



# Article Assessment of the Pitting, Crevice Corrosion, and Mechanical Properties of Low-Temperature Plasma-Nitrided Inconel Alloy 718

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Abstract: A comparative study on the mechanical properties, scratch resistance, and localized corrosion (pitting and crevice) of plasma-nitrided Inconel alloy 718 (UNS NO7718: IN 718) was carried out. Thermochemical treatment was performed at low temperatures (400 and 450 °C) for 4 h. The treatment formed layers with thicknesses of 7.17  $\pm$  0.89  $\mu$ m (400 °C) and 7.96  $\pm$  0.48  $\mu$ m (450 °C). The XRD and nanohardness analyses indicated the formation of a hard layer composed of the expanded austenite phase ( $\gamma_N$ ), CrN at 400 °C, and CrN +  $\gamma$  at 450 °C, with a maximum indentation hardness of 12 and 12.5 GPa, respectively, when compared to the 5 GPa substrate hardness. The scratching tests (2-8 N) showed that with increasing load, the nitrided surfaces had a transition from 100% microcutting to a combination of microplowing/cutting, with the presence of cracks. The critical load of the nitrided surfaces was 3 N for 400 °C and 4 N for 450 °C. The untreated condition maintained a crack-free combined mechanism regardless of the load. For the same load, the nitrided surfaces held lower coefficient of friction values and higher scratch resistance values, which were more pronounced at 450 °C. The linear polarization tests (3.56 wt.% NaCl) showed pitting corrosion in all samples, with the 450 °C condition being less resistant. Nitriding at 400 °C increased the crevice corrosion resistance of Inconel, while at 450 °C, it severely damaged it. Nitriding at 400 °C brought concomitant gains in hardness and scratch and crevice corrosion resistance when compared to the as-received IN 718.

Keywords: Inconel 718; plasma nitriding; nanohardness; scratch resistance; crevice corrosion

# 1. Introduction

Inconel 718 (UNS NO7718: IN 718) is a nickel-chrome-based austenitic superalloy hardened via precipitation [1]. It is commonly used in the aeronautic, aero-spatial, petrol, and gas industries [2–4]. These Ni-based alloys are widely employed in adverse conditions involving high pressure, temperatures between –250 and 750 °C, and aggressive environments, showing good corrosion resistance [1,2,5,6]. However, it also exhibits poor wearing performance, limiting its use in several applications [7].

Plasma nitriding has been established for decades as a successful method in surface engineering [8]. It aims to modify metallic alloy surfaces by introducing nitrogen to improve their tribological performance. When treated at low temperatures, a hard supersaturated interstitial solid solution layer (known as nitrogen-expanded austenite  $\gamma_N$  or S phase) might form on the surface of stainless steels [8–13] and Ni-Cr alloys [1,3,6,7,14–16]. When compared to the number of studies on stainless steel nitriding, as reviewed, for example, in [8], the research on Inconel alloy nitriding is sparse. Surface modification via the nitriding of



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). IN 718 has been developed through various techniques. Regardless of the type of nitriding, when it is carried out at temperatures  $\leq 450$  °C, the formation of a  $\gamma_N$  phase has been confirmed [1,3,6,7,14–17]. However, nitriding at a higher temperature (>450 °C) formed deleterious phases, identified as CrN, without the  $\gamma_N$  phase [4,6,7,14–16,18]. As for stainless steel nitriding, the growth in the layer thickness with increasing temperature or time was widely reported [7,14,18,19], following diffusion-controlled parabolic growth [6,19]. According to [18], time was more effective than temperature for increases in thickness. Besides, upwards of a two-fold hardness increase due to nitriding treatment is in agreement with all studies evaluating nitrided IN 718 Vickers microhardness, regardless of the layer thickness and composition [3,4,6,7,14–16,19]. Refs. [1,3–8,14–16,18] and Table 1 summarize the existing studies on the nitriding methods applied to IN 718 alloy, which evaluated wear and corrosion performance.

Table 1. Summary of Inconel 718 alloy nitriding research results in chronological order.

Ref.	Nitriding Process	Summar	y of Results
[19]	Plasma nitriding T; t: 550 to 750 °C; 1 to 16 h P: 8 mbar/6 Torr %: N <sub>2</sub> :H <sub>2</sub> ; 1:1, 1:3, 3:1, and 9:1	W	(Dry pin-on drum)—The nitride layer reduced the friction coefficient (CoF) by 3.7 times. Wear volume increase of up to 60% in nitrided samples, ascribed to the substrate fracture and separation.
[14]	Intensified plasma-assisted processing (IPAP). T; t: 450 and 490 °C; 3 h P: 50 mTorr	W	(Dry pin-on disc) The average CoF for the unprocessed and nitrided alloy is comparable, but the latter showed a tremendous improvement in wear resistance.
[1]	%: N <sub>2</sub> :Ar; 4:1 V: -1000 V	С	Open circuit potential (OCP): 0.1 N NaCl. The higher potential of nitrided IN 718 (+200 mV vs. $-25$ mV for untreated) suggests that IPAP nitriding at 450 °C has a beneficial effect on corrosion resistance.
[18]	Plasma DC T; t: 400 to 600 °C; 1 and 4 h. P: 500 Pa/3.75 Torr %: N <sub>2</sub> :H <sub>2</sub> ; 1:1 V: 500 V	W	(Dry pin-on disc) The CoF also decreased with hardness growth. The untreated specimens exhibit the highest wear rate that decreased upon an increase in the nitriding time and temperature.
[6]	Salt Bath nitriding—molten salt ( $M_2CO_3$ : M: K, Na, etc.), (CO(NH <sub>2</sub> ) <sub>2</sub> ), others. T; t: 425 to 500 °C; 4 to 16 h	W/C	(Erosion-corrosion: $3.5\%$ NaCl + $5 v\%$ H <sub>2</sub> SO <sub>4</sub> + Al <sub>2</sub> O <sub>3</sub> )—mass loss reduction (up to 77%) in samples nitrided up to 475 °C. Treatment at 500 °C increased mass loss from 1.5 to 3.25 times.
[1]	Ultrasonic nanocrystal surface modification (UNSM) and Gas nitriding (GN) T; t: 460 °C; 5 h	W	(Sliding dry wear: high-frequency reciprocating) Up to 98% reduction in the wear volume in both nitriding conditions. CoF remained around 0.8 in all conditions.
	P: 1 atm/760 Torr %: Ammonia	С	Both treatments increased corrosion resistance in Tafel tests (3.5% NaCl).
[4]	Liquid nitriding: KCNO, NaCNO, KCl, NaCl, K <sub>2</sub> CO <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , and Li <sub>2</sub> CO <sub>3</sub> T; t: 500 °C; 16 h	W/C	(Dry Ball-on-disk: at 25, 100, and 200 °C)—wear rate reduction of around 99.9% at all temperatures. (Erosion-corrosion: 3.5% NaCl + 5 HCl + SiO <sub>2</sub> )—nitrided alloy exhibits an improvement of almost 80.3% in the erosion-corrosion resistance compared with its untreated counterpart.

