



# Article High-Efficient Gas Nitridation of AISI 316L Austenitic Stainless Steel by a Novel Critical Temperature Nitriding Process

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Abstract: To improve the surface properties of austenitic stainless steels, a thick S-phase layer was prepared by using a novel critical temperature nitriding (CTN) process. The properties of the thick S-phase layer were optimized by controlling the process parameters. The microstructures and phase compositions of CTN-treated layers were characterized by the optical microscope, scanning electron microscope and X-ray diffraction, respectively. The surface properties, including corrosion and wear resistance, were systematically investigated by the electrochemical workstation, micro-hardness tester and ball-on-disk tribometer, respectively. The results showed that a thick S-phase layer with a thickness of 18 to 25 µm can be fabricated in a short time by critical temperature nitriding, which represented higher efficiency than conventional low-temperature nitriding. Although the most top surfaces of CTN-treated layers contain massive iron nitrides, there are no precipitates in the inner nitrided layer. The electronic work function calculated by first-principles method has confirmed that those iron nitrides had a slight influence on the corrosion resistance of nitrided layers. The optimized CTN-treated layer exhibited a comparable corrosion resistance and wear resistance as the low-temperature nitrided layer. The CTN process is considered a potentially highly efficient surface modification method for austenitic stainless steels.

Keywords: thick S-phase layer; nitriding; austenitic stainless steel; corrosion resistance; wear resistance

## 1. Introduction

Austenitic stainless steel (ASS) is one of the most important engineering materials which is widely employed in corrosion-resistant conditions due to their excellent corrosion resistance. However, their relatively low hardness limits their extensive applications under tribological conditions. Thanks to S-phase surface engineering, the problem above has been solved [1]. The ASS is carburized, nitrided or nitrocarburized under a certain condition and a special layer with high hardness and excellent corrosion resistance formed on the nitrided surface of ASS. This special nitrided layer is called an "S-phase" layer or nitrogen expand austenite ( $\gamma_N$ ) layer. The existence of an S-phase layer could perfectly increase the surface hardness of ASS without losing its excellent corrosion resistance. In the last few decades, research works on the nitriding of ASS have been widely concerned [2–5]. The effects of nitriding parameters on the formation behavior of S-phase layers have been clearly identified [6–8]. It was found that the corrosion resistance of the S-phase layer was significantly deteriorated after the precipitation of chromium nitrides (CrN or  $Cr_2N$ ). Therefore, the S-phase layer without precipitates was expected to be produced. All research works have proved that the precipitation-free S-phase can be only prepared under low-temperature conditions. However, the thickness of S-phase layers obtained by low-temperature nitriding is always unsatisfactory and it is usually less than 25 µm as



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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/). Li's statistical data [9]. The thicker S-phase layer requires a long-time nitriding treatment at low temperature. Obviously, it is hard to fabricate a thick S-phase layer by simply increasing nitriding temperature, prolonging nitriding duration as well as optimizing gas mixtures [10,11], since there is a limit of temperature and time for the nitriding of ASS, that is, the threshold T-t curve [12]. This reminds us how the S-phase layer without precipitates can be obtained only when the nitriding temperature and time lie below the threshold T-t curve. Breaking through the threshold T-t curve will cause the precipitation of chromium nitrides. There is a limitation in the thickness of the S-phase layer without precipitates due to the threshold T-t curve. In order to increase the thickness of S-phase layers, many other technologies, such as the plasma nitriding combined with surface nanocrystallization, have been developed to accelerate the nitriding kinetics of ASS [13,14]. It should be pointed out that these pre-treatments could increase the thickness of nitrided layers but result in an accelerated precipitation of chromium nitrides as well. Additionally, Wang et al. developed a new plasma arc source nitriding of ASS at low temperature [15,16]. The results show that the plasma arc source nitriding has great advantages to the thickness of S-phase layers as compared with the conventional glow-discharge plasma nitriding [15]. The plasma arc source nitriding is characterized by a higher voltage, lower treatment temperature and lower pressure than the conventional glow-discharge plasma nitriding, thus owns an intensified ion bombardment resulting in the thicker S-phase layer [16,17]. Nevertheless, the plasma arc source nitrided layer also contains massive nitrides [18]. In fact, the nitriding temperature is the most sensitive parameter to determine the thickness of nitrided layers of ASS. There exists a transition temperature of 450 °C, above which the growth kinetics of nitrided layers rapidly increases [19]. The threshold T-t curve exhibits an incubation time for the precipitation of chromium nitrides at a specific temperature. The higher the nitriding temperature, the shorter incubation time. If the short incubation time at high temperatures can be fully used, the thickest S-phase layer can be produced theoretically. For example, Li et al. conducted a high-temperature (560 °C) plasma nitriding on the AISI 316L ASS by hollow cathode heating and a thick S-phase layer of about 6  $\mu$ m was formed in a short time (30 min) [20]. Therefore, in this study, as inspired by the research above, we developed a novel critical temperature nitriding (CTN) process to prepare a thick S-phase layer on the AISI 316L stainless steel. During the CTN treatments, the nitriding temperature will be controlled and gradually decrease below the threshold T-t curve. The effects of ammonia flow on the microstructure of CTN-treated layers were analyzed. After that, the wear and corrosion properties of the thick S-phase layer were evaluated by experiments and theoretical calculations and were compared with those of conventional low-temperature nitrided layers.

