

Effect of QPQ nitriding time on microstructure and wear resistance of SAF2906 duplex stainless steel

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Abstract. QPQ salt bath treatment of SAF2906 duplex stainless steel was conducted at 570 °C for 60 min, 90 min, 120 min, 150 min and 180 min, followed by post-oxidation process with heating temperature of 400 °C and holding duration of 30 min. The effect of QPQ nitriding time on microstructure and wear resistance of SAF2906 duplex stainless steel was investigated by means of OM, SEM, XRD, microhardness test, adhesion strength test and wear resistance test. Microstructure observation showed outer layer was composed of Fe₃O₄. The main phase of the intermediate layer was CrN, α N and Fe_{2.3}N. The main phase of the inner layer was CrN and S. The adhesion strength test of the surface layer-substrate showed the QPQ treated samples have favorable adhesion strength of HF-1 level. With the increase of nitriding time, the growth rate of the compound layer gradually slowed down and the surface hardness first increased and then decreased, and the maximum hardness was 1283 HV_{0.2} at 150 min. The dry sliding results showed that the wear resistance of the QPQ treated samples was at least 20 times than that of the substrate, and the optimum nitriding time to obtain the best wear resistance is 150 min. The worn surface morphology observation showed the main wear mechanism of the substrate was plough wear, while micro-cutting is the main wear mechanism that causes the damage of the QPQ treated samples.

1. Introduction

Duplex stainless steels which have a two-phase microstructure consisting of ferrite and austenite and possess the excellent performance of ferritic and austenitic stainless steel are widely used in petroleum-refining, chemical and military industries, etc. [1-3]. The research and application of duplex stainless steels were conducted since 1930 s. With the progress of metallurgical technology, duplex stainless steels have been developed to the third-generation of super duplex stainless steel, whose pitting resistance equivalent number is over 40 [4]. SAF2906 super duplex stainless steel has better corrosion resistance, and it is suitable for deep water or seawater. However, deposited in joint action of multiple factors (e.g. corrosion, wear and overloading), SAF2906 duplex stainless steel, of whose low hardness and poor wear resistance, failed early. In industrial production, there are some enterprises using quench-polish-quench (QPQ) technology to improve wear resistance of stainless steels [5]. For example, the has been used QPQ technology treating engine valve materials of 5Cr21Mn9Ni4N austenitic stainless steel to increase its wear resistance under high temperature condition. The German textile machinery manufacturers also adopt QPQ technology to treat guide rail materials of 0Cr18Ni12Mo2Ti austenitic stainless steel for improving its wear resistance. Current opinion on the mechanisms of stainless steels possessing excellent wear resistance after QPQ treatment that has reached a unified is the formation of high-hardness and a certain thickness of



compound layer in its surface. The thicker the compound layer, the better the wear resistance. And some scholars are specialized in investigating the influence of nitriding time on surface layer thickness and wear resistance of stainless steel [6-7], the results show that when nitriding time is short, the compound layer is too thin to meet the requirement of the actual operating condition. Yet long nitriding time makes the growth rate of the compound layer slow down and the loose layer appear, and the nitrides in the compound layer grow and coarsen, which leads to the decrease of surface hardness. As a consequence, choosing the reasonable nitriding time is important for stainless steels to improve its wear resistance. At present, considerable researches on the effect of QPQ nitriding time on microstructure and wear resistance of stainless steels is mainly about single phase stainless steels such as austenite and martensite, and the research on SAF2906 duplex stainless steel is rarely done. Therefore, it is necessary to study the effect of QPQ nitriding time on the microstructure and wear resistance of SAF2906 duplex stainless steel.

2. Materials and methods

The material used in this investigation was SAF2906 duplex stainless steel, whose preparation method is as follows: first, the raw materials such as 316L stainless steel, chromium metal, iron- molybdenum, electrolytic nickel and nitride alloy were melted in 300 KW/30 Kg medium frequency induction furnace, the chemical compositions of the alloy was obtained by OES as shown in table 1. The as-cast sample was solid solution treated by KSS-1700 box-type resistance furnace at 1050 °C for 2h, then followed by water quenching. The heat treatment samples were cut into two groups: 10 mm×10 mm×10 mm and 30 mm×7 mm×6 mm. The former were used for optical microscopy and micro-hardness test, and the latter were used for adhesion strength and wear resistance test. Before QPQ treatment, all the flat surfaces of each sample were ground with various grades of SiC sandpaper up to 2500 grit and polished to a mirror finish using Cr₂O₃ solution, then followed by ultrasonically rinsing in acetone and alcohol for 10 min, and finally dried in air.

Table 1. Chemical compositions of SAF2906 DSS samples (wt.%).

C	Si	Mn	P	S	Ni	Cr	Mo	Cu	N	Fe
0.03	0.72	0.81	0.02	0.02	6.61	29.19	2.11	0.79	0.26	Bal.

The samples were nitrided at 570 °C for 60 min, 90 min, 120 min, 150 min and 180 min, then followed by the same post-oxidation process with heating temperature of 400 °C for 30 min. The CNO-concentration was kept at 33 %.