Ref.	Nitriding Process	Summar	ry of Results
[7]	Hot wall plasma nitriding (HWPN) T: t: 400, 450, and 500 °C: 6 h	W	(Pin-on disk)—The wear rates of samples nitrided at 400, 450, and 500 $^{\circ}$ C were about 3, 4, and 6 times lower compared to the untreated, and the CoF was reduced from 1 to 0.55.
[7]	P: 4 mbar/3 Torr %: N <sub>2</sub> :H <sub>2</sub> ; 3:1	С	(Tafel 3.5% NaCl)—the 400 °C-samples showed the highest potential ( $E_{corr}$ ) and lowest corrosion density ( $i_{corr}$ ), followed by 450 °C. Higher $i_{corr}$ and same $E_{corr}$ for 500 °C-samples compared to the untreated ones.
[3]	Arc Enhanced Glow Discharge plasma nitriding T; t: 450 °C; 1 to 2 h P: 0.01 mbar/0.75 Torr %: N <sub>2</sub> :Ar; H <sub>2</sub> ; 1:5.2:0.4 V: -250 V	W	(Dry pin-on disk)—nitriding increased the wear resistance significantly, so wear was not measurable.
[15]	Triode plasma nitriding (TPN) T: 400, 425, and 450 °C/700 °C t: 4 and 20 h/1, 2 and 4 h P: 0.4 Pa/0.03 Torr %: N <sub>2</sub> :Ar; 7:3 V = -200 V	С	(Linear polarization 0.1N NaCl)—Samples nitrided at 400 and 450 °C for 20 h kept the electrochemical behavior of the untreated sample, while the one nitrided at 700 °C-1 h reduced passivation considerably and increased i <sub>corr</sub> 11.5 times.

Table 1. Cont.

T: temperature, t: time, P: pressure, %: gas mixture composition, W: wear, and C: corrosion.

The results obtained (Table 1) revealed that several nitriding methods are effective for increasing IN 718 tribological performance and corrosion resistance when carried out at low temperatures ( $\leq$ 450 °C). These improvements are associated with  $\gamma_N$  formation. Another finding was that, unlike stainless steel nitriding [8,9,13,20], the precipitation of Cr nitrides in the Inconel nitrided layer does not always hamper corrosion resistance [1,6,14–16]. The explanation for this fact has not been reported.

In the literature, few studies evaluate crevice corrosion in Ni-based alloys [21,22]. Among the reports found, the study developed by Mulford and Tromans [21] on IN 600 and IN 625 stands out, and their results showed that although both alloys were resistant to crevice corrosion (at 20, 55, and 80 °C), IN 625 was more resistant due to Mo addition in the alloy. Miller and Lillard [22] found out that the higher the potential applied to the IN 625 alloy was (E < 0.40 V vs. SCE), the shorter the time for the appearance of crevice corrosion. It seems relevant to emphasize that the Inconel alloy nitriding studies listed above (Table 1) did not present crevice corrosion analyses. In fact, crevice corrosion evaluation is also scarce in nitrided stainless steel [9,10,20] despite nitrogen's beneficial and proven effects on this type of corrosion [23–26]. Thus, evaluating the IN 718 nitriding effect on this type of corrosion is necessary.

The literature review showed that the evaluation of wear had been addressed through various tests listed in Table 1, among which the scratch test has yet to be reported. Furthermore, few investigations evaluated the corrosion resistance of nitrided IN 718. It was studied through open circuit potential, the Tafel curve, and linear polarization tests. This panorama demonstrates that there are still several gaps to be filled in the characterization of nitrided IN 718. This study investigates the viability of nitriding a Ni53/Cr19/Fe19 (IN 718) alloy using DC plasma nitriding in an N<sub>2</sub>–H<sub>2</sub>–Ar atmosphere. Based on the literature (Table 1), two treatment temperatures were selected: 400 °C and 450 °C. This paper evaluates the scratch wear and pitting and crevice corrosion resistance in nitrided samples and correlates them with the microstructural and topographical characterization of the nitrided and untreated surfaces.

# 2. Materials and Methods

# 2.1. Materials

The material studied was an IN 718 (UNS NO7718) alloy, as received by the manufacturer (solubilization at 1089 °C for 1 h, followed by aging at 788 °C for 7 h). The alloy chemical composition was determined using the positive material identification technique (PMI, X-ray fluorescence XRF: Olympus Vanta series M, (EVIDENT EUROPE GMBH, Hamburg, Germany) (Table 2). The IN 718 was received in bars 14.6 cm in diameter, from which the 5 mm-thick disks were obtained via wire electro-erosion. Then,  $20 \times 20 \times 5 \text{ mm}^3$  pieces were produced via waterjet cutting.

Table 2. Percentages (wt.%) of the IN 718 alloy main elements.

Ni	Cr	Fe	Nb	Мо	Ti	Al	Со
53.45	18.28	18.81	4.94	2.83	0.93	0.5	0.23

# 2.2. Low-Temperature Plasma Nitriding (LTPN)

The samples were sanded using SiC paper up to #1200 in grain size. Next, they were cleaned with pure acetone in an ultrasound bath and dried in warm air. The samples were then immediately placed inside a pulsed cold wall DC reactor similar to the one used in previous research [10–13]. The plasma nitriding treatment was carried out in two phases (Table 3). The first phase was sputtering, which aimed to remove the passive layer and clean the surface. The second phase was the nitriding treatment at 400 °C and 450 °C, named N400 and N450, respectively. Cross-sections of the nitrided samples were prepared metallographically and attacked with oxalic acid (10% m/v, H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), applying a 5 V voltage for 10–15 s.