# 2. Experimental and Calculation Details

# 2.1. Sample Preparation

The AISI 316L ASS bar with a diameter of 20 mm was selected for substrate materials in this work with the chemical composition (wt.%) of 0.08C, 17.2Cr, 10.0Ni, 2.0Mo, 1.3Mn, 0.6Si and Fe balance. The AISI 316L ASS bar ( $\Phi$ 20 × 300 mm) was austenitized at 1050 °C for 0.5 h and then oil quenched (KR118H, KERUN Co., Ltd., Nanjing, China) to obtain a homogeneous substrate. After that, the disk samples with a thickness of 4 mm were cut from the quenched bars. Then the samples were mechanically ground with SiC paper (Water Proof Abrasive Paper, Hong Kong, China) down to 400 grade. Before gas nitriding, the grounded samples were immersed in a hydrogen chloride solution of 10 vol.% to remove the passive oxide film on the surface of the AISI 316L ASS. After acid picking, the samples were ultrasonically cleaned in ethyl alcohol (AR) and were put into the furnace as soon as possible to avoid the recovery of passive oxide film.

### 2.2. Gas Nitriding

Before the new critical temperature nitriding (CTN) process was developed, some primary characteristics of the gas nitrided behavior of AISI 316L ASS should be clarified

and the threshold T-t curve for the precipitation of chromium nitrides should be built. The conventional gas nitriding of AISI 316L ASS was carried out in the temperature range of 430–590 °C for different durations. The detailed nitridation parameters are listed in Table 1. The conventional gas nitrided samples were marked as GNT-t, where T was the nitriding temperature and t was the nitriding duration. The threshold T-t curve can be estimated by distinguishing the metallographic morphologies of conventional gas nitrided AISI 316L ASS (see Figure 1). Then, the new critical temperature nitriding was developed by controlling the nitriding temperature below the threshold T-t curve from 560 to 460 °C as shown in Figure 2. Three different CTN processes were carried out under different ammonia flows from 0.2 to 0.8 L/min, which were marked as CTN-M (the letter M stands for the ammonia flow). The duration of all CTN processes is 10.8 Ks (Kiloseconds). All gas nitriding processes were conducted in a quartz tube furnace and the heating rate was fixed to 13 °C/min.

#### 2.3. Characterizations

After gas nitriding, the cross-sections of nitrided layers were prepared by mechanically grinding and polishing for metallographic observations. The cross-sections were etched by a reagent containing 50 vol.% HCl + 25 vol.% HNO<sub>3</sub> + 25 vol.% H<sub>2</sub>O and observed by using optical microscopy (OM, Olympus GX51F, Olympus Corporation, Tokyo, Japan). The detailed morphologies of nitrided layers were observed by scanning electron microscopy (SEM, JEM-IT500, Japan Electron Optics Laboratory Co., Ltd, Mitaka, Japan) equipped with an energy dispersive X-ray analyzer (EDS) to check the distribution of the chromium (Cr) element in nitrided layers. An X-ray diffraction measurement (XRD, X'Pert Pro, Malvern Panalytical, Almelo, The Netherlands) with Cu-K $\alpha$  radiation was applied to identify the phase composition of nitrided layers. The diffraction angle was in the range of  $30^{\circ}$ – $90^{\circ}$ . The properties of nitrided layers were measured systematically including hardness, wear resistance and corrosion resistance. The microhardness of nitrided surfaces was determined with a microhardness tester (HVA-1000, Shanghai Lianer experimental Equipment Co., LTD, Shanghai, China) under an indentation load of 100 g for 15 s. Each hardness would be tested at least three times to ensure accuracy and the average values were used. To evaluate the corrosion resistance of gas nitrided AISI 316L steel, the anodic polarization tests were performed in static 3.5 wt.% NaCl solution using an electrochemical workstation (Corrtest CS350, Wuhan Koster Instrument Co., Ltd, Wuhan, China). A standard threeelectrode electrochemical cell was applied and the saturated calomel electrode, platinum electrode and samples were set as the reference electrode, counter electrode and working electrode, respectively. The exposed area of the sample was 3.14 cm<sup>2</sup>. The potentiodynamic polarization curves were collected after the stability of open circuit potential (OCP) was reached. The scanning rate was set as  $1 \text{ mVs}^{-1}$  in the range of -1.0 V to +1.0 V, relative to OCP. After corrosion tests, the corroded surfaces were observed and compared by using SEM. The wear tests were conducted by a ball-on-disk tribometer (CSM HT-1000, Anton Paar, Graz, Austria). During the tests, a rotated sample was slid against a stationary  $Al_2O_3$ ball at the speed of 200 r/min for 3600 s under a contact load of 20 N. All tests were conducted in the air. The diameter of the Al<sub>2</sub>O<sub>3</sub> ball used as a counterpart was 6 mm. All surface friction tests were performed in standard atmospheric conditions (temperature: 25 °C, air humidity: 75%–85%) and without the application of any additional lubrication. The wear rates,  $\eta$  (mm<sup>3</sup>·N<sup>-1</sup>m<sup>-1</sup>), were calculated by using the follow equation [21]:

