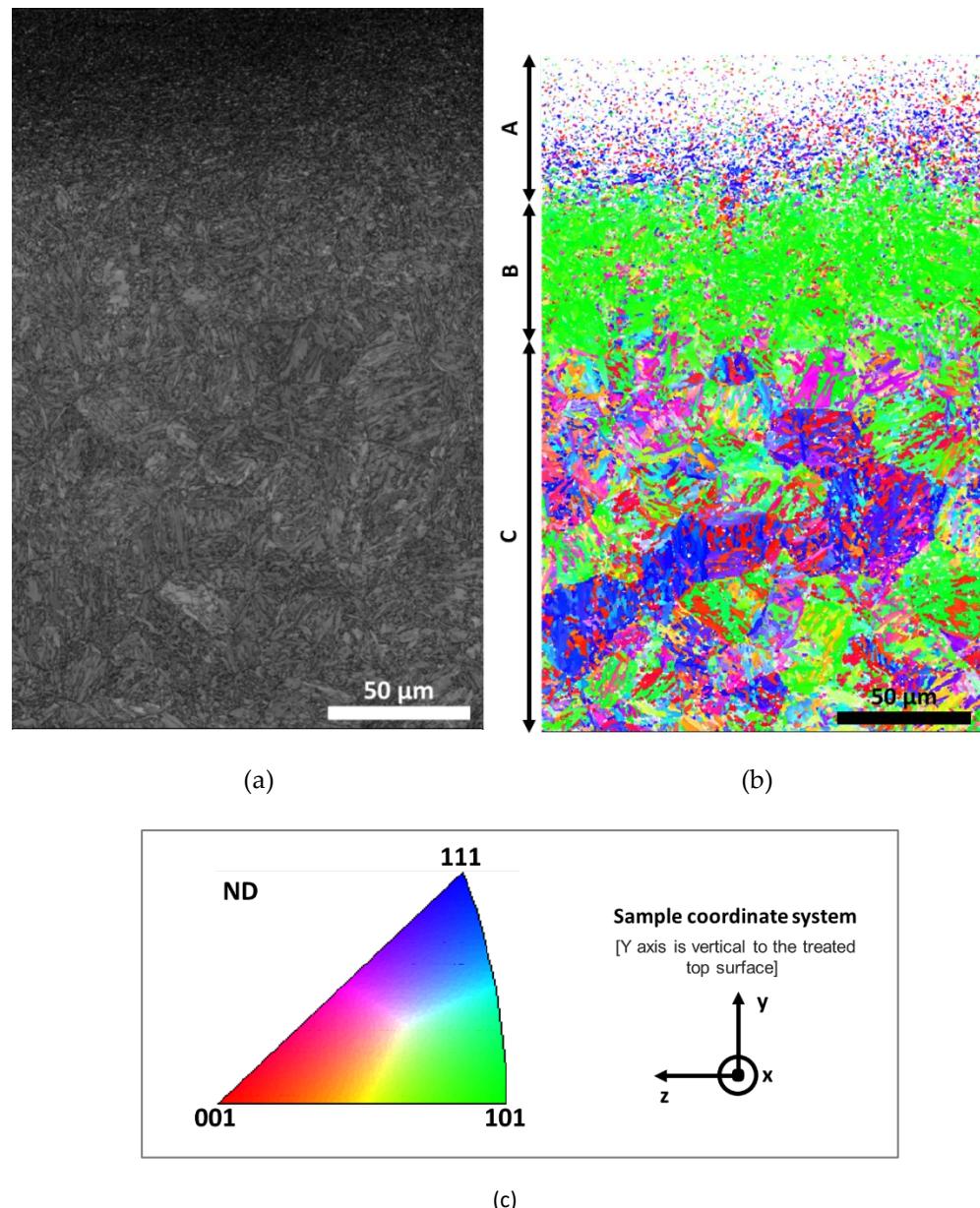
Tribocorrosion test was performed during stage 2 (i.e. under sliding, c.f. Fig. 3) of the experimental protocol. An alumina pin, with a diameter of 7 mm having a spherical tip with a radius of 100 mm, was selected to be the counter body for tribological tests. A normal force and rotation speed of respectively 5 N and 120 rpm were applied on the pin to have a wear track diameter of about 10 mm. The normal force corresponded to an average Hertzien pressure of 84 MPa. Sliding tests were performed either continuously or intermittently for the tribocorrosion tests. The sliding tests were conducted for 5000 cycles with a sliding distance of 157 m. In the continuous sliding, the pin was animated by a permanent rotation (i.e. the stop time  $t_{stop} = 0$  s). In the intermittent sliding, the pin rotated for 0.5 s first and then it kept immobile for another 20 s in order to evaluate the combined effect of corrosion and mechanical wear. The latency of one cycle is the delay separating two successive contacts, so that  $t_{lat} = t_{rot} + t_{stop}$ . During stage 2, the alumina pin was loaded on the sample surface and the sliding test was monitored by the OCP2 and EIS2 measurements. EIS2 measurement was acquired over the frequency range from 10 mHz and 10 KHz applied with sinusoidal voltage signal of 20 mV. For both corrosion and tribocorrosion experiments, tests are repeated three times and averaged in order to obtain statistically valid results.

The wear was quantified using white light interferometer measurements in three areas regularly positioned along the wear track. The total wear volume was determined by multiplying the area of the profiles by the sliding track perimeter. Finally, optical microscope and SEM were used to analyze the wear tracks.