#### Table 3. Conditions of the low-temperature plasma-nitriding process.

Condition	Sputter-Cleaning	DC Plasma Nitriding
Gas mixture $N_2/H_2/Ar$ (%)	0/75/25	75/20/10
T <sub>on</sub> (µs)	170-230	95–110 (400 °C), 160–200 (450 °C)
T <sub>off</sub> (μs)	210-250	250
Treatment time (h)	0.5	4
Temperature (°C)	300	400 (N400), 450 (N450)
Peak voltage (V)	500	500
Pressure (Torr)	2.5	2.8
Total gas flow rate (SCCM)	200	200

#### 2.3. X-ray Diffraction (XRD)

After the LTPN treatment, the phases formed in the nitrided layer were identified using grazing incidence X-ray diffraction (GIXRD: Shimadzu, model XRD-7000, Shimadzu Corporation, Tokyo, Japan) with Cu-K $\alpha$  radiation ( $\lambda = 1.54060$  Å; 30 kV; 30 mA) and a 3° incidence angle. The measurements were performed at the top of the sample's surface over the 2 $\theta$  range from 30° to 80°. The phase constituents of the XRD spectra were identified by comparing them with crystallographic powder data based on JCPDS cards: for austenite ( $\gamma$ ), 00-006-0696, and for chrome nitrides, 00-011-0065. The identification of the nitrogenexpanded ( $\gamma_N$ ) peaks was based on the literature [1,3,6,7,14–16]. The penetration depths for the angles (2 $\theta$ ) of 43.5° and 50.58° corresponding to the peaks of  $\gamma$ (111) and  $\gamma$ (200), respectively, were approximately 5.51 µm and 6.15 µm. These values were calculated using the X-Ray attenuation length tool available at CXRO (The center for X-ray optics, Berkeley, CA, USA) [27], considering Cu-K $\alpha$  radiation and 2 $\theta$  incidence. The depths were determined by considering the four main elements (Ni, Fe, Cr, and Nb) for the stoichiometric fraction of the IN 718 alloy. Additionally, the depth of  $2\theta = 37.5^\circ$  of the CrN compound was calculated,

assuming a layer composed solely of CrN, resulting in 4.30  $\mu$ m. These calculations were performed for 2 $\theta$  incidence.

#### 2.4. Microscopy Techniques

Optical microscopy (MO: Olympus BX51RF, Olympus Corporation Shinjuku Monolith, Tokyo, Japan) and scanning electron microscopy (SEM: Zeiss, model EVO MA 15, Carl Zeiss Ltd., Cambridge, UK) were employed to determine the layer thickness and to observe the microstructure and surfaces after the corrosion and scratch tests. Nitrogen profiles (weight percentage: wt.%) of the cross-sections were acquired using high-resolution field emission scanning electron microscopy FE-SEM (Tescan Lyra 3, TESCAN ORSAY HOLDING, Brno— Kohoutovice, Czech Republic) via energy-dispersive X-ray spectroscopy (EDX, Oxford XMAX 80, Aztec Software Oxford SP1 3.3, NanoAnalysis, Wiesbaden, Germany). Four linear EDX analyses and two mapping EDX analyses were performed for each nitriding condition on the cross-section of the samples at 15,000× magnification.

#### 2.5. Indentation Hardness

Hardness measurements were carried out at the top of the samples using instrumented nano-indentation equipment (Zwick-Roell ZNH nanoindenter<sup>®</sup>, GmbH & Co. KG, Ulm, Germany). The quasi-continuous stiffness measurement (QCSM) method was employed to measure hardness as a function of the tip penetration during loading. The QCSM method increases the accuracy of measurements when compared to cyclic load-unload typical tests [28]. This technique is ideal for measuring the mechanical properties of thin films, which change with indentation depth, such as in surface modification thermochemical treatments [28]. A diamond tip with Berkovich geometry was used, and the load was gradually increased over 24 cycles up to the 1000 mN (100 g) maximum load. A matrix of 25 indentations separated by a 100 µm gap was delineated in the regions of interest.

# 2.6. Scratch Test

Linear scratch tests were performed using a tribometer (CETR-UMT-2MT s/n T1471 Bruker Nano Inc., Campbell, CA, USA), applying a 2–8 N constant load at a speed of 0.017 mm/min. Three scratches (5 mm in length) were produced per load in each load/sample condition combination. The conical stylus (diamond Rockwell C) has an apex angle of 120°, and the cone ends in a hemispherical tip 200  $\mu$ m in radius. The friction coefficient (CoF) was recorded during scratching using a coupled load cell, which automatically measures tangential force and controls the normal force.

Scratch resistance was determined via the scratch hardness number ( $HS_P$ , in Pa) and abrasion factor ( $F_{ab}$ , nondimensional). The  $HS_P$  was determined following ASTM G171, according to Equation (1) [29]. A total of 25 measurements for scratch width were determined for each load/sample condition using an optical microscope with an incident light polarization filter (OM: Olympus BX51RF, Olympus Corporation Shinjuku Monolith, Tokyo, Japan).

$$S_{\rm P} = \frac{8P}{\pi w^2} \tag{1}$$

where P = normal force (N) and w = scratch width (m).

The friction factor ( $F_{ab}$ ) was determined following the procedures described by Rovani et al. [30]. The  $F_{ab}$  calculation followed Equation (2) [31].

H

$$F_{ab} = \frac{\text{area of groove} - \text{area of pile} - \text{up}}{\text{area of groove}}$$
(2)

The surface topography before and after the nitriding treatments was determined using an optical interferometer (Talysurf CCI Lite, M12-3993-03, green light, Taylor Hobson, Leicester, UK). The scratch cross-sections were determined by setting a  $0.8 \times 0.8$  mm<sup>2</sup> measurement area using  $1024 \times 1024$ -pixel resolution. Three measurements per load/sample condition combination were carried out in the scratch central region. The scratch 3D topog-

raphy and the surrounding flat surface were measured. Next, the mean plane was defined based on the unscratched area only. Finally, the groove and pile-up areas were calculated using the "profile extraction" tool by TalyMap<sup>®</sup> (Taylor Hobson, Leicester, UK).