$$\eta = \frac{\pi DS}{FL} \tag{1}$$

where F (N) is the normal contact load, L (m) is the sliding distance, D (mm) is the diameter of the wear tracks (6 mm in present work) and S (mm<sup>2</sup>) represents the cross-sectional area of the wear track which is measured by a profilometer (KLA-TENCOR ALPHASTEP P-7, KLA Corporation, Milpitas, CA, USA).



**Figure 1.** Microstructures of conventional nitrided layers formed on AISI 316L ASS under different conditions (nitriding temperature is in the range of 430–590 °C and nitriding time depends on the nitriding temperature). The symbol GNT-t reveals the nitriding parameters. GN stands for gas nitriding, the former number T is the nitriding temperature (°C) and the latter number t is the nitriding time (hour). The precipitation situation in nitrided layers is marked by frames with different colors. Green is free of precipitation, yellow stands for few of precipitation and red stands for full of precipitation.

Samples	Temperature (°C)	Time (h)	NH3 (L/min)
GN430	430	8, 11, 16, 24	
GN450	450	4, 8, 12, 16	
GN470	470	4, 8, 10, 16	
GN490	490	2, 3, 4, 8	
GN510	510	1/2, 1, 2, 4	0.8
GN530	530	1/2, 3/4, 1, 2	
GN550	550	1/4, 1/3, 1/2, 1	
GN570	570	1/12, 1/6, 1/4, 3/4	
GN590	590	1/60, 1/12, 1/4, 1/2	

Table 1. Detailed parameters of conventional gas nitriding of AISI 316L ASS.



**Figure 2.** (**a**) Experimental threshold T-t curve (green line) for the precipitation of chromium nitrides and (**b**) Schematic diagrams of critical temperature nitriding processes.

### 2.4. First Principles Calculations

To understand the effects of nitrides on corrosion resistance of nitrided layers, the electronic work functions (EWFs) of related phases formed in nitrided layers were calculated in the framework of first principles. There were four phases to be calculated: S-phase,  $\gamma'$ -Fe<sub>4</sub>N,  $\varepsilon$ -Fe<sub>3</sub>N and CrN. The crystalline structures of these phases were built according to descriptions in references [21–24]. It should be pointed out that the S-phase was treated as a solid solution with randomly distributed nitrogen atoms and closely distributed chromium atoms around nitrogen atoms. The crystalline structures of calculated phases are schematically listed in Table 2.

All calculations were performed with the DS-PAW code from HZWTECH based on density functional theory (DFT) [25,26]. The exchange-correlation potential was described by generalized gradient approximation (GGA) in the PBE formula. Ultrasoft pseudopotentials were applied to describe the electronic interaction. The bulk crystals of calculated phases were optimized under a cut-off energy of 500 eV. After geometry optimization, the surface slabs of calculated phases were built to calculate the EWFs. In the present work, low index surfaces, such as S-phase (111),  $\gamma'$ -Fe<sub>4</sub>N (111),  $\varepsilon$ -Fe<sub>3</sub>N (002) and CrN (111), were investigated. The k-point grids were set according to lattice parameters:  $3 \times 3 \times 3$  for S-phase,  $\gamma'$ -Fe<sub>4</sub>N and CrN and  $3 \times 3 \times 6$  for  $\varepsilon$ -Fe<sub>3</sub>N and  $2 \times 2 \times 1$  for all slab models. During the structural optimizations, the convergence criteria of energy and force were set as  $1.0 \times 10^{-4}$  eV and 0.05 eV/Å, respectively.