### 3. RESULTS and discussions

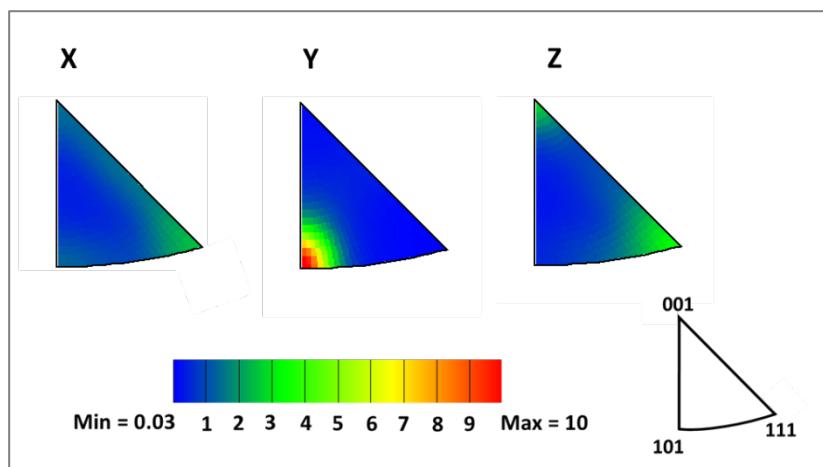
#### 3.1. Microstructure analyses

The EBSD examination on the cross-section, as shown in Fig. 4, reveals the depth-dependent gradient microstructures of the deformed layers on NP sample. The features of plastic deformation can be traced to a depth of about 110  $\mu$ m, in which two different zones can be clearly identified: Zones A and B. The zone A is extended over 56  $\mu$ m from the top surface. The detailed microstructure of this zone could not be distinguished neither in SEM micrographs (Fig. 3) nor in EBSD map (Fig. 4). This is related to several plastic deformation induced by the nanostructuration treatment. Similar microstructures results had also been reported in the literature of AISI 316L and AISI 304 stainless steels undergoing similar nanostructuring treatment [41-42].



**Fig. 4** EBSD map acquired in the cross-section of NP sample: (a) kikuchi pattern quality map, (b) IPF map shows martensite grains orientation and (c) stereographic triangle of IPF color map. Notice that the indexing rate was only of 82%.

Zone B is extended from 56  $\mu\text{m}$  to 110  $\mu\text{m}$  below the surface. Numerous small martensitic laths become visible (see Fig. 4 (a)). The prior austenite grain boundaries are still embedded in the distorted martensite grains but could be hardly identified. In this transitional zone, the martensitic laths have a mean size of 1.09  $\mu\text{m}$  with an aspect ratio of 1.9 and with a width of about 573 nm. In Fig. 4 (b), the colors represent the crystallographic orientation normal to the observed planes in the cross section of NP sample, is indicated in the stereographic triangle shown in Fig. 4 (c). As Fig. 4 (b) suggests, most of the martensite grains in the zone B have their crystallographic axes  $<101>$  parallel to the Y direction. A clear crystallographic texture in the zone B is recognizable as shown by the Inverse Pole Figure (IPF) charts in Fig. 5. These IPF were obtained from the EBSD map presented in Fig. 4.



**Fig. 5** Texture developed in zone B, represented by IPF, showing strong  $<101>$  //Y texture formation.

Zone C corresponds to the bulk material. Its microstructure remains close to the as-non treated material and reveals equiaxed PAG owning a means size of about  $25\text{ }\mu\text{m}$ , with an aspect ratio of 3. Inside the PAG, the martensitic laths are oriented at a combination of different crystallographic planes such as  $\{001\}$ ,  $\{101\}$ ,  $\{111\}$ . No preference grain orientations were identified in this zone. The martensitic laths are larger compared to those identified in the zone B, the width of which is about  $710\text{ nm}$ , and the average grain size is of  $1.53\text{ }\mu\text{m}$  with an aspect ratio of 1.9.

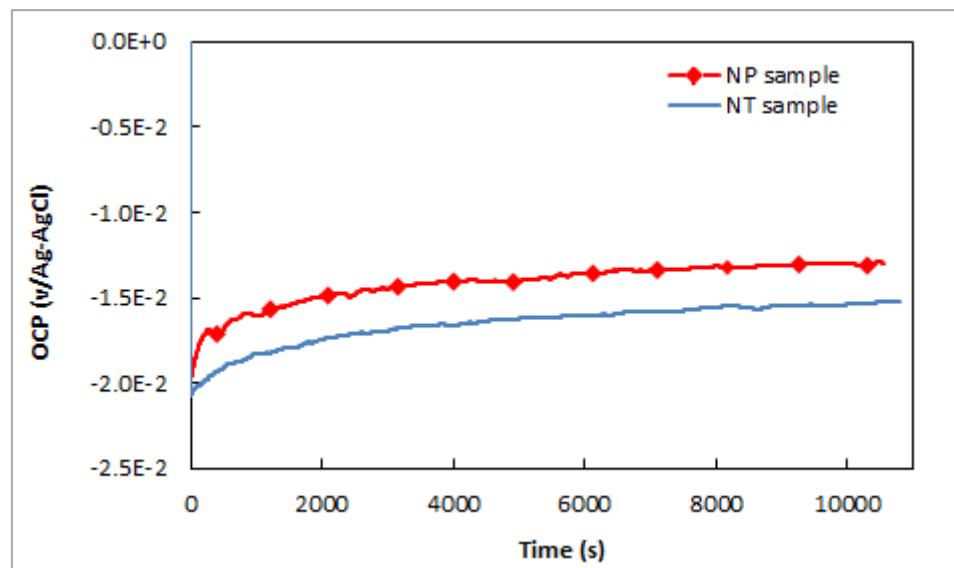
The average micro-hardness values obtained on NT and NP samples were  $260\text{HV}_{0.05}$  and  $550\text{ HV}_{0.05}$ , respectively. Thus, the surface hardness of the martensitic stainless steel was improved by 1.3 times more than that of the untreated steel, which can be ascribed to high plastic deformation resulting in nanostructuration of grains.