# 2.7. Electrochemical Techniques

For all localized corrosion tests, the samples were first mounted in epoxy resin, aiming to expose the region of interest with a 2.2 cm<sup>2</sup> fixed area. All potentials refer to the reference electrode: saturated calomel (SCE). A graphite bar was the counter electrode. All tests were evaluated in a NaCl 3.56 wt.% aerated solution at  $20 \pm 2$  °C and started after the open circuit potential (OCP) stabilization for an hour. Each experiment was repeated at least three times in order to check the reproducibility, and the scatter in the data was reported.

#### 2.7.1. Linear Polarization

Tests were performed in a glass cell filled with 150 mL solution. The potentiodynamic scanning (1 mV/s) started at -0.2 V vs. OCP and ended when reaching the transpassivation region (5000  $\mu$ A/cm<sup>2</sup> [32]). The main corrosion parameters, such as corrosion potential (E<sub>corr</sub>) and corrosion current density (i<sub>corr</sub>) in the Tafel region, passivation current density (i<sub>pass</sub>), and pitting potential (E<sub>pit</sub>), were determined according to the literature [10,13,32,33].

# 2.7.2. Potentiostatic Polarization

Potentiostatic polarization tests at 1.0 V were performed to evaluate susceptibility to crevice corrosion. This potential was chosen for comparison purposes since it is at the end of the untreated IN 718 passivation region. A Teflon crevice-former presenting three  $2.25 \times 6.25 \text{ mm}^2$  rectangular areas each was used. The contact between the crevice-former and the mounted sample surface was reached by applying 0.5 N torque with a nylon screw. The 3D topography of the crevice corrosion marks was analyzed using 3D interferometry.

#### 3. Results

# 3.1. X-ray Diffraction and Thickness Layer Analysis

The nitriding process formed a homogeneous and continuous layer (Figure 1). As reported in several studies [1,3,4,15,16,18,19], the nitriding treatments generate an outstanding superficial nitride layer (Figure 1). Growth in layer thickness with increasing temperature, as widely reported in the literature [7,14,18,19], was observed. However, the increase was insignificant in this case when considering the standard deviation in Figure 1. The high dispersion in the N400 condition is associated with the noteworthy differences in the layer thickness influenced by the crystallographic orientations of the austenitic microstructure (Figure 1a), which has also been reported in other studies [6,16]. The arrows in Figure 1 indicate the presence of intermetallic precipitates, mainly composed of Ni, Al, Ti, and Nb. Their semi-quantitative compositions were identified using SEM-EDX, for which the values (wt.%) ranged from 0.99–50.89% for Ni, 0.27–0.44% for Al, 1.02–5.65% for Ti, and 4.74–72.65% for Nb. Those intermetallic compounds, known as  $\gamma'/\gamma''$ , resulted from the IN 718 precipitation hardening treatment.

Figure 2 shows SEM cross-section micrographs on the left side, their respective EDX line scans, and the EDX maps for nitrogen on the right side. The nitrogen concentration (wt.%) as a function of depth from the surface shows a plateau trend, which correlates with the thickness of the nitride layer for both samples. The nitrogen content ranges from 2 to 10 wt.% in both nitrided layers (Figure 2). These results are consistent with the nitrogen distribution obtained through EDX mapping.



**Figure 1.** Cross-section OM micrographs of the nitrided layers at (**a**) 400  $^{\circ}$ C and (**b**) 450  $^{\circ}$ C. Nitrided layer thickness values correspond to the white layer that stands out from the substrate.



**Figure 2.** Cross-section SEM micrographs, their EDX line scans, and mapping for nitrogen (wt.%): plasma nitriding at (**a**) 400 °C and (**b**) 450 °C.

Figure 3 shows the X-ray diffraction spectra of the material, as received from the manufacturer, and the nitrided conditions. Nitriding at 400 °C generated a layer composed of N-expanded austenite ( $\gamma_N$ ), chromium nitride (CrN), and austenite ( $\gamma$ , with increased full width at half maximum (FWHM)), which agrees with several works on IN 718 treated with LTPN [1,3,6,7,14,15]. However, nitriding at a higher temperature (450 °C) formed deleterious phases that were identified as CrN without the  $\gamma_N$  phase, as reported in other studies, and this increased the temperature or treatment time [4,6,7,14–16,18]. The broader,

asymmetric, and lower intensity austenite peaks  $\gamma$  in the N400 and N450 spectra do not represent substrate influence since the XRD penetration depths are less than the nitrided layer thickness (details in Section 2.3) [3,15].



Figure 3. X-ray diffraction patterns.

The lattice parameters of intermetallic precipitates, such as  $\gamma'(Ni_3(Al,Ti))$  and  $\gamma''(Ni_3Nb)$ , are similar to those of the  $\gamma$  matrix and, therefore, cannot be resolved under XRD (Untreated: Figure 3) [3,15]. Regarding this finding, Tao et al. [15] identified the formation of N-modified precipitation-strengthening phases using grazing-angle XRD and TEM analysis. The appearance of nitrided  $\gamma'/\gamma''$  or N-modified intermetallic precipitates was not confirmed in this study.

# 3.2. Indentation Hardness and Scratch Resistance

Indentation hardness was measured on the top of the sample surfaces. The nitrided samples showed higher hardness profiles when compared to the as-received IN 718 (Figure 4a). The indentation size of both N400 and N450 (Figure 4c,d) was reduced when compared to the untreated samples (Figure 4b). Increased hardness on the surface nitrided at 400 °C is explained by the formation of the  $\gamma_N$ , for which nitrogen saturation increased crystalline lattice stress [3,4,6,7,15,16]. However, the presence of CrN precipitates in the N400 layer also contributes [3,14,15]. On the other hand, the hardness of N450 is related to hard compound-layer (CrN) formation; the distribution of this within the layer prevents free dislocation movement, which has been extensively studied [3,7,14,16,18,19]. It is relevant to highlight that the Berkovich tip penetration depth remained within the nitrided layers (Figure 4a) but beyond 10% thickness [28]. Consequently, the substrate influenced the indentation measurement in both of the nitriding surfaces.

Moreover, the micrographs in Figure 4c–d exhibited the topography of the grain boundaries on the nitrided surfaces in contrast with the untreated sanded topography (Figure 4b). Further topographic information can be found in Table 4. The parabolic profile of the indentation hardness profiles as a function of depth (Figure 4a) responded to the significant effect of surface roughness due to nitriding treatment, as reported in other studies [3,14,15,18,28]. In addition, the indentations in the rougher nitrided surfaces also showed the non-negligible dispersion of the indentation hardness depth curves.