Phases	Form	iula	For	nula
	Fe <sub>23</sub> Cr <sub>6</sub>	Ni <sub>3</sub> N <sub>12</sub>	Fe <sub>22</sub> Cr	Ni <sub>3</sub> N <sub>12</sub>
S-phase	۵۵۵۵۵ ۵۵۵۵۵ ۵۵۵۵۵ ۵۵۵۵۵ ۵۵۵۵۵ ۵۵۵۵۵			
	Fe <sub>22</sub> Cr <sub>7</sub>	Ni <sub>3</sub> N <sub>8</sub>	Fe <sub>21</sub> Cr	<sub>8</sub> Ni <sub>3</sub> N <sub>8</sub>
γ'-Fe <sub>4</sub> N				
	Fe <sub>17</sub> Cr <sub>5</sub>	Ni <sub>2</sub> N <sub>8</sub>	Fe <sub>16</sub> Cr	<sub>6</sub> Ni <sub>2</sub> N <sub>8</sub>
ε-Fe <sub>3</sub> N				
	Cr <sub>32</sub> N <sub>32</sub>	100 at.%	Cr <sub>31</sub> 1	FeN <sub>32</sub>
CrN				

Table 2. Crystalline structures of calculated phases.

## 3. Results and Discussions

### 3.1. Microstructures of Conventional Gas Nitrided Layer of AISI 316L ASS

Figure 1 gives the cross-sections of nitrided layers formed on AISI 316L ASS by the conventional gas nitriding process. It can be seen that the CrN will gradually precipitate from the S-phase layers with the elevated temperature or prolonged time. For the thickness of nitrided layers, high temperature is indeed beneficial for the growth of nitrided layers, but it also easily leads to CrN precipitation. Taking the GN510-4 sample for instance, the thickness of the nitrided layer reaches more than 25 µm, however, massive CrN precipitations appear in the nitrided layer. In order to minimize the CrN precipitation, low-temperature nitriding is commonly required. But the disadvantage of low-temperature nitriding is also obvious, namely, it loses the growth rate of nitrided layers. Taking the GN430-24 sample, for example, a long-time nitriding (24 h) only brings a precipitation-free layer of 15  $\mu$ m. Therefore, a novel critical temperature nitriding process will be developed to balance the CrN precipitation and the nitriding efficiency. By microstructural observations, three typical morphologies can be classified as shown in Figure 2a. They are free of precipitation, few of precipitation and full of precipitation. Based on nitriding temperatures and durations of precipitation-free samples, the threshold T-t curve can be obtained. The novel high-efficient gas nitriding called critical temperature nitriding (CTN) will be conducted under the critical T-t curve by fully using the high-temperature range (see Figure 2b).

## 3.2. Microstructures of Critical Temperature Nitrided Layers

Figure 3 shows the cross-sectional microstructures of critical temperature nitrided (CTNed) layers of AISI 316L ASS. A white and homogeneous nitrided layer was displayed

after etching. No obvious precipitation of CrN (black spots in the nitrided layer) was found in the CTNed layers, which is quite similar to the conventional low-temperature nitrided (LTNed) layer as shown in Figure 3d. This shows the success of the CTN processes. With the decrease of the ammonia flow, the CTNed layers show different characteristics. For the CTN-0.8 sample, there was still a trace of CrN precipitate in the nitrided layer due to the high ammonia flow and the short incubation time of precipitation at high temperatures. When the ammonia flow decreases to 0.4 L/min, the precipitation of CrN has been greatly restrained. It indicates that decreasing ammonia flows could prolong the incubation time of precipitation due to the reduced nitriding potential. It should be pointed out that the higher ammonia flows than 0.4 L/min leads to the brittleness of nitrided layers (see notches in Figure 2a,b). Further decreasing the ammonia flows to 0.2 L/min could improve the toughness of nitrided layers. The nitrided layer of the CTN-0.2 sample shows a compact and precipitation-free appearance as the LTNed sample (GN430-24), which is believed to have a similar performance. Most importantly, the new CTNed layer is thicker than the LTNed layer, but the nitriding time is shorter, indicating its high efficiency.



**Figure 3.** Cross-sectional microstructures of critical temperature nitrided AISI 316L ASS under ammonia flows of (**a**) 0.8 L/min, (**b**) 0.4 L/min and (**c**) 0.2 L/min. (**d**) The cross-sectional microstructure of low-temperature gas nitrided AISI 316L ASS for comparison.

