Properties of stainless-steel surface after hollow cathode assisted plasma nitriding

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Abstract

AISI 304 stainless steel was nitrided at different temperature in the plasma equipment using a new auxiliary device. The proposed hollow cathode auxiliary device improves the plasma density, thereby accelerating the nitriding process. The modified surface was characterized by x-ray diffraction, scanning and transmission electron microscopies, atomic force microscopy, surface microhardness testing. Electrochemical corrosion test was used to measure the localized corrosion resistance of the samples. Single S-phase layer without the CrN precipitation was obtained by hollow cathode plasma nitriding at 450°C, which improved the microhardness, wear and corrosion resistance of the steel surface. Nitriding at higher temperature of 550°C resulted in substitution of the S-phase towards layer composed from CrN and α-Fe phases, improving the microhardness but decreasing the corrosion resistance.

1. Introduction

Known for exceptional corrosion resistance and excellent mechanical properties, austenitic steel is the most widely used in petroleum, chemical and food industries type of stainless steel [1, 2]. However, poor tribological properties of austenitic stainless steels limit their application in engineering fields. Thus, many mechanical parts, made out of austenitic steel, are often occluded or stuck [3, 4]. Increasing surface hardness [5] and groove texture with a careful design [6] may improve the tribological properties of the steel significantly. Nitriding, being one of the modern metal surface heat treatment method, enhances steel surface hardness and wear resistance. Compared with gas nitriding technology, plasma nitriding has higher thermal efficiency, better sample geometry suitability and less energy consumption [7, 8].

One of the methods to increase the nitriding temperature and thus, improve the efficiency of nitriding process is implementation of the hollow cathode auxiliary device [9]. Many kinematic models have been suggested to explain the temperature change [10] and ionization [11, 12] under the hollow cathode effect. A typical hollow cathode discharge structure includes two cathodes and an anode. When the electrode is energized, the cathode emits electrons that move toward the anode. When the two cathodes are close, the electrons emitted by one cathode will enter the electric field of the other cathode, and receive repulsive force. Then electrons return to the original cathode electric field, gain potential energy and move to the anode again. This repeated movement of electrons will collide with neutral particles, making the particles easier to be excited and ionized [12–14]. In the negative glow, the movement of positive ions are dominated by diffusion. The combination of two negative glow zones enhances the light intensity, which increases gas ionization rate, assisting in sample heating and energy consumption reduction [15].

During the nitriding process, many parameters such as temperature, nitriding time, pulsed power supply and arrangement of cathode have a great influence on the surface morphology, mechanical properties and corrosion resistance of the samples [16]. Y Hoshiyama et al showed, that prolonging of the nitriding time
increased the hardness of the nitrided layer [17]. Nevertheless, Naeem et al [18] pointed out that keeping constant the time-averaged current of the pulsed DC power supply duty cycle decreased the surface hardness. Obviously, based on the hollow cathode effect, a reasonable cathode arrangement can improve the gas ionization rate and thus the diffusion efficiency. However, there are few reports about the hollow cathode discharge with interval arrangement of cathodes and anodes.

In this paper, a modification of hollow cathode auxiliary device by its surrounding with the anode rods and cathode tubes was developed to increase the plasma density and accelerate the nitriding rate. Nitriding temperature was changed to verify the efficiency of the experimental equipment and explain the effect of the diffusion temperature on the ion diffusion process.

2. Experimental procedure

2.1. Materials
The diameter and thickness of the AISI 304 stainless steel, utilized in this work, were 20 mm and 8 mm, respectively. The chemical composition of the samples is shown in table 1. Before the experiment, the surface of samples was polished with sandpaper to the mirror-like state.

2.2. Nitriding process and setup
The nitriding process was accomplished by LDMC-20 pulsed plasma unit. The hollow cathode plasma treatment equipment is shown in figure 1. An auxiliary device had a cylindric structure consisting of a base, surrounded by cathode tubes and anode rods; and a round top cover.