### 3.2. Corrosion tests

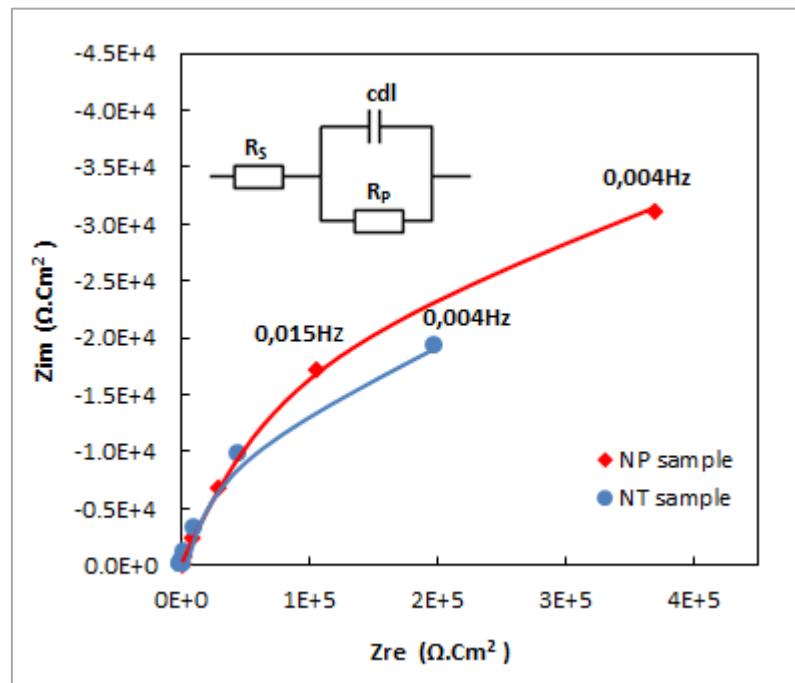
The corrosion behavior was investigated using the open circuit potential measurements (OCP1). The OCP1 evolution as a function of time during the first hour of immersion of NT and NP samples in boric acid and lithium hydroxide solution are presented in Fig.6 (a). For all samples, the OCP1 increases and then stabilizes suggesting a stable electrochemical state at the surface by the formation of natural passive films. This figure shows that NP sample exhibits a better behavior than NT one. In fact the OCP1 of NP sample is stabilized at higher potential ( $-0.13\text{ v/Ag-AgCl}$ ) compared to NT sample ( $-0.15\text{ v/Ag-AgCl}$ ). In addition, the necessary time to form an initial passive layer are 2000 s and 1400 s for NT and NP samples, respectively. These values indicate that the recovery rate of the surface by the protective film on the NP sample is 1.4 time faster than on the NT one. This is related to the significant increase in Cr, Mo and Ni contents of the NP martensitic stainless steel (Table 1). They increased by 20%, 97% and 98%, respectively, due to the Nanopeening treatment. Indeed, the increase in Cr, Ni and Mo contents increases the repassivation rate of the oxide film and corrosion resistance [43-44]. In fact Mo incorporated into the surface layer may accelerate the formation of the passive film. It may improve depassivation resistance due to the different oxidation states:  $\text{Mo}^{+4}$  and  $\text{M}^{6+}$ . The oxides of  $\text{Mo}^{+6}$  in the passive film reduce  $\text{Cl}^-$  ion penetration. The presence of Ni stabilizes the passive film because it may decrease the dissolution rates of Fe and Cr.

The corrosion resistances of NT and NP samples were further evaluated through electrochemical impedance spectra measurements (EIS1) when a stable potential (OCP1) was reached. Fig. 6 (b) shows that NT and NP samples behaved the similar Nyquist impedance plots and the same equivalent electrical circuit performed with ZView2 software. The equivalent circuit (EC) is made up of the solution resistance ( $\text{Rs}$ ) in series with a parallel association of the double layer capacitance ( $\text{Cdl}$ ) and the polarization resistance

( $R_p$ ).  $R_p$  is proportional to the corrosion resistance of the surface. The  $R_p$  obtained on NP sample was  $915.68 \text{ K}\Omega \cdot \text{cm}^2$ , clearly greater than that of NT sample ( $527.78 \text{ K}\Omega \cdot \text{cm}^2$ ). This means that both samples resisted to corrosion and the nanopeneed layer improved the corrosion resistance of AISI 420 steels. The resistance enhancement obtained in the case of NP sample is mainly due to the superior Cr, Mo and Ni contents.



(a)

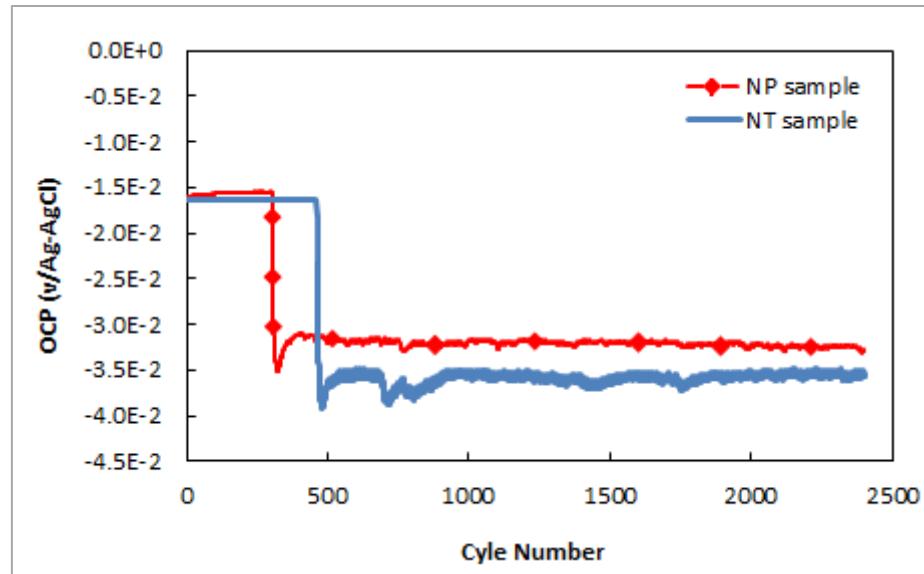


(b)