Figure 4 shows the SEM image and elemental distribution of the nitrided layer of the CTN-0.2 sample. There exists a thin film on the top of most nitrided layers. A similar thin film was observed by Paweł Kochmański et al. when they treated martensite stainless steel by gas nitriding. The thin layer was identified as  $\varepsilon$  nitride [27]. The EDS map shows the uniform distribution of elements except nitrogen. Although there is massive nitride precipitation, no obvious segregation of chromium can be observed, which is beneficial to maintain the high corrosion resistance.



Figure 4. SEM image and elemental distribution of the nitrided layer for the CTN-0.2 sample.

## 3.3. Phase Compositions of Critical Temperature Nitrided Layers

The depth-related XRD patterns of CTNed AISI 316L ASS are shown in Figure 5 and the XRD patterns of the LTNed sample (GN430-24) are inserted for comparison. As the normal nitrided phases, the S-phase and CrN (ICSD 053146) are detected on all nitrided surfaces of AISI 316L ASS. Apart from these normal nitrided phases, massive iron nitrides, such as  $\gamma'$ -Fe<sub>4</sub>N (ICSD 060195) and  $\varepsilon$ -Fe<sub>3</sub>N (ICSD 79981), can be detected on the CTNed surfaces compared with the LTNed ones. The formation of iron nitrides is attributed to the high-temperature stage of the CTN process. Much research have proved that the  $\gamma'$ nitride is usually formed at the nitriding temperature higher than 470 °C [6,28] and the  $\varepsilon$  nitride comes from the S-phase by a faulting mechanism [29]. With the decrease of ammonia flows, the amount of iron nitrides, especially  $\varepsilon$  nitride, was greatly reduced, which corresponds to the improvement of toughness in nitrided layers. When the nitrided surfaces were slightly polished (the thickness of removed layers was less than 5  $\mu$ m, and the thin film shown in Figure 4 was completely removed), a single S-phase structure appeared on both the polished surfaces of CNed and LTNed samples. It indicates that all nitrides were concentrated on nitrided surfaces and the CNed sample had a similar inner nitrided layer as the conventional LTNed one. Unlike the plasma nitriding, massive iron nitrides concentrate on the gas nitrided surface formed a thin film due to the lack of ion etching (see Figure 4). The effects of these iron nitrides on the wear and corrosion resistance of nitrided layers will be evaluated in the following sections.



**Figure 5.** Depth-related XRD patterns of gas nitrided AISI 316L ASS at (**a**) nitrided surfaces and (**b**) polished surface. The polished surface is produced by mechanical grinding and the thickness of the removed layer was less than 5  $\mu$ m.

## 3.4. Nitridation Efficiency of Critical Temperature Nitriding Processes

Figure 6 shows the statistical plot of the thickness of nitrided layers produced by conventional gas nitriding and critical temperature nitriding. For the conventional gas nitriding, especially low-temperature gas nitriding, the thickness of precipitation-free nitrided layers is hard to surpass at 15  $\mu$ m. Further, when increasing the temperature or prolonging the time, the CrN will precipitate from the S-phase layer. It shows clearly that

the CTN process can break the limitation in the layer thickness of the precipitation-free S-phase. The maximum thickness of the single S-phase layers can reach 25  $\mu$ m. Most importantly, the CTN process can fabricate the thick S-phase layer in a short time, which shows a high nitridation efficiency.



**Figure 6.** Statistical plot of the thickness of nitrided layers produced by conventional gas nitriding and critical temperature nitriding.

## 3.5. Corrosion Resistance of Critical Nitrided Layers

Figure 7 shows the potentiodynamic polarization curves of CTNed layers compared with the untreated and LTNed ones. Based on the polarization curves, the polarization parameters were estimated by the Tafel method and are listed in Table 3. As shown in Figure 7a, unlike the untreated sample, all nitrided ones evidently exhibited a passivation region with a slowly increased anodic current density after corrosion potential. Then, the anodic current density rapidly increased due to the breakdown of passive films. All passivation regions of nitrided samples can be divided into two stages, indicating a typical local solution-repassivation process. The lower anodic potential stage (from corrosion potential to -0.06 V) results from the corrosion of iron nitrides, while the higher anodic potential stage (from -0.06 to 0.51 V) corresponds to the corrosion of the S-phase. Comparing the anodic polarization curves of LTNed and CTNed samples, it can be found that the existence of iron nitrides ( $\gamma'$ -Fe<sub>4</sub>N and  $\varepsilon$ -Fe<sub>3</sub>N) has little influence on the corrosion resistance of nitrided surfaces. The iron nitrides also show a good passivity similar to the S-phase and the CrN leads to the local corrosion and rapidly increased anodic current density at anodic potential of -0.25 V. When the most top thin film is removed, as shown in Figure 7b, all nitrided samples exhibit a similar polarization curve due to the similar S-phase composition in nitrided layers. The S-phase shows an evidently passivation characteristic with lower anodic current density than the untreated AISI 316L ASS. In addition, by eliminating the negative effect of CrN on the corrosion resistance, the corrosion potential of nitrided layers shifts to a positive direction and the corrosion current is reduced (see Table 3), which indicates the improved corrosion resistance. It is generally believed that the low-temperature nitriding is the main technique to prepare the S-phase layer with excellent corrosion resistance. Our present results show that the CTNed samples exhibit a comparable corrosion resistance to the LTNed one, which reveals that the CTN process is a potential technology to prepare the thick S-phase layer in high efficiency.



