Corrosion Behavior of Active Screen Plasma Nitrided 38CrMoAl Steel under Marine Environment

Yang Li¹,², He Yongyong¹, Mao JunYuan¹ and Zhang Lei²
¹State Key Laboratory of Tribology, Tsinghua University, Beijing, 100084, PR China
²Department of Materials Science and Engineering, Yantai University, Yantai, 264005, PR China

Abstract. The 38CrMoAl steels were nitrided at different temperatures for 7 h using active screen plasma discharge. The analysis showed that the thick compound layer composed of ε-Fe₂₃N and γ′-Fe₄N was formed on the surface. The corrosion behavior was evaluated by measuring the anodic polarization curves in natural sea water (similar 3.5% NaCl solution), and observation of corroded surface were conducted. The electromechanical measurements indicated that the corrosion potential of the nitrided specimens shifted to a nobler value compared to that of untreated specimens. Passive regions were also observed in the polarization curves for all the nitrided specimens. These results indicate that active screen plasma nitriding can enhance the corrosion resistance of the 38CrMoAl steel under marine environment.

1. Introduction
Plasma nitriding is an effective surface modification technique to improve the surface hardness and corrosion resistance of various steels. By the nitriding process, the α-Fe solid solution becomes enriched with nitrogen and, if the chemical potential of nitrogen in the nitriding atmosphere is sufficiently high, different iron nitrides may form. Many researches have been made to investigate the effects of processing parameters on the microstructures and properties of modified layers formed on various steels by nitriding over past several decades [1-3]. Nitrided layers can be subdivided into a diffusion layer and a compound layer which consist predominantly of iron nitrides ε-Fe₂₃N and γ′-Fe₄N and a diffusion layer. The diffusion layer determines the strength of the nitrided layer, as well as its fatigue strength, while the compound layer determines the tribological characteristics and corrosion resistance. Recent years, many results have been published about the influence of various nitriding techniques on the corrosion behaviors of stainless steels [4-6]. However, very little work about corrosion behavior of nitrided low alloy steels has been done on these aspects [7]. For instance, A. Basu et al. [8] studied the effect of plasma nitriding on the corrosion resistance of high carbon low alloy steel. The evident improvement of corrosion resistance was due to the maximum coverage of nitrides after nitrided at 560 oC for 5 h. Basso et al. [9] reported the plasma nitrocaburizing of AISI H13 tool steel with different processing time from 2 to 20 h and the influence of microstructure of nitrided layer on its corrosion behavior.
Corrosion behavior of nitrided low alloy steels depends on the type of the nitride formed in the compound layer. Nitrided steels are more resistant to general corrosion in comparison with untreated ones, but are subjected to pitting corrosion. The objective of this paper is to investigate the effect of
active screen plasma nitriding on the corrosion resistance of 38CrMoAl low alloy steel in 3.5% NaCl solution.

2. Experiments
The chemical composition of the 38CrMoAl steel used for plasma nitriding is (wt%): 0.37–0.42 C, 1.30–1.60 Cr, 0.70–1.10 Al, 0.50–0.80 Mn, 0.30–0.46 Si and Fe balance. The diameter of 25 mm steel bars were cut into 6 mm thick discs. The surfaces of specimens were mechanically polished to a mirror finish before being placed into the nitriding chamber.

The nitriding was performed in active screen discharge plasma nitriding furnace at temperatures ranging from 500 to 530°C for 7 h. The N₂ and H₂ gas was used as nitriding agent to provide active nitrogen atoms for diffusion into the substrate. The working pressure during nitriding was 500 Pa. The microstructure of the nitrided specimens was investigated using optical microscopy and scanning electron microscopy (SEM). X-ray diffraction (XRD) analysis was carried out to determine the phase composition in the nitrided layer produced by nitriding. The electrochemical experiments were performed with the CHI660e electrochemical working stations in solution of 3.5% NaCl at room temperature. All potentials recorded throughout the test are with respect to a saturated calomel electrode (SCE).

3. Results and Discussion
The cross sections of the 38CrMoAl steels nitrided at 500°C and 530°C for 7 h are presented in Fig.1. The nitrided layer are consisted of the outer compound zone, a thin and dense white layer, and the inner diffusion zone in accordance with usually nitrided low alloy steels. Metallographic observation shows that the thickness of the compound layer is changed from 7 to 11 μm with the nitriding temperature increased from 500°C and 530°C. It can be seen that the layer thickness increases with the increasing operating time and treatment temperature [10].

