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The Effect Of Ammonia Water On The Microstructure And Performance Of Plasma Electrolytic Saturation Nitriding Layer Of 38CrMoAl Steel

Xiao-Zhen Hua\textsuperscript{a}, Lang Zhou\textsuperscript{a}, Xia Cui\textsuperscript{a}, Ai-Hua Zou\textsuperscript{a}, Wu-Bo Xu\textsuperscript{a}, Xian-Liang Zhou\textsuperscript{a,b,*}

\textsuperscript{a} School of Materials Science and Engineering, Nanchang Hangkong University, Nanchang 330063, China
\textsuperscript{b} Key Laboratory of Nondestructive Test, Ministry of Education, Nanchang 330063, China

Abstract

38CrMoAl nitriding layer had been prepared by plasma electrolytic nitriding under different concentration of ammonia water. The layer structure, surface and phase composition had been analyzed by OM, SEM, XRD, respectively. Deeper analysis about element distribution in layer had been implemented by GDOES. The layer corrosion resistance had been measured by Parstat2273 Electrochemical workstation. Microhardness and the wear properties of specimens were also evaluated. The experiment results show that: the nitriding layer consist mainly of Fe\textsubscript{2}N and Fe\textsubscript{3}N, the layer thickness is 85±5 to 165±15\textsubscript{C}m and the cross-section microhardness of the layer is 650-1023HV after treated 10min at 220V. When the concentration of ammonia water drops to 40%, FeO is observed in outer-layer. The intensity of the maximum diffraction peak changed with the varying of nitrogen concentration. With the increasing of ammonia water concentration, the thickness of uniform and compact the white layers increases, the diffusion layers consist of needle nitrides and small carbides first increases then decreases, the distance for the biggest microhardness position to the surface increases obviously. After treated at 60% ammonia water, the layer thickness would get 165\textsubscript{C}m, the diffusion layer reach 114\textsubscript{C}m, microhardness of the layer reach 1023HV while the substrate hardness remain 310HV. Compared with the treated sample, the untreated wearing weight increase 4.5 times. The corrosion potential had been improved greatly from -523.4mV to -464.1mV. The white layer reaches 52\textsubscript{C}m while the ammonia water reaches 70. However the diffusion layer is thinner, so the layer thickness decrease gradually.

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Keywords: Ammonia water; 38CrMoAl steel; plasma electrolysis; nitriding layer; microstructure; corrosion resistance; wear resistance

* Corresponding author. Tel.:+135-7629-8956; fax:+0-791-395-3320.
E-mail address:zhouxl209@163.com (X.L.Zhou).
1. Introduction

38CrMoAl steel is a kind of medium carbon alloy steel, which is the most typical nitriding steel (Zhou Shang qi et al., 2002). The main purpose of the nitriding can improve the surface hardness, wear resistance and corrosion resistance, while heart of the nitriding parts can maintain high strength and toughness. With the development of the industry, the gas nitrocarburizing, gas nitriding and plasma nitriding process (J.J. Jeong et al., 2002), (A. L. Yerokhin et al., 2001) were investigated extensively, However, The shortcomings of the traditional nitriding process required a long production period, high energy consumption, easy to deformation, low production efficiency, high cost of the process (A. Leyland et al., 1999). Plasma electrolysis technology (P. Gupta, G et al., 2007), (C. Tsotsos et al., 2001), (E.I. Meletis et al., 2002) can solve these problems, the workpiece is placed in an electrolyte through arc discharge in a few minutes can obtain very high hardness, wear resistance, corrosion resistance of nitriding layer. The performance of the nitriding layer is mainly affected by process parameters of voltage, processing time, current density, frequency and electrolyte composition. At present, the process parameters study focused on the effect of voltage, current and frequency on the microstructure and properties of layer. However, the influence and role of electrolyte in the structure and performance of layer has not been reported hitherto in the literature. At the same time, the research focused on carburizing, carbonitriding (X. Nie et al., 2001), (M. Tarakci et al., 2005), (F. Cavuslu et al., 2011), (L. Wang et al., 2005) and plasma electrolysis nitriding is less.