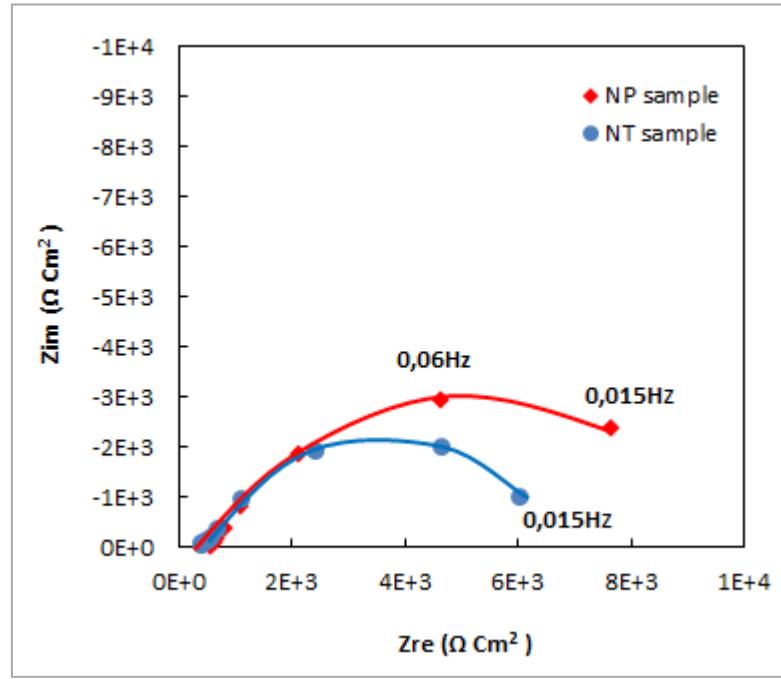
**Fig. 6** Corrosion tests without mechanical loading: (a) open circuit potential as a time function, (b) electrochemical impedance spectra (Nyquist plot) of NT and NP AISI 420 samples, immersed in boric acid and lithium hydroxide solution.  $Z_{\text{im}}$  and  $Z_{\text{re}}$  are, respectively, the imaginary and the real part of the impedance.

### 3.3. Tribocorrosion tests under continuous sliding

During the tribocorrosion tests under continuous sliding at 5 N and 120 rpm, the evolution of OCP2 potential is monitored as a function of cycle numbers as shown in Fig.7 (a).



(a)



(b)

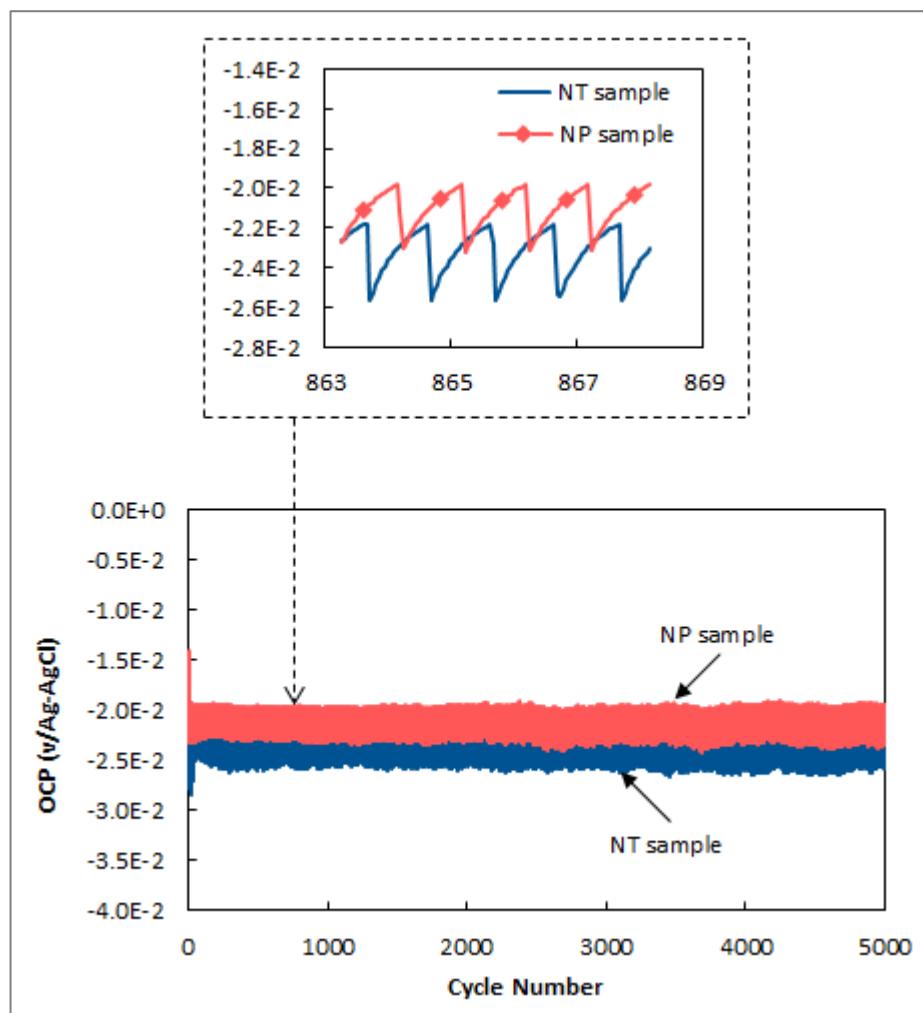
**Fig. 7** Tribocorrosion tests under continuous sliding (a) open circuit potential evolution, (b) electrochemical impedance spectra (Nyquist plot) of NT and NP samples, immersed in boric acid and lithium hydroxide solution..