**Figure 4.** (a) Indentation hardness curves as a function of the indentation depth (QCSM method) (Error bars represent standard deviation). Instrumented nano-indentation matrix with enlarged indentation mark: (b) untreated; (c) N400; (d) N450.

**Table 4.** Roughness results (±represents standard deviation):  $S_q$  (root mean square height),  $S_{sk}$  (skewness),  $S_{ku}$  (kurtosis),  $S_z$  (maximum height),  $S_{dq}$  (root mean square surface slope), and  $S_{dr}$  (developed interfacial area ratio).

Condition	S <sub>q</sub> (μm)	$S_{sk}$	S <sub>ku</sub>	S <sub>z</sub> (μm)	S <sub>dq</sub>	S <sub>dr</sub> (%)
Untreated	$0.0127 \pm 0.0009$	$-0.19\pm0.03$	$4.14\pm0.09$	$0.151\pm0.006$	$0.0116 \pm 0.0008$	$0.0067 \pm 0.0009$
N400	$0.0148 \pm 0.0002$	$0.11\pm0.08$	$4.58\pm0.24$	$0.228\pm0.011$	$0.0135 \pm 0.0004$	$0.0091 \pm 0.0005$
N450	$0.0146 \pm 0.0002$	$-0.02\pm0.03$	$3.58\pm0.06$	$0.174\pm0.004$	$0.0138 \pm 0.0001$	$0.0095 \pm 0.0002$

Scratch resistance was evaluated by producing constant load scratches from 2 N to 8 N on the sample surfaces. The first column in Figure 5 shows the topography results obtained using 3D interferometry before the test. The results of roughness characterization are presented below (Table 4). The second column in Figure 5 corresponds to the 3D reconstruction of a scratch section. The reconstruction of the mean cross-section profile along the scratch is shown in the third column. The results shown (Figure 5) correspond to a representative sample of each condition evaluated at 8 N. The same procedure was adopted for all loads (2–8 N), the results of which are summarized in the graphs below (Figure 6).



**Figure 5.** A sequence of surface analysis using 3D interferometry before and after the scratch tests: initial topography and the reconstruction of scratches and their cross-sections: (**a**) untreated, (**b**) N400, (**c**) N450 (the results presented in this figure correspond to the 8 N load).



**Figure 6.** (a) Scratch depth as a function of abrasion factor ( $F_{ab}$ ). (b) Coefficient of friction as a function of the scratch hardness (HS<sub>P</sub>). Error bars represent confidence intervals.

Table 4 shows the most relevant roughness parameters describing the topographic changes due to the nitriding process. The S<sub>q</sub>, S<sub>z</sub>, S<sub>dq</sub>, and S<sub>dr</sub> values of N400 and N450 confirmed a general increase in roughness. S<sub>dq</sub> is a general measure of the slopes that compose the surface. S<sub>dr</sub> represents the percentage of the additional surface area contributed to by the texture in comparison with an ideal plane of the measurement region. Both results are coherent with the grain boundary topography observed in the reconstruction in Figure 5b,c. In particular, the surfaces nitrided at 450 °C are characterized as being normally distributed since S<sub>sk</sub> and S<sub>ku</sub> are close to 0.00 and 3.00, respectively. Thus, the topography developed in N400 is characterized by the predominance of peak structures (S<sub>sk</sub> > 0), which agrees

with the presence of excessively high peaks ( $S_{ku} > 3.00$ ) and the maximum surface heights (highest  $S_z$ ).

The graph below (Figure 6a) depicts the scratch depth (in the cross-section) as a function of the abrasion factor ( $F_{ab}$ ) in all sample conditions and loads. The  $F_{ab}$  values indicate the predominant scratch wear mechanism. As shown in Figure 6a, a zero (0) value indicates pure microploughing wear, while a value of one (1) represents pure microcutting wear (Figure 6a). During the scratch tests, the friction coefficient (CoF) was recorded, and the results (as a function of scratch hardness (HS<sub>P</sub>)) are represented in Figure 6b for all conditions.

All samples showed increased scratch penetration as a function of load increase (Figure 6a). Regarding IN 718 (untreated), we observed that  $F_{ab}$  hardly depends on the load, keeping values around 0.25–0.4, showing a tendency for plastic deformation mechanisms without crack formation (microploughing). The nitrided surfaces presented cracks at the sides of the scratches from the 3 N load for N400 and from 4 N in N450. At low loads, the pure microcutting mechanism operates in both nitrided conditions, within the 2–4 N range for N400 and only 2 N in N450. From the loads mentioned, a mixed mechanism predominates with a plowing tendency when the load grows. When considering the penetration depth, the substrate did not influence the tests up to 4 and 5 N in N400 and N450, respectively. This occurred because the scratch depth did not exceed 10% of the nitride layer thickness [28]. Consequently, from those loads upwards, the substrate influenced the abrasion response on the nitrided surfaces.

At similar loads, the CoF (Figure 6b) was always lower for the nitrided surfaces when compared to the untreated ones. In addition, the CoF values were lower in the N450 condition when compared to N400. The surface hardening effect (Figure 6b) as a result of nitriding was observed since the nitrided surfaces presented higher scratch hardness values  $(HS_p)$  than those observed on the untreated surface. Additionally, the N450 condition showed a tendency for higher HS<sub>p</sub> mean values when compared to N400.

## 3.3. Linear Polarization

The most representative polarization curves of each condition are presented in Figure 7. The most relevant corrosion parameters are shown in Table 5. The tests revealed that the general corrosion resistance, measured based on the  $i_{corr}$ ,  $E_{corr}$ , and  $C_o$  parameters, is comparable between the untreated and the N450 conditions. The N400 samples showed  $E_{corr}$  values close to that of the untreated material and higher  $i_{corr}$  and  $C_o$  values. An increase of several orders of magnitude was observed for current density from E > 0.25 V in the nitrided conditions (Figure 7). Regarding N450, the appearance of bubbles on the surface of the samples was observed due to water oxidation reactions and the hydrolysis of the alloy metals [10,33]. Simultaneously, on the auxiliary electrode's surface, bubbles ascribed to oxygen and water reduction reactions were also observed from E > 0.25 [33]. The phenomena described did not occur when the current density increased in the N400 condition (E > 0.30 V). Therefore, it is possible to affirm that in the 0.65–1.00 V potential range for N400, second passivation occurred—actually, a pseudo-passivation—since the current was ~100  $\mu$ A/cm<sup>2</sup> (Table 5).