This method of cathode and anode localization allows to generate an electric field, which drags the electrons toward the anode, incrementing collisions with gas molecules, and thus, increasing the plasma density. Arslanbekov et al [14] suggested several models to determine the electron distribution function of a similar close-packed cathode and anode devices from a physical point of view. Enclosing these tube rods in a cylindrical shape supported the expansion of the plasma discharge to the center of the setup, forming a uniform negative glow discharge in the central area, and improve the quality of nitriding. The number of cathode tubes was higher than the number of anode rods, which possibly increased the area of the glow discharge. The apertures on the cathode tubes also form the discharge effect, which increased plasma density. Meanwhile, these cathode tubes and anode rods generated heat after formation of the discharge effect, assisting the device heating and heat transfer from the device towards samples, accelerating the nitriding rate. It is worthwhile noting that the shape and the size of the screen may affect the thickness of the nitrided layer. The distance between the cathodic screen and the upper surface of the sample has an effect on the particle size of the sample surface [19].

In this paper, the disk-shaped insulating base was made out of mica, with an outer radius of 170 mm, an inner radius of 130 mm, and a height of 30 mm. There were 22 cathode tubes and 11 anode rods respectively, both made of AISI 304 stainless steel. The length of the tubes was 300 mm, the inner radius was 5 mm and the
The wall thickness was 3 mm. The diameter of the apertures on the cathode tube was 4 mm, and the pitch was 8 mm. The length and the radius of anode rods were 270 mm and 5 mm, respectively. The distance between two anode rods, an anode rod and a cathode tube were 9.8 mm and 12.8 mm, respectively. Auxiliary equipment was placed in the nitriding furnace with a sample table inside. The samples were in a floating potential. Ammonia was utilized as nitriding gas with a flow rate of 500 sccm. The plasma nitriding process was executed at two temperatures, 450 °C and 550 °C, respectively. The voltage, pressure, duty cycle and current were adjusted to 800 V, 300 Pa, 60%, and 10 A. The process in both cases lasted for six hours.

The auxiliary device is composed of closely-arranged anodes and cathodes, which greatly improves the efficiency of the hollow cathode effect and makes the gas introduced more easily to be ionized. The device improved the nitriding efficiency, which means that the nitriding sample can be prepared in a shorter time and more energy can also be saved. Shortening the diffusion time also means reducing the use of ammonia.

2.3. Characterization methods
X-ray diffraction analysis was performed on a Bruker D8-advance x-ray diffractometer with Cu Kα radiation and 2θ ranging from 30° to 70°. A FEI Quanta 200 FEG scanning electron microscope (SEM) equipped with energy dispersive spectroscopy was used to measure the surface, cross-sectional morphology and distribution of various chemical elements in the samples. A JEOL JEM-2100 transmission electron microscope (TEM) was used to characterize the structure of the samples. The detailed surface topography was measured using a NanoScope III atomic force microscope.

The localized corrosion resistance of the samples was measured at room temperature by CS-350 electrochemical workstation with a standard three-electrode system. NaCl with concentration of 3.5 wt% was used as the corrosion solution. The effective area of working electrode was about 10 mm².

3. Results and discussion
3.1. XRD analysis
The diffusion mechanism can be explained by ‘sputter-deposition’ model proposed by Saeed A [20]. The ion bombarded the cathode tubes, and the particles sputtered during the bombardment adsorbed nitrogen in the plasma space and deposited on the surface of the sample. The particles deposited on the surface of the sample decomposed at a specific temperature, and the nitrogen adsorbed in it was released and deposited on the surface of the sample [15]. Hubbard P et al [21] pointed out that the nitrogen penetrating the sample comes from sputter deposition and the active nitrogen-containing particles formed by nitrogen ion recombination.

Figure 2 shows the XRD patterns of the untreated and treated samples at 450 °C and 550 °C. The untreated sample exhibits two distinct peaks on XRD pattern at 43.68° and 50.8°, respectively. This indicates that the sample was mainly composed by austenite. An α-peak, which corresponds to martensite phase formed during the grinding process [22], also presents on the pattern at 44.56°. The relative peak’s height of these two phases indicates that the content of martensite phase in the metal matrix was much lower than austenite.
For the sample nitried at 450 °C, two new peaks designated by S (111) and S (200) phases appeared on the pattern at 40.8° and 46.32°, respectively. The angle values, corresponding to new phases, appeared to be smaller than the angle values of austenite peaks in untreated samples. This shifting of the austenite peaks can be explained by nitrogen supersaturation in the metal lattice [23]. It is worth noting that these two peaks belong to the face-centered cubic structure, which correlated with the experimental results published by Romero et al [24]. The metastable 'expanded austenite' phase called S-phase can be used to explain the formation of these peaks appeared at the nitriding temperature of 450 °C [25–27]. With the increase of temperature, the amount of S-phase decreases significantly, while the diffraction peaks of the CrN and α-Fe phase appeared at about 44.2° and 63.6°. It seems that the supersaturated nitrogen was released from the crystal lattice and form CrN combined with the chromium in the matrix [28].
3.2. Cross-section morphology and chemical composition