When the sliding starts, the OCP2 decreases to reach the lowest value of -0.37 and -0.32 V/Ag-AgCl for NT and NP samples, respectively, which corresponds to the increase

of corrosion rate. In fact, the passive film was destroyed by sliding. The wear track became uncovered by the protective layer and the bare metal was attacked by the aggressive environment of boric acid and lithium hydroxide solution. After 72 cycles, the OCP2 stabilizes at -0.35 and -0.32 V/Ag-AgCl for NT and NP samples, respectively. The EIS2 measures the impedance of the metal/solution interface in order to identify the surface state and determine the corrosion resistance of samples under continuous sliding as shown in Fig. 7 (b). The experimental data was simulated by the equivalent circuit EC. The resistance  $R_p$  for both NT and NP samples was about 6700 and 10036  $\Omega \cdot \text{cm}^2$  respectively, proposing an active surface state [36]. The  $R_p$  of NP sample was slightly higher than NT sample, which suggested the improvement of corrosion resistance under a continuous friction. This improvement was attributed to the difference of the oxide layer composition (c.f. Table 1). In fact, the passive layer on NP samples was more stable due to the highest Cr, Ni and Mo contents compared to NT one. That may also be ascribed to the oxide debris remained in the wear track to form a barrier layer counter instead of being injected.

#### 3.4. Tribocorrosion tests under intermittent sliding

The OCP2 evolutions versus time of both NT and NP samples under intermittent sliding at 5 N and 120rpm are presented in Fig.8. For both NT and NP samples, a sudden decrease of the OCP2 is observed when sliding starts. The OCP2 drop to -0.28 and -0.23 V/Ag-AgCl for NT and NP samples, respectively. Then, it is fluctuating in phase with the alumina pin rotation ( $t_r$ ) and stop ( $t_{stop}$ ). The fluctuations were attributed to the passivation-activation transitions of the wear track in a tribocorrosion system. Indeed, the passive film was removed by mechanical wear during  $t_r$  indicating an active state of wear track. Then the dissolution of the material was produced inside the wear track, confirming the OCP2 drop. During  $t_{stop}$ , OCP2 increased which indicated that the wear track was repassivated. In such intermittent sliding tests, EIS measurements could not be performed because of the fluctuations and non-stationary OCP2 in a single cycle.

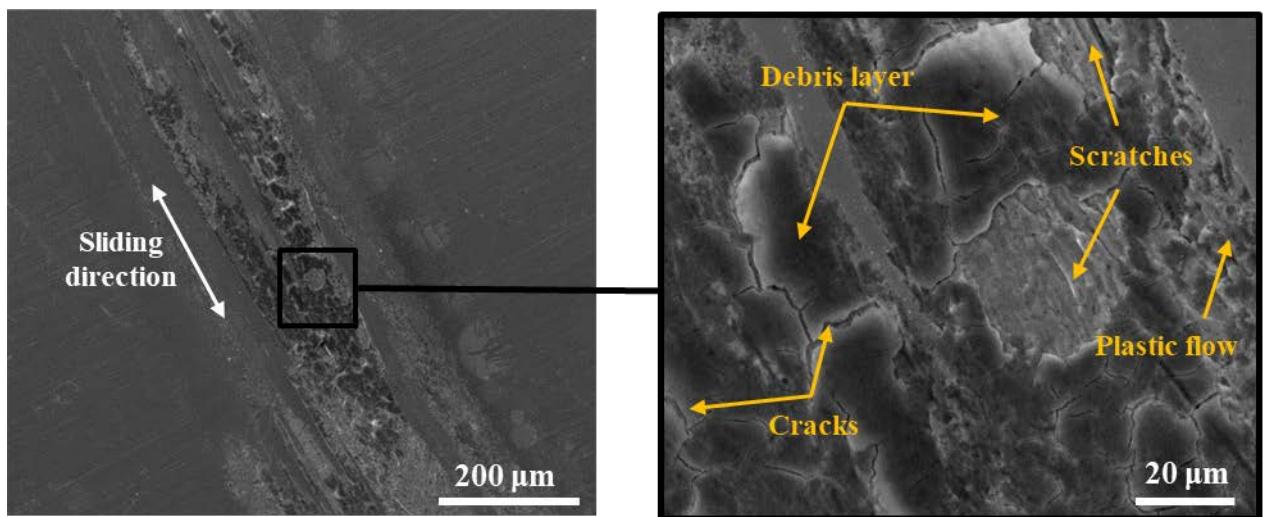


**Fig. 8** Tribocorrosion tests under intermittent sliding: open circuit potential evolution, of NT and NP samples, immersed in boric acid and lithium hydroxide solution..

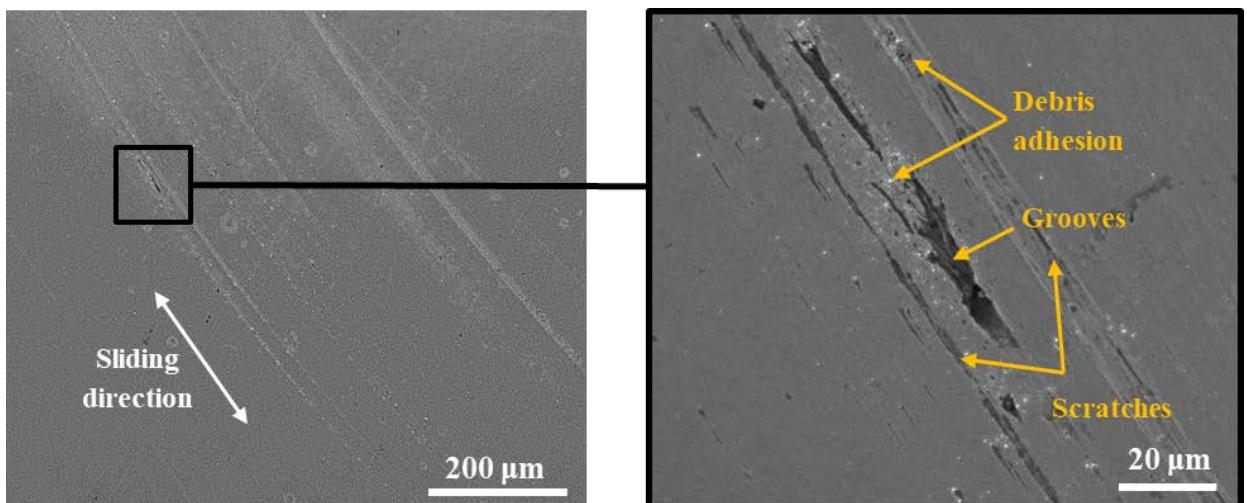
### 3.5. Surface and morphological characterization

In order to understand the surface wear mechanisms, the wear tracks on NT and NP samples were analysed by SEM micrographs. They are presented in Fig. 9 and 10 under continuous and intermittent sliding, respectively.