Plasma electrolysis technology often choose source of the carbon and nitrogen is commonly glycerol, ethanolamine, urea, formamide etc. Compared with them, ammonia water is a kind of pure nitrogen source, the cost is low and ammonia water as nitrogen source has not been reported hitherto in the literature. Base on the effect of electrolyte systems on the microstructure and performance of plasma electrolytic saturation nitriding layer of 38CrMoAl steel. We choose ammonia water as nitrogen source. Nitriding treatment of 38CrMoAl steel through self-developed of the plasma electrolytic permeability apparatus in different ammonia water concentration was studied in this paper. Influences of ammonia water on structure morphology, thickness, hardness, corrosion resistance and wear resistance of plasma electrolytic saturation nitriding layer of 38CrMoAl steel, which is an important basis for study of the electrolyte.

2. Experimental materials and methods

Substrate material used in this study was 38CrMoAl steel that had a shape of approximately 2mm×12mm×15mm. All the samples were ground by 180 and 600 grit SiC paper and cleaned by ethyl alcohol before the plasma electrolytic surface saturation nitriding treatment. The chemical composition (Bal. Fe) of 38CrMoAl steel is given in table 1.

Table 1  Chemical composition of 38CrMoAl steel ( wt%)

<table>
<thead>
<tr>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>1.48</td>
<td>0.2</td>
<td>0.9</td>
<td>0.3</td>
<td>0.35</td>
<td>0.03</td>
<td>0.035</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Nitriding was performed in aqueous medium with a nominal chemical composition of ammonia water, water, quantitative additives. The electrolyte was prepared by solving first additive in water and then 40%, 50%, 60% and 70% ammonia water was added to the solution. In this aqueous solution, electrolytic conductivity was attained by addition of additive, and ammonia water acted as a nitrogen source. In this study nitriding treatment was used self-developed of the plasma electrolytic permeability apparatus with a DC power supply, at the same time, Titanium plate as an anode and sample as a cathode.
After that, 220V DC was applied to the sample and immersed slowly into the electrolytic, the sample placed below the liquid level 4-10mm. In the vicinity of the sample, the hydrogen film rapidly formed with surface temperature rose slowly. Once stable arc discharge is formed on the sample, and then started time. The samples were subjected to the nitriding treatment in different ammonia water solution for 10min, and were quenched in the solution to room temperature by shutting down the power supplied. Following quenching, the samples were removed from the clamping device and cleaned by ethyl alcohol.

Rigaku X-ray diffractometer(D8X) was employed for the phase characterization of nitriding layer of the samples. The diffract conditions are that it takes CuKα radiation source, graphite monochromator, working voltage for 40kV, working current for 40mA, scanning speed for 8°/min and the step size of 0.02°. Before the mesurements, samples were ground on wet emery paper down to 2000 grit, then polished and etched with 4% Nital. Philips SU1510 scanning electron microscope (SEM) was used to examine the microstructure of the cross-section and surface topography of the samples. The presence of possible elements in the layer was confirmed via energy dispersive X-ray spectroscopy (EDS). Depth profile analysis of the layer was qualitatively performed using RF-Glow Discharge Optical Emission Spectrometry (RF-GDOES). The thickness of the nitried layer was measured under an optical microscope. The hardness of the nitrided layer was measured by a HX-1000 hardness tester equipped with a Vickers diamond indenter with a load of 100g and a time of 10s. In addition, the corrosion behavior of the samples has been evaluated using Parstat2273 Electrochemical workstation in 3.5% NaCl saturated solution at 25°C in a three-electrode electrochemical cell with a scan rate of 1mv/s which was characterized potentiodynamic polarization curves. The sample is the working electrode, a saturated calomel electrode (SCE) was used as a reference and a platinum as a counter electrode. Finally, wear tests on untreated and treated samples were evaluated using a reciprocating sliding machine under dry pure slide conditions. The tests were performed at room temperature and atmospheric pressure using a WC balling of 45 mm diameter at a rotate speed 234 r/min under a normal load of 50 N.