**Figure 7.** Poteniodynamic polarization curves of (**a**) nitrided surfaces and (**b**) polished surfaces of the CTNed and LTNed AISI 316L ASS. A commonly used low-temperature nitriding process (GN430-24) is selected as a reference to evaluate the improvement of the novel critical temperature nitriding.

Table 3. The polarization parameters of untreated and nitrided AISI 316L ASS.

Samples	Corrosion Potential (V)	Corrosion Current Density (A/cm <sup>2</sup> )
Untreated	-0.38518	$5.0995 \times 10^{-6}$
GN430-24 (nitrided surface)	-0.89202	$1.7399  imes 10^{-5}$
CTN-0.2 (nitrided surface)	-0.88578	$5.1024 imes10^{-5}$
CTN-0.4 (nitrided surface)	-0.66256	$5.4824 imes10^{-5}$
CTN-0.8 (nitrided surface)	-0.9173	$1.9674  imes 10^{-5}$
GN430-24 (polished surface)	-0.33879	$3.7034  imes 10^{-7}$
CTN-0.2 (polished surface)	-0.39407	$1.2909  imes 10^{-8}$
CTN-0.4 (polished surface)	-0.49179	$1.2446  imes 10^{-5}$
CTN-0.8 (polished surface)	-0.57112	$6.8901  imes 10^{-7}$

Figure 8 shows the SEM images of corroded surfaces of the untreated and CTNed AISI 316L ASS. It can be seen that the pitting corrosion is the common mode for the untreated AISI 316L ASS (see Figure 8a). After CTN treatment, the corrosion pits can still be found on the corroded surface, indicating that the unchanged corrosion mode is the untreated AISI 316L ASS (see Figure 8b). In addition, the grain boundaries clearly appear on the corroded surface, which is attributed to the multi-phase composition on the CTNed surfaces. For the S-phase layer underneath the nitrided surfaces, the corroded surface shows a similar morphology as the untreated AISI 316L ASS but has shallow corrosion pits (see Figure 8c). The corroded morphologies are consistent with the polarization curves. The enlarged morphology of corrosion pits for the CTN-0.2 sample is shown in Figure 8d and the elemental distributions are displayed in Figure 8e, f. The Cr and O elements mainly accumulate in the corrosion pits, which indicates that the corrosion will occur preferentially in the Cr-rich area. In other words, the Cr-rich nitrides or CrN formed in the Cr-rich area deteriorate the corrosion resistance of the nitrided layers. It should be pointed out that the formation of nitrides does not mean that the corrosion resistance is reduced. As shown in Figure 8d, the uncorroded area is covered by massive iron nitride particles. The small difference in the anodic current density between CTNed surfaces and the S-phase layer underneath indicates the slight influence of iron nitrides on the corrosion resistance of nitrided layers (see Figure 7). Therefore, only the formation of chromium-rich nitrides is harmful to the corrosion resistance of AISI 3161 ASS.



**Figure 8.** SEM images of corroded surfaces of the (**a**) untreated AISI 316L ASS, (**b**) CTN-0.2 and (**c**) polished CTN-0.2 samples. (**d**) Enlarged morphology of local area marked by a square in (**b**); (**e**,**f**) are EDS maps of Cr and O distributions in (**d**), respectively.

# 3.6. Wear Resistance of Critical Temperature Nitrided Layers

Figure 9 shows the surface micro-hardness of the nitrided AISI 316L ASS. After gas nitriding, the surface hardness of AISI 316L ASS was greatly improved. All nitrided samples exhibited a high surface hardness of more than  $1000 \text{ HV}_{0.1}$ , and the surface hardness of the CTN-0.8 sample reached 1468 HV<sub>0.1</sub>. The surface hardness of CTNed samples was generally higher than that of the LTNed sample (GN430-24) due to massive iron nitride precipitation, which indicates higher brittleness. By reducing the ammonia flow, the brittleness of the CTN-0.2 sample decreased compared with the CTN-0.8 sample.