Under both continuous and intermittent sliding, the wear tracks have scratches parallel to the sliding direction which proved an abrasive wear mechanism in both NT and NP samples. In fact, the pin mechanical action caused two-body abrasive wear. After the removal of local passive film, the wear debris was generated from bare metal. Then, three-body wear occurred when this debris was free to roll and slide down the sliding surfaces. This debris acted as an additional abrasive and created scratches. Besides, the abrasive wear seems to be more pronounced for NP samples due to the major scratches and the presence of grooves in the wear track under both continuous (Fig. 9 (b)) and intermittent sliding (Fig. 10 (b)), respectively. Indeed, the grooving process was a result of three-body abrasive wear during sliding. The abrasion wear could be caused by a large amount of oxide debris. A Cr-rich oxide debris were created from treated passive layer were. These hard oxides leaded to the pronounced abrasion forming the appearance of deep grooves. In addition, adhesive wear mechanism was observed in the wear tracks.

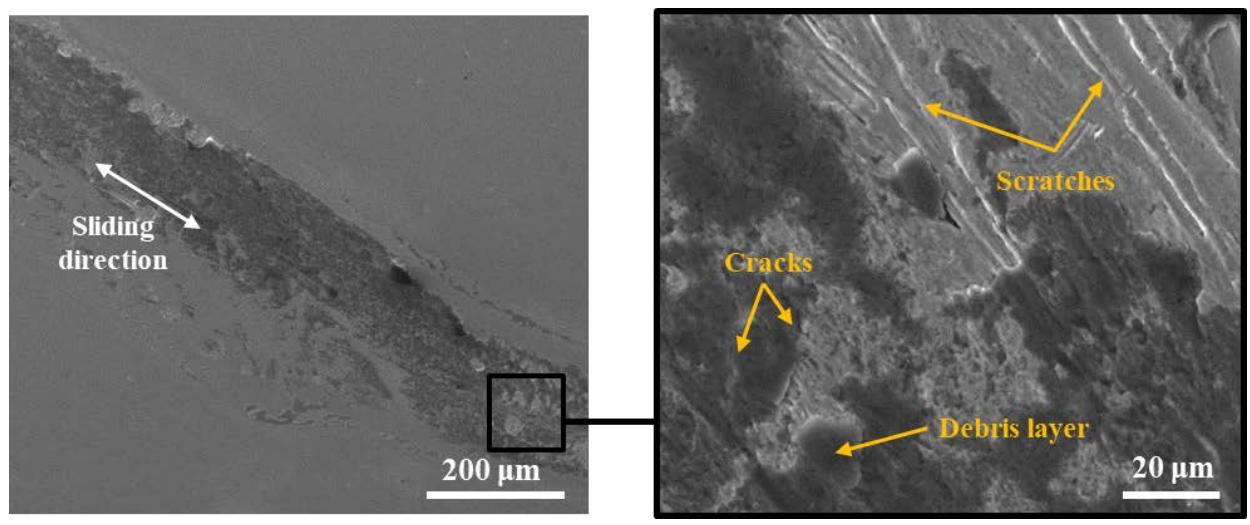


(a)



(b)

Fig. 9 SEM micrographs of the wear tracks observed in (a) NT and (b) NP samples under continuous sliding.



(a)

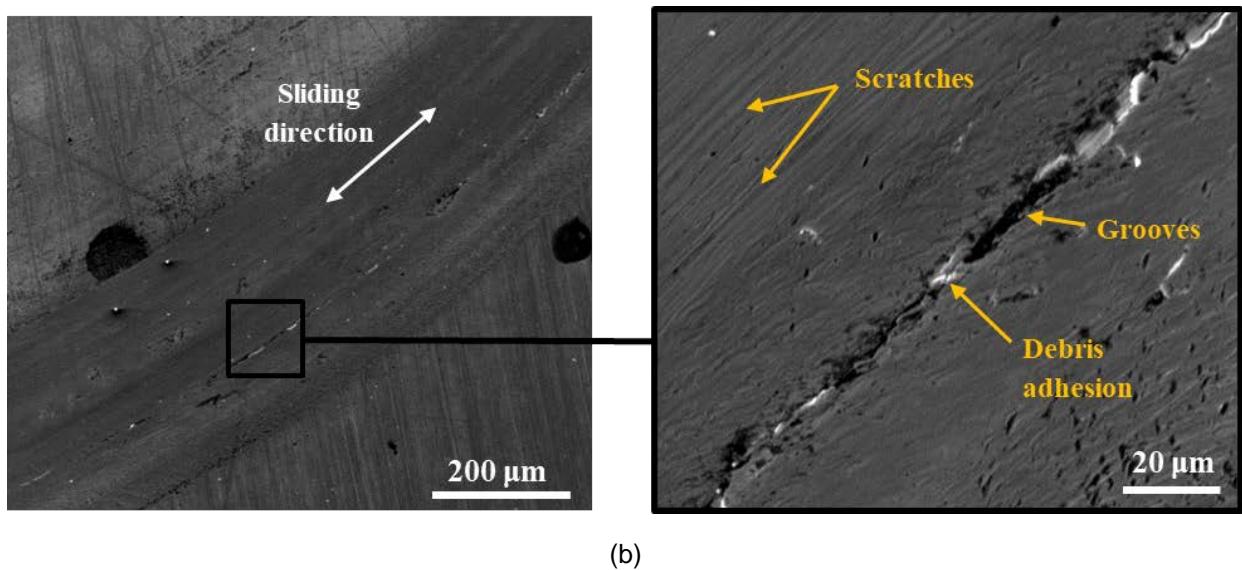


Fig. 10 SEM micrographs of the wear tracks observed on (a) NT and (b) NP samples under intermittent sliding.