3. Experimental results and analyses

3.1 Optical texture and microhardness

The microstructures of plasma electrolytic saturation nitriding layer of 38CrMoAl steel under 40%, 50%, 60% and 70% ammonia water are shown in Fig. 1(a-d). It can be seen from the pattern that four regions appear in the nitrided layers in Fig. 1(a-d), namely: (1) the outside is loose layer, (2) uniform and compact the white layers, (3) the diffusion layer consist of needle-like nitrides and small carbide, and (4) the transition zone between the layer and the substrate, presumably rich in small nitrides and carbide. Although it is difficulty to distinguish region the transition zone and the substrate, presumably rich in small nitrides and carbide. The thickness of the nitrided layers thickness depending on ammonia water concentration. From figures, in the same voltage and the processing time, the thickness of layers shows a variation tendency, which first increases to the maximum value and then decreases with the increasing of ammonia water concentration. It is estimated that the thickness values of nitrided layers from 85±5 to 165±15μm. In addition, variation curve of the thickness values of the white layers and the diffusion layers under different concentration of ammonia water are shown in Fig. 2(b).
Fig. 1 Optical micrographs of the nitrided layers under different concentration of ammonia water: (a)40%; (b)50%; (c)60%; (d)70%

Fig. 1(a-d) shows that the layers contained uniform and compact the white layer, the diffusion layer consist of needle nitrides and small carbide on the surface of the samples, although there is no big difference between the treated samples under different concentration of ammonia water. All of the samples contained some tiny porosities dispersed the thickness was about 3−5μm in the loose layers. The different of surface concentration and temperature which resulted in the intensification of the etched and consequently surface loosen. Fig. 1(a) shows that the thickness of the layer was evaluated about 85μm and the thickness of the white layer was about 25μm. When the concentration of ammonia water increased to 60%(fig. 1(c)), the thickness of the layer increased to 165μm, the thickness of the white layer reached to 46μm and the thickness of the diffusion layer increased to the maximizing 114μm(fig. 2(b)). As seen from fig. 2(a), when the concentration of ammonia water continue increased to 70%, the thickness of the layer reduced to 118μm, the thickness of the white layer continue to increase to 60μm. It is related to percentage ration of water and surface concentration of nitrogen in the electrolyte. The same conditions of treating time and voltage, the higher ammonia water concentration decreased the resistance between the sample and the solution, meanwhile high surface concentration of nitrogen is the other important factor that provides the driving force for diffusion. Percentage ration of water decreased with the increasing of ammonia water concentration, surface temperature decreases, which lead to the reduction of the diffusion coefficient, thus suppressing diffusion of nitrogen. When the concentration of ammonia water reached 60%, surface concentration of nitrogen and surface temperature is obtained in
perfect balance, thus thickness of the layer is the greatest. The microstructure of the substrate was mostly continued of lath martensite under different concentration of ammonia water.

![Graph](image)

Fig. 2: The variation curve of the thickness of the layer under different concentration of ammonia water: (a) the layer; (b) the white layer and the diffusion layer.

Fig. 3 shows the cross-section microhardness indentation variation from the outer layer to the interior for the sample treated in 60% ammonia water. It can be seen from the pattern that the microhardness of region 1 of the white layer is 681 HV, the microhardness of region 2 of the diffusion layer is 913HV and the hardness of region 3 of the transition zone is 824HV. While the microhardness of the untreated is 310HV, the microhardness of the layer was more than 2.5 times of matrix. Fig. 4 also shows the curve of the microhardness variation from the surface to the interior for the sample treated under 40%, 50%, 60%, 70% ammonia water. The results indicate that the microhardness of the samples treated under different concentration of ammonia water shows a same variation tendency, which first increases to maximum value, decreases and then quenching hardness stabilizes with the increase of distance to surface. The cross-section microhardness of the layer is 650-1023HV. The tendency of microhardness variation is in good agreement with the metallographic analysis.

![SEM Image](image)

Fig. 3 SEM image of the treated at in 60% ammonia water, showing the microhardness indentation variation from the outer layer to the interior.
Further finding from Fig.4, when the concentration of ammonia water drops to 40%, the biggest microhardness was 913HV, which obtained distance from surface at a distance of 30μm. With the increasing of ammonia water concentration, the distance for the biggest microhardness position to the surface gets bigger. When the ammonia water reaches 70%, the biggest microhardness was 981HV, which obtained distance from surface at a distance of 75μm. It’s about the white layer. Hardness measurements showed that the microhardness of the surface layer in the white layer is much lower than that of the diffusion layer due to part of the nitrogen atoms recombine into N₂ in the grain boundary of the white layer, to escape from the surface of the formation of the micro hole, and then these tiny holes merged to form the channel perpendicular to the surface, which resulted in loose structures in the surface. It is evident that the biggest microhardness first increases then decreases with the increasing of ammonia water concentration. In the same condition of discharge voltage and worked time, due to higher nitrogen potential may promote formation of the white layer with the increasing of ammonia water concentration, the diffusion coefficient, the mobility of the nitrogen atoms and the rate of diffusion decreases and the formation of nitrides and carbides refrains with decreasing temperature, which results in the porosity layer forms by the molecularized of the more nitrogen atoms and influences on enhancement of microhardness of the layer. Take together, when the concentration of ammonia water drops to 60%, microhardness of the layer reached 1023HV. This illustrates that hardness is affected synthetically by ammonia water concentration and the surface temperature.