Figure 9. Surface micro-hardness of the critical temperature nitrided AISI 316L ASS.

Figure 10 gives the friction coefficient and cross-sectional profiles of wear scars for the untreated and nitrided AISI 316L ASS. For the untreated sample, the friction coefficient gradually decreases from 0.75 to 0.5 as the sliding distance, which corresponds to the typical running-in stage during the wear test. After the running-in stage, the friction coefficient tends to stabilize due to the formation of oxide film on the worn surfaces. The infrequent

oscillation in the friction coefficient can be attributed to the compaction and delamination of wear debris which is called "oxidation–scrape–reoxidation" theory [30,31]. For the nitrided samples, the friction coefficient was rapidly stabilized after a short running-in stage due to their high hardness to hold thick oxide film [30]. The friction coefficient of CTNed samples (about 0.8) was higher than that of the LTNed sample (close to 0.5), which reveals a different wear mode due to different hardness. It should be noted that the friction coefficient for the CTN-0.8 sample was more stable than that for the CTN-0.2 sample. It implies that the abrasive wear dominates the worn surface of the CTN-0.8 sample due to its higher hardness than the CTN-0.2 sample (see Figure 8). The cross-sectional profiles of wear scars reveal the intensity of the wears. It was found that the wear depth of the CTN-0.2 sample was quite close to that of the GN430-24 sample, indicating a comparable wear resistance. In addition, the high hardness of the CTN-0.8 sample corresponded to the high brittleness, which results in a deeper wear depth than the CTN-0.2 sample.



**Figure 10.** Friction coefficient of untreated and nitrided AISI 316L ASS sliding with  $Al_2O_3$  ball for 3600 s. (a) Untreated AISI 316L ASS, (b) GN430-430, (c) CTN-0.8 and (d) CTN-0.2 samples. The cross-sectional profiles of wear scars are shown in the insets.

Figure 11 shows the wear rates of the untreated and nitrided AISI 316L ASS after sliding with an  $Al_2O_3$  ball for 3600 s. It can be seen that the GN430-24 sample had the lowest wear rates among all tested samples. Due to the brittleness of CTNed samples caused by iron nitride precipitations, the wear rate of CTNed samples was a little higher than that of the LTNed one. It should be noted that by optimizing the ammonia flow, the brittleness on the nitrided surface of the CTNed sample can be significantly reduced. The wear rate of the CTN-0.2 sample was very close to that of the GN430-24 sample, which is an order of magnitude lower than that of the untreated AISI 316L ASS. Our present results reveal that the CTN process can fabricate a thick nitrided layer with high wear resistance and high corrosion resistance on the surface of AISI 316L ASS. Most importantly, the CTN process is characterized by high efficiency.



**Figure 11.** Wear rate of the untreated and nitrided AISI 316L ASS after sliding with Al<sub>2</sub>O<sub>3</sub> ball for 3600 s.

#### 4. Discussion

# 4.1. Distribution of Chromium in Nitrided Layers

The general viewpoints demonstrated that the CrN precipitation was the primary cause for deteriorating the corrosion resistance of nitrided austenitic stainless steels since it would cause the depletion of chromium in the matrix. In the present work, besides the expected S-phase and CrN, massive iron nitrides also precipitated on CTNed surfaces. Whether these iron nitrides affect the corrosion resistance of nitrided layers should be evaluated. Here, we calculated the partitioning enthalpy of chromium between S-phase and nitrides by assuming the following reaction:

$$S_{high} + N_{low} \rightarrow S_{low} + N_{high}$$

where  $S_{high}$  and  $S_{low}$  represent the S-phase with high and low chromium content, respectively.  $N_{high}$  and  $N_{low}$  are nitrides (CrN,  $\gamma'$ -Fe<sub>4</sub>N and  $\varepsilon$ -Fe<sub>3</sub>N) with high and low chromium content, respectively. This gives the partitioning enthalpy of chromium  $\Delta H_p$  as:

$$\Delta H_p = E_{\rm S_{low}} + E_{\rm N_{high}} - E_{\rm S_{high}} - E_{\rm N_{low}}$$

where  $E_{S_{low}}$ ,  $E_{N_{high}}$ ,  $E_{S_{high}}$  and  $E_{N_{low}}$  are the total energy for the corresponding calculated models. The positive  $\Delta H_p$  indicates that the chromium atoms prefer to stay in S-phase.