The adhesive wear was proved by the formation of oxide debris on NT samples under continuous and intermittent sliding as shown in Fig. 9 (a) and 10 (a), respectively. The debris was oxidized and then delaminated by the adhesive sliding to form the oxide layer. The wear mechanism of the oxide layer was cracking and delamination through sliding. For NP samples, debris adhesion was presented in the wear tracks due to plastic deformation of the oxide debris between sliding surfaces under continuous and intermittent sliding as shown in Fig. 9 (b) and 10 (b).

### 3.6. Wear analyses

Typical tribocorrosion protocol was used to calculate the contribution of wears [37]. The total wear loss ( $W_{tr}$ ) is the amount of four components according to Eq. (1).

$$W_{tr} = W_{act}^c + W_{repass}^c + W_{act}^m + W_{repass}^m \quad (\text{Eq 1})$$

Where  $W_{act}^c$  is the mass loss of active material by corrosion,  $W_{repass}^c$  is the mass loss of repassivated material by corrosion,  $W_{act}^m$  is mass loss of active material by mechanical wear and  $W_{repass}^m$  is the mass loss of repassivated material by mechanical wear.

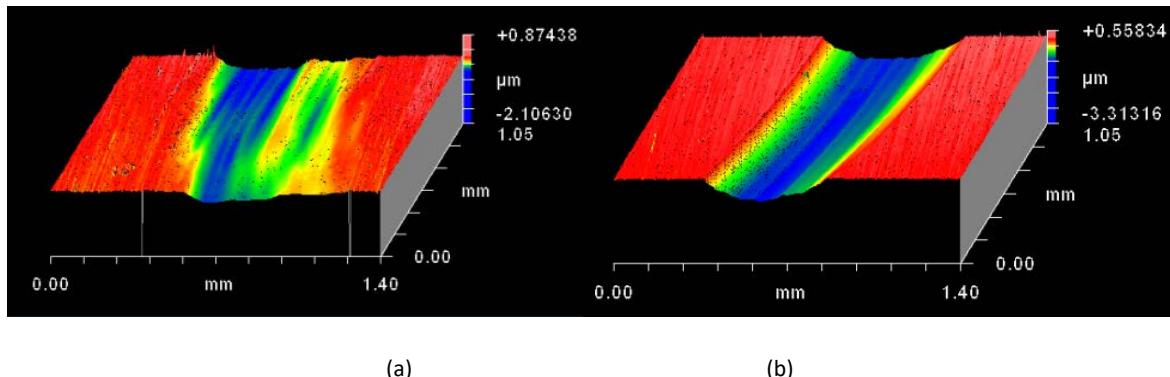


Fig. 11 3D plot wear track profile obtained on NT samples (a) under continuous and (b) intermittent sliding.

Fig. 11 and 12 show the 3D wear track profile obtained under continuous and intermittent sliding in NT and NP samples, respectively. Three 3D profiles were revealed from each wear track, which allowed determining the total volume of the wear track  $W_{tr}$ .

The total wear determined from topographical measurements is summarized in Fig. 13 and Table 2. From these results, one can conclude that the nanopeening treatment can

greatly improved the tribocorrosion of AISI 420 steel. Indeed, it enables a decrease of about 20 % on the total wear under both continuous and intermittent sliding.

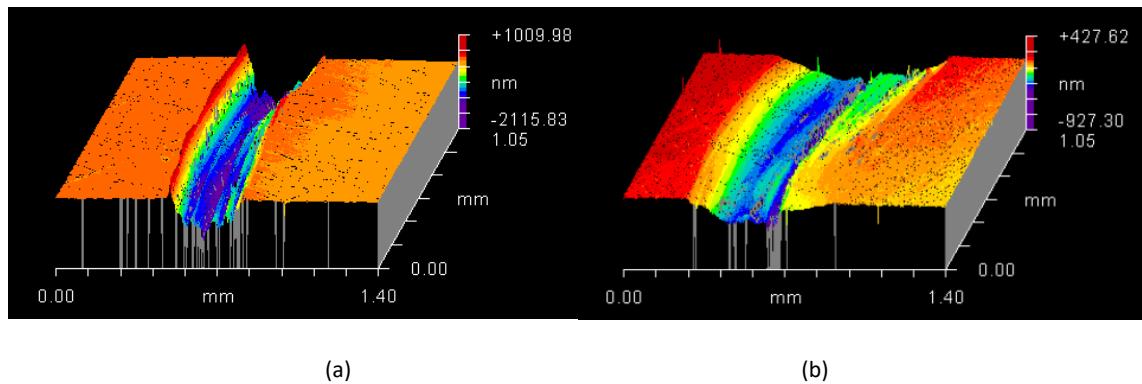


Fig. 12 3D plot wear track profile obtained on NP samples (a) under continuous and (b) intermittent sliding.