3.2 Phase and element analysis

The X-ray diffraction (XRD) patterns of the untreated and treated samples under 40%, 50%, 60% and 70% ammonia water are shown in Fig.5. It can be seen from the diffraction pattern that there is a clear difference between untreated and treated samples. The dominant phases formed on 38CrMoAl steel were found to be a mixture of Fe₂N, Fe₃N, Fe₃C, AlN and FeO confirmed. As it can be seen in Fe-N phase diagram, Fe₂N, Fe₃N phase were formed with N soluble in α-Fe. When the concentration of ammonia water drops to 40%, FeO is observed in outer-layer. When the concentration of ammonia water is more than 50%, FeO is not detected, although there is no big difference between the treated samples under 50%, 60% and 70% ammonia water. As a result of the lower ammonia water, water content is higher in the electrolyte, the higher the surface temperature, the surface is more vulnerable to the oxidation reaction.
As it can be seen in Al-Fe phase diagram, 1% Al being dissolved in solid solution with α-Fe, at the same time, Al, Cr and Mo has a strong affability for nitrogen, the formation of AlN for the treated sample was observed which changed the solubility of some phase of nitrides.

As shown in Fig.5, cementite was detected for treated samples under different concentration of ammonia water. As a result of higher carbon concentration can lead to the expansion of the lattice parameter with the diffusion of carbons in the grain-boundary sites of the austenite forming cementite in the diffusion layer. It can be seen from Fig. 1 that there are some dark areas in the diffusion layer with different microstructure that might be a lot of needle-like nitrides, small carbides and martensite structure was obtained by quenching directly after nitrided, at the same time, some retained austenite is always present in the case of high carbon content in the diffusion layer. Needle-like nitrides are related to ferrites of the microstructure are lath-like. At the same time it can be attributed to diffusing and infiltrate of nitrogen which results in the increasing of content of Al, Cr and C in the diffusion layer. However, the brittle of the nitrided layer increased with increasing needle-like nitrides. XRD analyses showed that the intensity of the major peak attributed to Fe2N, Fe3N, Fe3C, first increases then decreases with the increasing of ammonia water concentration. It was observed that the major peak changed with changing thickness of the nitrided layer. Take together. When ammonia water is low, at the same treating time and voltage, the surface is more vulnerable to the oxidation reaction. With the increasing of ammonia water concentration, the oxidation of reaction is the fainter.

Fig. 5. XRD patterns of the untreated 38CrMoAl and treated samples under 40%, 50%, 60% and 70% ammonia water.

Fig. 6 shows the variation curve of the main elemental concentration depth profiles of the nitrided sample in 60% ammonia water by RF-GDOES. As seen from fig. 6(a), the content of nitrogen was continuously decreased, while the content of Fe was gradually increased with increasing of the distance to surface. From fig. 6(a), the contents of carbon, chromium and aluminum at first decreased in the white layer then increased in the diffusion zone, last come down to the content of substrate. It shows that the formation of carbonitride(especially chromium ) has changed element distribution of originality state in matrix after nitriding treatment. Thus, the white layer was mostly constituted of the mixed phase of Fe2N and Fe3N. The contents of carbon, chromium and aluminum increased in the diffusion zone led to the formation of carbonitride increased which would cause layer maintain relatively high hardness. However,
the thickness of the layer can not be fully agreement with the optical texture analysis. The other parameters constant, due to the test specimen by GDOES required bigger for size which caused surface temperature decreased and the thickness of the layer decreased. In fig 6(a), the higher nitrogen content in surface layer was affected by part of the nitrogen atoms recombine into $N_2$ in the grain boundary and the equipment to be charged with nitrogen in test.