The micrographs (Figure 8) evidenced that the passivation layer failure occurred mainly due to the localized pitting corrosion in all samples. For this reason, the passive layer breakdown potential was named  $E_{pit}$  in the curves of Figure 7 and Table 5. The N450 nitriding revealed a sharp decrease in pitting resistance, observed as (i) a significantly lower  $E_{pit}$  value when compared to the untreated and N400 samples (Table 5); (ii) the formation of larger pits (Figure 8c), and (iii) greater pit nucleation density. On the other hand, the N400 samples showed slightly lower  $E_{pit}$  values than those presented by the untreated IN 718 (Table 5). On both nitrided surfaces, the pits were observed as starting mainly at the grain boundaries and were larger than those found in IN 718. However, the N400 condition showed lesser pit density when compared to the untreated and N450 conditions.



**Figure 7.** Polarization curves of untreated and nitrided samples (3.56 wt.% NaCl,  $20 \pm 2$  °C, 1 mV/s).

	Fable 5. Summary of	f E <sub>corr</sub> ,	icorr, (	$C_0$ , $i_{\text{pass}}$ ,	and Epit	parameter values	$(\pm r\epsilon)$	presents stand	ard c	deviation	).
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Parameter	Untreated	N400	N450				
E <sub>corr</sub> (V)	$-0.174 \pm 0.037$	$-0.14\pm0.02$	$-0.13 \pm 0.03$				
$i_{corr}$ ( $\mu A/cm^2$ )	$0.015\pm0.002$	$0.025\pm0.001$	$0.015\pm0.003$				
$C_o \text{ (mm/year)} \times 10^{-4}$	$1.57\pm0.24$	$2.55\pm0.12$	$1.59\pm0.35$				
Passivation region (V)	0.00-1.00	0.00–0.25 * 0.65–1.00	0.00-0.25				
$i_{pass}$ ( $\mu A/cm^2$ )	$4.827\pm3.432$	$0.26 \pm 0.15 \ * 176 \pm 44$	$0.141\pm0.091$				
E <sub>pit</sub> (V)	$1.131\pm0.004$	$1.109\pm0.005$	$0.26\pm0.042$				
*—Pseudo-passivation.							



**Figure 8.** Micrographs of surfaces after the linear polarization tests: (**a**) Untreated, (**b**) N400 and (**c**) N450.

## 3.4. Crevice Corrosion

The potentiostatic polarization curves with crevice formers are shown in Figure 9 (representative curve of each sample). The N400 condition showed lower current densities than the untreated material, presenting improvements in crevice-corrosion resistance. However, the N450 condition showed very high current densities, reaching 50,000  $\mu$ A/cm<sup>2</sup> from the beginning of the polarization. Such densities indicate very high corrosion rates that go over the potentiostat tolerance limit, provoking the suspension of the measurement.



Figure 9. Potentiostatic polarization curves (1.00 V) in tests with crevice-former.

Crevice corrosion marks are seen in Figure 10. A reconstruction of the micrographs of the corrosion marks obtained using optical microscopy is shown in Figure 10 (center). On the left of Figure 10, the details of a corroded region analyzed using 3D interferometry can be observed. The micrographs of the untreated and N400 conditions revealed that the corrosion occurred preferentially on the boundaries of the crevice-former. The 3D interferometry analysis only evidenced a severe and profound attack in the untreated material (Figure 10a). The N400 samples did not present deep crevice corrosion but had extended corrosion in the surrounding areas of the crevice-former's contour (Figure 10b).



**Figure 10.** Potentiostatic polarization curves (1.00 V) of tests with crevice former: (**a**) untreated, (**b**) N400, and (**c**) N450.

The N450 sample tests were interrupted due to high current densities: only a few seconds were enough to generate corrosion on the whole surface, as observed in the

macrography (Figure 10c) (right side). Pitting corrosion was not observed inside or outside the crevice areas in any sample. This finding confirms that the potentiostatic test at 1.00 V exclusively evaluated the behavior of the material concerning the localized crevice corrosion.

## 4. Discussion

# 4.1. X-ray Diffraction and Thickness Layer Analysis

The modification of surfaces of Inconel alloys using nitriding has been developed through different techniques (Table 1). The main common microstructural changes observed in Inconel alloy nitriding studies are (i) the dislocation, loss of symmetry, and generalized widening of the  $\gamma(111)$  and  $\gamma(200)$  crystallographic peaks in the XRD spectrum (Figure 3); (ii) the presence of CrN and  $\gamma_N$  peaks (Figure 3); (iii) the formation of a nitride layer differentiated from the substrate (Figure 1).

Regarding the first change, (i) the peak characteristics indicate an alteration in the crystalline lattice parameter due to the introduction of nitrogen via microstresses, non-homogeneous chemicals, and microstructural composition, or the residual stress related to chemical gradients and crystalline lattice anisotropic expansion [3,6–8,10,11,13,34]. The peaks referring to the  $\gamma_N$  phase (Figure 3) appear due to the formation of the nitrogen interstitial solid solution in the austenitic structure of Inconel alloys, as reported by [1,3,6,7,14,15]. Regarding the second change (ii), the simultaneous presence of peaks referring to the CrN phases in N400 and the disappearance of the  $\gamma_N$  peaks in N450 indicate  $\gamma_N$  phase degradation in CrN +  $\gamma$ . This was observed when IN 718 was nitrided at higher temperatures ( $\geq$ 450 °C) [4,6,7,14,18,19] and also for longer periods (>8 h) [6,19]. A more detailed discussion on the formation of the  $\gamma_N$  phase and CrN is given elsewhere [3,6,15,34].