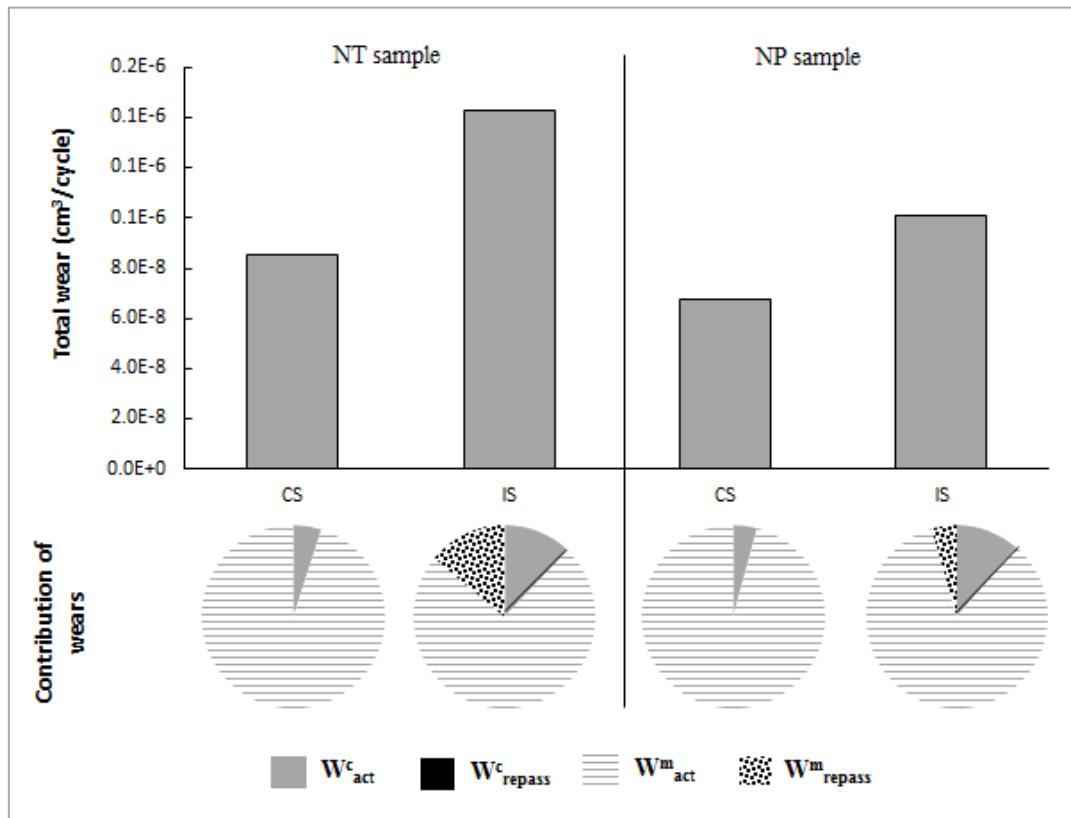


Fig. 13 Contribution of wear obtained on NT and NP samples under continuous and intermittent sliding against alumina pin (5 N, 120 rpm) in boric acid and lithium hydroxide solution.

Table 2 Tribocorrosion components obtained on NT and NP samples under continuous and intermittent sliding

Sliding	NT samples		NP samples	
	Continuous	Intermittent	Continuous	Intermittent
W <sup>c</sup> <sub>act</sub> (cm <sup>3</sup> /cycle)	4.24E-08	1.73E-07	2.86E-08	1.14E-07

$W_{repass}^c$ (cm <sup>3</sup> /cycle)	-	1.65E-11	-	6.89E-12
$W_{act}^m$ (cm <sup>3</sup> /cycle)	8.10E-07	1.06E-06	6.48E-07	8.49E-07
$W_{repass}^m$ (cm <sup>3</sup> /cycle)	-	1.99E-07	-	4.51E-08

Under continuous sliding, both ( $W_{act}^c$  and  $W_{act}^m$ ) contributions decreased with treatment (c.f. Table 2). However, the  $W_{act}^c/W_{tr}$  and  $W_{act}^m/W_{tr}$  ratios for both NT and NP samples were almost identical of about 0.04 and 0.9, respectively. Under intermittent sliding, the improvement of resistance wear was marked by the decrease of all contributions, especially mechanical ones  $W_{act}^m$  and  $W_{repass}^m$ . The mechanical resistance improvement led to a work-hardened and nano-grained surface layer. In fact, the impact of high-energy balls led to severe plastic deformation [45]. This mechanism contributed to the formation of nano-sized grains and hardness rise. In addition, the propagation of high density dislocations promoted the diffusion of Cr, Mo and Ni to form protective mixed oxides in the treated surface, which explain the higher content of those elements and consequently the corrosion resistant improvement [27, 46].

#### 4. CONCLUSIONS

The effect of nanopeening treatment on the tribocorrosion behavior of martensitic AISI 420 steel was studied in this work. The EBSD examinations showed that the nanopeening treatment produced a microstructural changes in the surface layer with a depth of about 110  $\mu$ m. A severe plastic deformation was obtained in the zone extended to 55  $\mu$ m from the top surface of samples in which the martensitic grains could not be identified. Therefore, the micro-hardness values in nanopeened sample (550 HV<sub>0.05</sub>) were higher than that obtained in the non-treated one (260 HV<sub>0.05</sub>).

The tribocorrosion tests were conducted, in pin-on-disc tribometer, at room temperature in boric acid and lithium hydroxide solution. The tests were carried out under continuous and intermittent sliding at constants load of 5 N and rotating speed of 120 rpm. The results showed that:

- Under both continuous and intermittent sliding, wear mechanism was dominated by abrasion and adhesion mechanism. However, the wear of nanopeened sample was dominated by abrasion, which may give rise to the effect of hard oxide debris.
- The three-dimensional surface profiles of the wear tracks were performed to determine the total wear loss. The tribocorrosion protocol was applied to calculate the different contributions of wear. The tribocorrosion behavior of AISI 420 was improved by applying the nanopeening treatment. Under continuous sliding, both mechanical and corrosion contributions of wear decreased with a similar contribution/total wear ratio. Under intermittent sliding, all wear contributions decreased after the treatment, which greatly ameliorated the mechanical resistance of repassivated surface.

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