The cross-section morphology has been investigated by SEM imaging, shown in figure 3. An approximately 6 μm thick S-phase layer obtained at 450 °C could be observed in figure 3(a). Williamson et al [29] pointed out that, compared with the diffusion rate of nitrogen in fcc austenite, the diffusion rate of nitrogen in S-phase was faster and the activation energy was lower. The thickness of the diffusion layer obtained at 550 °C was about 33.9 μm, which was marked by a yellow line. The increased temperature makes the ammonia passed into the device have higher energy and be easier to ionize, so the plasma nitrogen content is higher and it is easier to deposit on the sample surface, making the diffusion layer thicker. It could be seen from figure 3 that the black dot-like phase precipitated from the nitrided layer at 550 °C, highlighted by green frames. Actually, the black part of the diffusion layer shown in figure 3(b) and the morphology in figures 3(c), (d) was a mixture of CrN and α-Fe.

Based on the analysis of XRD patterns, the black dot-like precipitated phase was related to CrN. Cr is the matrix component in 304 steel. Different nitriding temperature affects the thickness and the phase composition of the diffusion layer. However, in the process of combining chromium and nitrogen to form chromium nitride, the movement of chromium is on the nanometer level and will not affect the relatively macroscopic surface scan results. Therefore, Cr percentages is similar at different nitriding temperatures and different sampling points. Although there was no significant difference between the chromium content of the diffused layer and the substrate, as shown in table 2, the uneven distribution of chromium content can still reduce the corrosion resistance of the surface.

The chemical composition of the samples was analyzed by energy dispersive x-ray spectroscopy (EDS) in five sampling points and shown in table 2. The formation of nitrided layer was a complex process performed under high temperature and specific pressure, which involved several reactions taking place simultaneously at the boundary between the gas and the metal phases [30]. By analyzing the differences in elemental composition at different sampling points, the effect of the diffusion temperature on the nitriding layer can be inferred. The high values of carbon and oxygen contents are probably due to a surface contamination. First sampling point was located on the S-layer of the sample treated at 450 °C. The nitrogen content of the S-layer is 6.65 wt%, which is higher than that for the matrix (fifth sampling point), and the chromium and nickel content was lower. Same

| Table 2. Chemical compositions (wt%) of the different area from the figure 3. |
|-----------------|---|---|---|---|---|---|
|                | C  | N  | O  | Cr | Ni | Fe  |
| Area 1         | 10.55 | 6.65 | 5.82 | 16.33 | 6.08 | 54.56 |
| Area 2         | 13.84 | 8.21 | 6.55 | 15.96 | 5.10 | 50.34 |
| Area 3         | 8.03  | 7.32 | 5.52 | 16.11 | 6.24 | 56.78 |
| Area 4         | 3.69  | 2.51 | 3.44 | 17.37 | 7.35 | 65.65 |
| Area 5         | 3.59  | 1.25 | 3.14 | 17.43 | 7.38 | 67.21 |

Figure 4. Cross-sectional field TEM micrograph and SAED pattern from the near surface of the nitrided samples at (a), (b) 450 °C and (c), (d) 550 °C.
distribution of chemical elements was found in samples nitrided at 550 °C. The deeper the nitrided layer, the lower the nitrogen content, and the higher the chromium and nickel content. This can be attributed to the nitrogen diffusion into the samples from the surrounding media, which concentration decreases with the nitrogen ions penetration depth.

Figure 3(f) shows the EDS line scan on cross-sectional of the nitrided layer of the 450 °C samples. The scan position was shown in figure 3(a) by a red line. The content of iron within 6 μm from the surface (thickness of the diffusion layer) is slightly lower than the content in the matrix. The nitrogen content decreased significantly at 6 μm from the surface of the sample. This phenomenon is consistent with the diffusion principle mentioned in section 3.1.