Finally (iii), the formation of a surface layer well differentiated from the substrate (Figures 1 and 2) was already reported in several studies [1,3,4,15,16,18,19]. According to Kovací et al. [18] and Aw, Batchelor, and Loh [19], a separate layer occurs as a consequence of the high speed of the sputtering-redeposition process and the fast reaction between N and Cr, which favor the formation of CrN instead of  $\gamma_N$ . The preferential electrochemical attack of the layer-substrate interface (Figures 1 and 2) may be associated with CrN nucleation, as reported in [18,19]. According to Kovací et al. [18], this does not allow the N to penetrate deeply into the surface and does not allow the diffusion layer to become too narrow. Only two nitriding studies on IN 718 have evaluated nitrogen distribution in the nitrided layer. Mondragon-Rodriguez et al. [3] observed a uniform distribution of N in the nitrided layer at 450 °C in IN 718, similar to Figure 2. Already in the work of Zhang et al. [1], the N distribution followed a linear decreasing trend from the surface to a depth of ~50% of the thickness of the nitrided layer. The remaining 50% of the layer exhibited an approximately constant N value (2-3 at.%). The discrepancies with Zhang et al. [1] may be attributed to the effect of residual stresses from the surface previously treated by UNSM from nitrogen diffusion.

On the other hand, other authors also evidenced differences in layer thickness (as observed in Figure 1a, N400), attributed to the presence of slip lines or crystallographic orientations within the layer [6,14] and in the substrate [5,16]. In both situations, these lines appear due to the difficulty of the  $\gamma$ -FCC structure to deform and the formation of pile-up gaps and dislocations resulting from the introduction of nitrogen [16,34]. At higher nitriding temperatures (in this case, 450 °C, Figure 1b), extensive CrN precipitation and  $\gamma_N$  degradation occurred, promoting lattice relaxation and achieving a uniform layer thickness in N450.

# 4.2. Indentation Hardness and Scratch Resistance

Upwards of a two-fold increase in hardness due to the nitriding treatment (Figure 4) is in agreement with all studies evaluating nitride Inconel alloy microhardness [3,4,6,7,14–16,19]. The severe distortion of the crystalline reticulate by N diffusion promotes solid solution strengthening. Moreover, the intrinsic higher hardness of CrN [1,4] and their distribution

in the layer enables the precipitation hardening mechanism [7,14,16,18,19]. However, increased nitriding temperature did not cause significant differences in hardness despite the layer composition in the N450 condition (CrN +  $\gamma$ ). According to Tao et al. [15], the close hardness values (HV<sub>0.01</sub>: 1570 and 1671) in nitriding treatments at 400 °C for 20 h and 450 °C for 20 h resulted from significant substrate influence (thinner layers of 4 and 7 µm, respectively). In this study, the similar indentation hardness values at a contact depth of <1 µm are due to the effect of high roughness (Table 4) [28]. In contact, depths of >1 µm are already influenced by the substrate (penetration in excess of 10% of the thickness), and values that were slightly higher were observed in the N450 condition, similar to those obtained in [15].

Increased roughness due to nitriding treatment (Table 4) is a well-known and widely reported finding [1,3,7,11,15,17,18,34]. Regarding Inconel alloys, the studies found in the literature [1,3,7,15,18,34] have evaluated the R<sub>a</sub> parameter. However, a broader analysis of topographic changes, such as the one in this study (Table 4), was never reported (to the author's knowledge). In addition, to increase mean roughness ( $S_q$ ,  $S_z$ ), the nitriding treatment increased the root mean square surface slope  $(S_{dg})$  and the real contact area  $(S_{dr})$ . The untreated surface was characterized by the predominance of deep valley structures, which were confirmed by the  $S_{sk} < 0$  and  $S_{ku} > 3.00$  parameters. The higher temperature (450 °C) promoted uniformity in the distribution of the peaks and valleys ( $S_{sk}$  and  $S_{ku}$ close to 0.00 and 3.00; a normal distribution). Nitriding at 400  $^\circ$ C was more severe in promoting topographic changes, differentiated by the predominance of peaky structures (S<sub>sk</sub> > 0, S<sub>ku</sub> > 3.00, highest Sz). According to Kovací et al. [18], the increased process parameters (time and temperature) intensify ion bombarding and the fast cathodic pulverization, which cause changes to the surface texture. In addition to sputtering effects, other studies [3,15,17,34] reported that increased roughness is mainly related to nitrogen diffusion (causing microstructure expansion or swelling). These reasons justify the more significant topographic changes in N400 than in N450 due to the formation of the  $\gamma_{\rm N}$  + CrN layer.

Increased surface roughness is usually related to a higher wear volume and friction coefficient (CoF) due to raised contact areas between the tribological pairs [1,35]. Kapoor et al. [35] established that the wear volume should increase with the roughness slope and decrease with increases in hardness. Thus, a higher CoF would be expected, and the scratch wear resistance in nitriding conditions would decrease based solely on the topographic changes already discussed (Table 4, Figure 5). However, over a two-fold hardness increase (Figure 4) on the nitrided surfaces predominated regarding tribological behavior. Zhang et al. [1] observed that the increase in hardness (1.9 times) due to surface modification (ultrasonic nanocrystal) was compensated for by an increase in roughness (Ra increase of five times), resulting in similar performances from the point of view of the wear for IN 718 (polished surface). This study obtained improved scratch resistance with nitriding treatment, evidenced by the decreased penetration depth, increased scratch hardness  $(HS_P)$ , and reduced CoF (Figure 6). These results agree with the studies put forward by Kovací et al. [18], Maniee et al. [7], and Aw, Batchelor, and Loh [19], in which nitrided IN 718 presented a lower CoF and lower wear when compared to the as-received material in dry pin-on-disk wear tests (Table 1). Thus, in this study, the nitriding treatments improved the surface mechanical resistance and remarkably influenced the scratch resistance. The roughness and topographical changes after nitriding did not negatively affect tribological performance.

However, little difference was observed in the scratch depth between N400 and N450, which agrees with the similar indentation hardness and layer thickness. On the other hand, the N450 samples showed lower CoF and higher HS<sub>P</sub> values than N400 in loads of  $\geq$ 5 N (Figure 6b). Both results can be explained, as proposed by Aw, Batchelor, and Loh [19], since, for equivalent hardness, the negative effect of the topography of surfaces nitrided at 400 °C predominates (peak predominance). Nitriding resulted in wear micromechanism changes when compared to the untreated material (Figure 6a). The adhesive-abrasive combined mechanisms in untreated and nitrided IN 718 (using different techniques) were identified

by [1,14,16]. All those authors identified lower adhesive wear contributions on nitrided surfaces, with a consequent reduction in CoF and wear rate in dry tests. Likewise, in scratch tests, mixed micromechanisms prevailed in the IN 718 and nitrided conditions (Figure 6a), in which microcutting predominated with a tendency to crack in low load conditions (2–4 N). However, despite the gain in scratch wear resistance with nitriding, microcutting + cracks might provoke higher losses due to wear with increased time/distance/severity in the tribological test, as pointed out by Zhang et al. [1].