![Graph](image1)

![Graph](image2)

Fig. 6 Elements distribution in 60% ammonia water: (a) Fe, N; (b) C, Al and Cr;

### 3.3 Polarization parameters

Experimental results showed that the concentration of ammonia water reach 60%, which was the optimum proportion of the electrolyte. Thickness and microhardness of the layer was better at 220 V for 10 min. So corrosion resistance and wear resistance of the treated of the sample in 60% ammonia water was determined. The potentiodynamic polarization curves for the untreated and treated samples in 60% ammonia water are shown in Fig.7. In addition, electrochemical measuring results in 3.5% NaCl solution are listed in Table 2. It is seen that the corrosion potential increases from -523.4mV for the untreated of 38CrMoAl steel to -464.1mV for plasma electrolytic saturation nitriding treatment in 60% ammonia water. The passivating phenomenon can be found in polarization curve with the very narrow passivating range and thereafter anode currents increase rapidly. However, self-corrosion current density decreases from 0.0061mA.cm$^2$ to 0.0037mA.cm$^2$ with increasing of potential. These results imply that the sample of plasma electrolytic saturation nitriding treatment in 60% ammonia water shows the better performance in corrosion-resistant than the sample of untreated. Due to $Fe_2N$ and $Fe_3N$ in the white layer ensures good anti-corrosion property (Cui G D et al., 2008). In addition, high nitrogen and carbon atoms filled in grain boundaries and defects in the diffusion layer, which resulted in crystalline structures become denser. Therefore, it can largely improve corrosion resistance of 38CrMoAl steel.
3.4 Wear resistance

The sliding wear tests results of the treated in 60% ammonia water and untreated samples is shown in Fig. 8. The biggest wearing weight of the sample is 0.75mm$^3$ after treated 10min at 220V. Compared with the treated sample, the untreated wearing weight increase 4.5 times. It can be seen from that the wear resistance of the treated 38CrMoAl steel is improved obviously and becomes increasingly better with the wear time. Largely, this is because needle-like nitrides, small carbides (Fe$_3$C) and martensite phases in the layer can increase the hardness obviously. Thus, efficiently reduces intense adhesion wear. The mixed phase of Fe$_2$N and Fe$_3$N in the layer caused the higher internal stress among the phases and it was unfavorable to increase the wear resistance. There was a possible correlation with the releases of the internal stress. There is a big difference about the wear resistance between the treated and untreated sample, we need to perform more detailed studies on microstructure.
4. Conclusion

(1) The thickness values of nitrided layers from 85±5 to 165±15μm under different concentration of ammonia water. With the increasing of ammonia water concentration, the thickness of layers shows a variation tendency, which first increases to the maximum value and then decreases, the thickness of uniform and compact the white layers increases, the diffusion layer consist of needle nitrides and small carbides increases then decreases. When the concentration of ammonia water reached 60%, surface concentration of nitrogen and surface temperature is obtained in perfect balance, the thickness of the layer increased to 165μm and the diffusion layer increased to the maximum 114μm. The white layer reaches 52μm while the ammonia water reaches 70. However the diffusion layer is thinner. Thus the thickness of layer increases with the increasing of nitrogen concentration and surface temperature.

(2) The cross-section microhardness of the layer is 650-1023HV under different concentration of ammonia water. Microhardness first increases to maximum value then decreases with the increasing of distance to surface. With the increasing of ammonia water concentration, the biggest microhardness first increases then decreases under different concentration of ammonia water, the distance to the surface gets bigger. When the concentration of ammonia water drops to 60%, microhardness of the layer reached 1023HV.

(3) The nitrided layer was mostly constituted of the mixed phase of Fe₂N and Fe₃N. When the concentration of ammonia water drops to 40%, FeO is observed. The intensity of the maximum diffraction peak changed with the varying of nitrogen concentration.

(4) Compared with the treated sample, the untreated wearing weight increase 4.5 times. The corrosion potential had been improved greatly from -523.4mV to -464.1mV. It is shown that the samples after plasma electrolytic saturation nitriding treatment can largely improve corrosion resistance and wear resistance of 38CrMoAl steel.

Fig. 8 Variation in the wear volume loss for the untreated and treated samples in 60% ammonia water
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References