TEM analysis was performed on the nitrided samples to analyze the sample microstructure. Figure 4 shows TEM morphology of the nitrided layer and the corresponding selected area electron diffraction (SAED) of the samples nitrided at different temperature. The structure of the samples nitrided at 450 °C consisted from dislocations found from the bright-field TEM image (figures 4(a), (b)). The corresponding SAED indicated that the diffraction spots had a face-centered cubic structure, which is in consistence with the XRD results, confirming that the nitrided layer mainly composed of face-centered cubic S-phase. For the samples nitrided at 550 °C, SAED analyses showed the formation of CrN and α-Fe phases (figures 4(c), (d)). Due to chromium

Figure 5. SEM surface morphology and corresponding EDS microanalysis of (a), (b) untreated samples, nitrided samples at (c), (d) 450 °C and (e), (f) 550 °C.
diffusion, CrN is able to form and the surrounding Cr-poor FCC austenite structure tends to transform in the BCC structure.

3.3. Surface topography and hardness

Figure 5 shows SEM surface morphology and corresponding EDS elemental analysis. Due to some surface contamination, the carbon content on the surface of untreated samples is higher than that for AISI 304 steel. Boundaries of austenite grains could be observed on the surface of the nitrided samples, which is because of the formation of the S-phase \[31\] and the nitrogen ions impact \[32, 33\] during the nitriding process. The formation of the S-phase is associated with the transformation of austenite into a bcc structure, which is consistent with the observation of the formation of S-phase in the nitrided samples. The hardness of the untreated and nitrided samples at 450°C and 550°C is shown in Figure 7. The hardness of the nitrided samples is significantly higher than that of the untreated sample, indicating the improved wear resistance and corrosion resistance of the nitrided samples.

Figure 6. Surface topography AFM images of the samples nitride at 450 °C (a) 3D image magnified 3000 times, (b) 2D image magnified 3000 times, (c) 3D image magnified 30000 times, (d) 2D image magnified 30000 times.

Figure 7. Surface microhardness of the untreated and nitrided samples.
of S-phase causes plastic deformation and rotation of the grains at the surface owing to austenite lattice expansion. This means that the increased diffusion temperature led to an increase in the surface roughness. The measurement values confirmed this, which were 20 nm (Ra) for untreated, 192 nm (Ra) for 450 °C, 306 nm (Ra) for 550 °C, respectively. It could be found from the results of EDS that the nitrogen content on the surface of the sample increased with the increase of diffusion temperature. The increased roughness will increase the corrosion area of the sample in the electrochemical experiment, but this is not a key factor affecting the corrosion resistance of the material.

Atomic force microscopy method is usually used to study the micro-topography and nano-roughness of the sample surface [34, 35]. Galeano-Osorio et al. [7] studied AFM images and pointed out that the increase in roughness directly related to the processing temperature. In the previous work, the surface roughness of the polished sample presented an average surface roughness of 2.95 nm (Ra) with no obvious morphology differences among the grains [36]. The surface morphology of the sample taken under the tapping mode of AFM is shown in figure 6. Using the AFM to magnify the surface morphology of the sample 3,000 times, the peak-shaped grains and valley-shaped grain boundaries could be observed from figure 6(a). The difference between the highest and the lowest point was 328 nm and the roughness value was 33.7 nm (Ra). Due to the diffusion of nitrogen, the microscopic roughness of the surface increased, which also caused the expansion of the crystal lattice. Therefore, the S-phase appeared on the surface of the samples, nitrided at 450 °C, was described as a metastable supersaturated solid solution of nitrogen in the austenite lattice. As shown in figure 6(d), when the surface of the sample was magnified to 30,000 times, granular protrusions can be observed, which may be due to the nitrogen diffusion. The nitrogen entering the lattice cannot exist stably. When the temperature rises, nitrogen with higher energy combines with chromium in the matrix to form CrN.