Figure 12 schematically shows the migration of chromium atoms among the formed phases in nitrided layers. The calculated reactions and results are listed in Table 4. It can be seen that the migration of chromium atoms between S-phase and  $\gamma'$ -Fe<sub>4</sub>N is reversible due to the low partitioning enthalpy being close to zero. In addition, the chromium atoms prefer to diffusion into the S-phase from the  $\varepsilon$ -Fe<sub>3</sub>N nitride. The chromium atoms will finally prefer to diffusion into CrN due to the remarkable negative partitioning enthalpy between CrN and other phases. This implies that the formation of iron nitrides ( $\gamma'$ -Fe<sub>4</sub>N and  $\varepsilon$ -Fe<sub>3</sub>N) cannot cause the depletion of chromium in the matrix. The CrN has more power to adsorb chromium atoms and its existence plays a key role in determining the corrosion resistance of nitrided ASS. This explains why the CTNed surface shows a similar polarization behavior as the LTNed surface (see Figure 6a), although they contain massive iron nitrides.



Figure 12. Schematic diagram of chromium partitioning between S-phase and nitrides.

Table 4. Calculated enthalpy of chromium atoms partitioning between S-phase and nitrides.

Reactions	$\Delta H_p$ , eV
$S (Fe_{22}Cr_7Ni_3N_{12}) + Cr_{31}FeN_{32} \rightarrow S (Fe_{23}Cr_6Ni_3N_{12}) + Cr_{32}N_{32}$	-0.194
$S (Fe_{22}Cr_7Ni_3N_{12}) + \gamma' (Fe_{22}Cr_7Ni_3N_8) \rightarrow S (Fe_{23}Cr_6Ni_3N_{12}) + \gamma' (Fe_{21}Cr_8Ni_3N_8)$	0.043
$S \left(Fe_{22}Cr_7Ni_3N_{12}\right) + \epsilon \left(Fe_{17}Cr_5Ni_2N_8\right) \rightarrow S \left(Fe_{23}Cr_6Ni_3N_{12}\right) + \epsilon \left(Fe_{16}Cr_6Ni_2N_8\right)$	0.359

## 4.2. Electronic Work Functions of Formed Phases in Nitrided Layers

To further evaluate the effects of nitrides on corrosion resistance of nitrided layers, the electronic work functions (EWFs) of related phases formed in nitrided layers were calculated as shown in Figure 13. It can be seen that the EWF of the S-phase (4.0054 eV) is very close to that of  $\gamma'$ -Fe<sub>4</sub>N (3.8681 eV) and  $\varepsilon$ -Fe<sub>3</sub>N (4.0771 eV). The EWF of CrN depends on the terminal element on the surface. The Cr-terminated surface has a very low EWF of 2.1541 eV compared with the N-terminated surface of 9.1157 eV. The EWF represents the energy difference between the vacuum level and the Fermi level, which is also an energy barrier to losing electrons. The higher the EWF, the harder it is to lose electrons. This means that the Cr-terminated CrN is prone to corrosion. Especially when CrN coexists with the S-phase, the great difference in EWF between them will enhance the electrochemical corrosion tendency. On the contrary, the similar EWF between the S-phase and iron nitrides will not cause additional electrochemical corrosion, which has little influence on the corrosion resistance of nitrided layers of ASS. Therefore, the existence of CrN will greatly deteriorate the corrosion resistance of nitrided layers.



**Figure 13.** The electronic work functions (EWFs) of related phases formed in nitrided layers of AISI 316L ASS.

### 5. Conclusions

A novel critical nitriding process was proposed and conducted on the AISI 316L austenitic stainless steel. A thick S-phase layer with excellent wear resistance and corrosion resistance was fabricated in high efficiency. The results were summarized as follows:

- 1. Based on the threshold T-t curve for the gas nitriding of AISI 316L austenitic stainless steel, a novel critical temperature nitriding process has been designed and been used to fabricate the thick S-phase layer successfully.
- The maximum thickness of the S-phase layer without precipitations can reach 25 μm by the critical temperature nitriding process.
- 3. The critical temperature nitrided surface inevitably contains massive nitrides, which is mainly composed of iron nitrides. Those iron nitrides have little influence on the corrosion resistance.
- 4. The CTN-0.2 sample shows a comparable corrosion resistance as the conventional low-temperature nitrided one, as well as an excellent wear resistance. Its wear rate is an order of magnitude lower than that of the untreated AISI 316L austenitic stainless steel.
- 5. The critical temperature nitriding process is a high-efficient surface modification method for austenitic stainless steels.

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