![Figure 1. Cross-sections images of nitrided 38CrMoAl steel.](image-url)

X-ray diffraction patterns obtained from the specimens nitrided at different temperatures are presented in Fig.2. The X-ray analysis confirmed the presence of ε-Fe₂₃N and γ′-Fe₃N phases in the compound layer formed at the surface region for all nitrided specimens. The details of the surface properties are given elsewhere [7, 10].
Figure 2. XRD patterns of the specimens nitrided at 500 °C and 530 °C for 7 h.

Fig.3 shows the polarization curves for the untreated and nitrided specimens at temperatures of 500°C and 530°C measured in 3.5 % NaCl solution. The 38CrMoAl substrate has a corrosion potential of -540 mV and exhibits a fast corrosion current increase as the potential. The corrosion potential for the nitrided specimens at 500°C and 530°C temperatures is -310 mV, -200 mV respectively and is higher than that of 38CrMoAl steel. This result showed that the compound layer formed during nitriding treatment caused the corrosion potential of the nitrided 38CrMoAl steel shift in the noble direction evidently.

Figure 3. Potentiodynamic curves of anodic polarization of the different specimens in marine solution.

In contrast to the untreated 38CrMoAl steel, all the nitrided specimens show a passivation behavior in the potential range from -200 mV to 350 mV the resulted in a very low anodic current in the passive regions. Clearly, the existence and thickness of compound layer plays an important role in determining the corrosion resistance of the nitrided specimens. These results are in agreement with the observations provided by Wen [11]. Ensinger et al. [12] also concluded that a dense nitrided layer irrespective of the type of the nitrides would always enhance corrosion resistance of steel.
Figure 4. SEM images of the different specimens after polarization tests.

Figs. 4 showed the corroded surface morphologies of the unnitrided and nitrided specimens, which had been subjected to the anodic polarization measurements up to a potential of 700 mV. From Fig. 4a it can be seen that a large amount of patches of corrosion product and pits were left on the surface of the unnitrided specimen and this showed that severely general and pitting corrosion happened simultaneously during polarization test in 3.5% NaCl solution. The nitrided specimen at 530 °C for 4 h (Fig. 4b) which has a lower dissolution current, shows considerably lower amount of pits regarding the other specimens. Once these pits were formed in some weak locations and penetrated through the compound layer they would expanded in the matrix under the compound layer because the compound layer is nobler than substrate. The results obtained in the present investigation were similar to those previously published for the nitrided low alloy steels [7, 10, 11]. A. Alsaran et al. [13] indicated that the presence of many pits distributed on the surface is a typical result of chloride attack. The enhanced corrosion resistance can be attributed to the presence of a nitride layer rich in ε-nitride on the surface. As nitride is a noble phase, the formation of more nitride helps to cover the surface from corrosion attack and therefore the corrosion resistance improves with the increase in nitriding temperature (Fig. 4c). This has been well-documented in literatures and is also demonstrated in this study by corrosion tests in sodium chloride solution [7, 10]. The local conditions are altered such that further pit growth is promoted. The anodic and cathodic electrochemical reactions that comprise corrosion separate spatially during pitting. The common cathodic reactions that must accompany the dissolution occurring in the pit, such as the oxygen reduction reaction (O$_2$+2H$_2$O+4e$^-$→4OH$^-$), result in a local increase in the pH at the cathodic sites. The acidity developed in the pit is not neutralized by the cathodic reaction because of the spacial separation of the anodic and cathodic reactions.

4. Conclusions

The 38CrMoAl substrate exhibits very poor corrosion resistance in the 3.5% NaCl solution with high dissolving rate. It can be clearly seen that nitriding processing led to a higher corrosion potential and an evident passive region with a very low passive current density in the polarization curves compared to those of the un-nitrided specimen. Hence, the higher corrosion potential and low passive current density of the nitrided low alloy steel can be explained by the formation of a dense compound layer on the nitrided substrate surface during nitriding. The results indicate that the plasma nitriding can significantly improve the corrosion resistance of the 38CrMoAl steel.

5. References

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