The infiltration of specific elements on the metal surface may greatly improve the surface hardness [37]. Microhardness measured on the surface of the samples is shown in figure 7. The microhardness value measured at the surface of samples nitrided at 550 °C was 1280 HV0.1, which was more than five times higher than that for the untreated samples: 230 HV0.1. Due to the solid solution strengthening [31] and work hardening [31, 38], the microhardness value of samples treated at 450 °C was 960 HV0.1, which reflected the hardness of the S-phase. An increase of the nitriding temperature increased the microhardness of the sample surface.

### 3.4. Corrosion resistance properties

When corrosion phenomena occurs, N alloying can widen the passive range and enhance corrosion resistance [31]. The corrosion resistance of the nitrided layers is essentially affected by the surface topography and the
The chemical composition of the layers [39]. It can be seen from the results of the polarization experiment shown in figure 8, table 3 that the corrosion resistance of samples treated at 550 °C was the lowest: the corrosion potential was $-0.398 \text{ V}_{(SCE)}$ and corrosion rate was 0.106 mm/year. The decrease of local corrosion resistance in those samples can be attributed to the precipitation of the CrN phase caused by uneven distribution of the Cr element in the nitrided layer. The corrosion potential of the untreated samples was $-0.324 \text{ V}_{(SCE)}$. A clear passivation zone appeared to be on the polarization curve and the pitting potential was about $0.35 \text{ V}_{(SCE)}$. For the samples nitrided at 450 °C, the corrosion potential increased to $-0.265 \text{ V}_{(SCE)}$. Both the minimum corrosion current value ($3.83 \times 10^{-7} \text{ Amp/cm}^2$) and the maximum impedance value (68113 Ohms/cm²) appeared on samples treated at 450 °C. This proves that the corrosion resistance of S-phase was better. When the diffusion temperature is below 450 °C, the S phase is relatively stable [40]. A reasonable theory [41, 42] shows that the nitrogen in the stainless steel will dissolve and react with $\text{H}^+$ during the electrochemical experiment by the reaction of $\text{N} + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NH}_4^+$. This neutralizes the acid near the corroded surface. A passivation layer is formed on the surface of the sample, thereby reducing the rate of pitting corrosion. Comparing the EDS microanalysis of the sample surface nitrided at 450 °C in figures 5 and 9, it can be seen that the content of each element does not change significantly. Nitrogen reacted with $\text{H}^+$ during the corrosion process, so the surface nitrogen element content decreases slightly after corrosion.

Figure 9. SEM micrographs and EDS microanalysis of the (a), (b) untreated samples, nitrided samples at (c), (d) 450 °C and (e), (f) 550 °C after polarization measurement.
Figure 9 shows the samples surface micro-morphology and corresponding elemental composition after electrochemical corrosion. There were obvious pitting pits on the corroded surface of the untreated samples. Compared with samples treated at 450 °C, more corrosion cracks appeared on the surface of samples treated at 550 °C. The precipitation of CrN caused the decrease in intergranular corrosion resistance. The fact that the Cr content soared to 40.92 wt% (figure 9(f)) supports this conclusion. However, the elemental content of samples nitrided at 450 °C has not changed significantly compared with untreated samples. Baba et al. [43] proposed that the supersaturated nitrogen in the S-phase reacted with hydrogen ions, which decreased the growth rate of the pit, meaning that the formation of the S-layer improved the corrosion resistance.

4. Conclusions

AISI 304 stainless steel was nitrided using a new auxiliary device with hollow cathodes tubes and anodes rods. Through this special electrode arrangement, the gas ionization ratio is greatly increased, thereby accelerating the nitriding process. The samples prepared under different diffusion temperature verify the effectiveness of the auxiliary device.

When the nitriding temperature increased from 450 °C to 550 °C, due to the increase in nitrogen energy, the thickness of the nitrided layer increased from 6 μm to 33.9 μm. The phase composition changed from single S-phase to a mixed phase composed of CrN, α-Fe and residual S-phase, the surface roughness doubled, the surface microhardness increased from 960 HV0.1 to 1280 HV0.1. The samples nitrided at 450 °C showed great corrosion resistance in electrochemical corrosion experiments. Through a series of methods to characterize the samples, it is proved that a diffusion layer with moderate thickness, uniform components, high hardness and good corrosion resistance can be produced by the new nitriding device. For the AISI 304 stainless steel, relative to the higher temperature, the samples prepared at 450 °C have higher hardness and better corrosion resistance.

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