#### 4.3. Linear Polarization

The linear polarization curves corresponding to IN 718 before and after nitriding are presented in Figure 7. The best performance of the N450 condition, when compared to the N400 condition up to the 0.20 V potential (that is, in  $E_{corr}$ ,  $i_{corr}$ , and  $C_0$ ), might be related to the better stability of the oxide layer formed on the surface composed of CrN (N450), as observed by Xue et al. [4] in salt bath-nitrided IN 718. Further studies are required to confirm this hypothesis. However, significant differences were observed for the Tafel region in both nitriding conditions when compared to the untreated IN 718.  $E_{pit}$  values close to the untreated condition (Table 5 and lower pit nucleation density in N400 (Figure 8b) indicate some improvements in pitting resistance in a NaCl (3.56 wt.%) solution. This result is ascribed to the  $\gamma_N$  phase, which demonstrated resistance to localized corrosion in Inconel [7,14–16] and other stainless-steel alloys [8–13,20] due to nitrogen enrichment. Nitrogen plays a role in neutralizing local pit acidification in anodic areas; further explanations can be found in other sources [23–26]. The polarization results revealed that CrN precipitation at 400 °C for 4 h (XRD results, Figure 3) is still insufficient to cause substantial damage to corrosion performance. These results agree with those reported in previous studies [15,16].

An increased treatment temperature from 400 to 450 °C resulted in a passivation region and pitting corrosion resistance reduction. Chrome depletion in many matrix areas, resulting from CrN formation, might cause such detrimental corrosion effects. Similar results were previously reported by [7,15,16] when they obtained a nitride layer (without  $\gamma_N$ ) due to an increase in nitriding temperature (Table 1). Otherwise, the preferential pit nucleation at the grain boundaries of the nitrided surfaces (Figure 8) was already reported by Xue et al. [4] for IN 718 treated by liquid nitriding. According to [4], this results from the concentration of lattice defects, such as dislocation at the grain boundaries, which reduces the corrosion potential when compared to neighboring grains, forming galvanic micropiles. This effect was also reported by Calabokis et al. [10] in nitrided UNS S32507 steel and by Berton et al. [13] in nitrided AISI 409.

# 4.4. Crevice Corrosion

Few studies in the literature have evaluated crevice corrosion in Ni-based alloys [21,22]. In fact, the research into Inconel alloy nitriding (Table 1) does not assess crevice corrosion. This study is the first to approach crevice corrosion in these nitrided alloys, according to the author's knowledge. Miller and Lillard [22] evaluated the crevice corrosion behavior of IN 625 in synthetic seawater. Through potentiostatic tests in a potential lower than the transpassivation potential, the authors of [22] found out that, regardless of the potential applied, a more profound attack occurs closer to the crevice opening (as shown in Figure 10a,b). According to Miller and Lillard [22], corrosion always starts inside the crevice, with a superficial attack. Then, over time, the attack moves toward the opening, where it propagates and deepens.

The results in Figures 9 and 10 showed that the formation of a layer composed of  $\gamma_N$  and CrN (N400) increases crevice corrosion resistance in IN 718. Nitriding at 450 °C harmed the resistance seen in the excessive current density. These results agree with the reduction in the passivation region and higher current densities in the linear polarization tests (N450: Figure 7, Table 5). Both results are due to the presence of Cr-depleted zones as a consequence of the transformation  $\gamma_N \rightarrow \text{CrN} + \gamma$ , already reported.

In fact, nitrided stainless-steel crevice corrosion evaluation is also relatively scarce in the literature [9,10,20]. Studies by Fossati et al. [9] and Bottoli et al. [20] reported crevice corrosion in modified AISI 316L via gaseous nitriding treatments [20] and glow-discharge nitriding [9], and Calabokis et al. [10] evaluated it in LTPN UNS S32750 duplex stainless steel. Studies [9,10,20] evidenced an improvement in crevice corrosion resistance due to the formation of  $\gamma_N$ . Nitrogen positively affects the passive layer resistance and its repassivation, which has been confirmed by several studies [23–26]. In agreement with this study, CrN precipitation in AISI 316L was seen to be harmful to crevice corrosion [9] due to the formation of Cr-depleted zones around the CrN precipitates.

Therefore, the results confirmed that a layer composed of  $\text{CrN} + \gamma$  (without  $\gamma_{\text{N}}$ ) significantly reduced localized pitting and crevice corrosion resistance in IN 718. An improvement in the crevice corrosion resistance of IN 718 was obtained after nitriding at 400 °C, which was confirmed by a reduction in current density in potentiostatic tests (Figure 9) and a reduction in crevice corrosion depth (Figure 10).

#### 5. Conclusions

The LTPN treatment produced layers with thicknesses of  $7.17 \pm 0.89 \ \mu\text{m}$  (400 °C) and  $7.96 \pm 0.48 \ \mu\text{m}$  (450 °C) composed of an N-expanded austenite phase ( $\gamma_N$ ) and CrN at 400 °C, and CrN +  $\gamma$  at 450 °C.

Surface hardening due to nitriding is associated with the solid-solution strengthening and precipitation-hardening mechanisms, with a maximum indentation hardness of 12 GPa (400 °C) and 12.5 GPa (450 °C), respectively, when compared to 5 GPa for substrate hardness. Surface hardening prevails in the tribological response in scratch tests against the effect of an increase in roughness (higher  $S_q$  and  $S_z$ ) and topographic changes ( $S_{ku}$ ,  $S_{sk}$ ,  $S_{dq}$ , and  $S_{dr}$ ) resulting from nitriding.

The nitriding condition at 450 °C showed slightly higher scratch resistance and a lower CoF compared to the N400 condition, with significant damage to localized pitting and crevice corrosion resistance when compared to IN 718. Those results are a consequence of the CrN +  $\gamma$  hard layer, which generates chromium-depleted regions around the CrN precipitates.

Even with CrN precipitation, the  $\gamma_N$  formation in N400 results in better performance regarding localized crevice corrosion (corrosion wear not measurable and a lower current density) without hampering the electrochemical behavior ( $E_{corr}$ ,  $i_{corr}$ ,  $C_o$ , and  $i_{pass}$ ) of the untreated material.

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