The cross-section microstructure of the QPQ treated samples after inlaying, grinding, polishing and etching was observed by XJP-300 optical microscopy and S-3000N scanning electron microscopy, and measured the compound layer thickness by image analysis software of Image-Pro Plus. The phase compositions of the surface layer were identified by X'Pert Pro MPD X-ray diffractometer with Co K α radiation in the range of glancing angles from 20° to 100°. The adhesion strength test of the surface layer-substrate adopted HRC indentation method commonly used in engineering. The test load was 150 kgf. The indent morphologies of the treated samples were observed under 100 times of optical microscopy, then compared with criteria morphologies of evaluating adhesion strength [8-9], and the adhesion level of the surface layer was obtained. The surface hardness of the samples was measured by MVC-1000D1 micro-hardness tester with 200 g load for 15 s, taking five readings to determine the arithmetic mean value as the surface hardness. Dry-sliding tribological tests were carried out on MMS-2A wear test machine. Before test, the substrate and treated samples were cleaned by alcohol and weighed. During test, a 40 mm diameter GCr15 steel ball rotated at a speed of 200 rpm on the surface of the samples. The test load was 50 N. After 60 min, the samples were removed from the wear test machine. They were cleaned and dried, and measured by FA2014 photoelectron analytical balance with an accuracy of 0.1 mg, then calculated mass loss to characterize its wear resistance. In

order to reduce the influence of test error on the results, the average mass loss was calculated by three parallel experiments carried out under the same condition.

3. Results and discussions

3.1. Metallographic observations

Figure 1 shows the cross-sectional microstructure of SAF2906 duplex stainless steel nitrided at 570 °C for different time (60 min, 90 min, 120 min, 150 min and 180 min). From the outmost surface to the core, a thin outer layer, intermediate layer, inner layer were formed. The outer layer is too thin to differentiate by optical microscopy, while the intermediate layer and inner layer can be distinguished from color after etching, but the appearance is still unclear. So as to clearly observe the morphology of different layers, the sample nitrided for 150 min was selected for SEM observation, the result is shown in figure 1(f). It can be seen from the figure that the outer layer is a black banding layer, whose thickness is about 2 μm. In order to furtherly determine the phases in the outer layer, the samples of nitrided only and QPQ treated were selected (nitriding time of 150 min) for XRD test, and the results were depicted in figure 2. The main phases of the surface layer nitrided only was CrN, αN (expanded martensite), Fe₂₋₃N and S (expanded austenite). In addition to CrN, αN, Fe₂₋₃N and S, the surface layer QPQ treated also has some Fe₃O₄. Therefore, it can be inferred that the outer layer is composed of Fe₃O₄, which was produced in the post-oxidation process, and this finding is consistent with previous reports [10-11], namely, the outer layer is an oxide layer. Nitriding treatment is the most important procedure of QPQ treatment, and its purpose is to form a certain thickness and high-hardness of nitrided layer. As shown in figure 2a, the nitrided layer consists of CrN, αN, Fe₂₋₃N and S. Due to the nitrogen concentration in the surface layer gradually declines from the outmost surface to the core, the hardness of the surface layer also drops. Besides, the nitrogen concentration in the inner layer has a significant drop, which leads to the hardness of the inner layer, whose effect on improving wear resistance is small, is far lower than that of the intermediate layer. Therefore, the intermediate layer also called compound layer, is the expected microstructure by nitriding treatment, and its main phases are high-hardness nitrides of CrN and Fe₂₋₃N, which plays a leading role in wear resistance. The inner layer, also called diffusion layer, is a black zone between the intermediate layer and the substrate, and its main phases are low-hardness phase of S and fine precipitate of CrN. Compared with common microstructure of diffusion layer, the diffusion layer of SAF2906 duplex stainless steel is discontinuous and composed of two parts: black region "1" and white region "2", which is closely related to the substrate phases of ferrite and austenite. This may be attributed to that the original microstructure of "1" region is ferrite, and its solubility of nitrogen is small, which results in nitrogen diffusing into ferrite combining extremely easily with high concentration of chromium to form chromium nitride and subsequently leads to Cr-depleted areas in the matrix and deteriorates its corrosion resistance, after reagent etching, the region appears "dark". The original microstructure of "2" region is austenite, and its solubility of nitrogen is higher than that of ferrite, more nitrogen atoms can be furtherly dissolved into austenite, which increases its corrosion resistance. Therefore, the region becomes "bright" after reagent etching. It is also obtained from figure 1 that when nitriding time is 60 min, the thickness of the compound layer is thin. With the extension of nitriding time, its thickness increases significantly. When nitriding time is over 120 min, its thickness increases slowly. The thickness of the compound layer is shown in figure 1, it was approximately 9.35 μm, 12.15 μm, 14.20 μm, 15.71 μm and 16.53 μm, respectively. Obviously, with the increase of nitriding time, the growth rate of the compound layer gradually slows down. The reason for the phenomenon is due to the extension of nitriding time, the nitrides formed on the surface of SAF2906 duplex stainless steel increases, which results in diffusion resistance of nitrogen increasing and the formation ability of nitrides reducing.

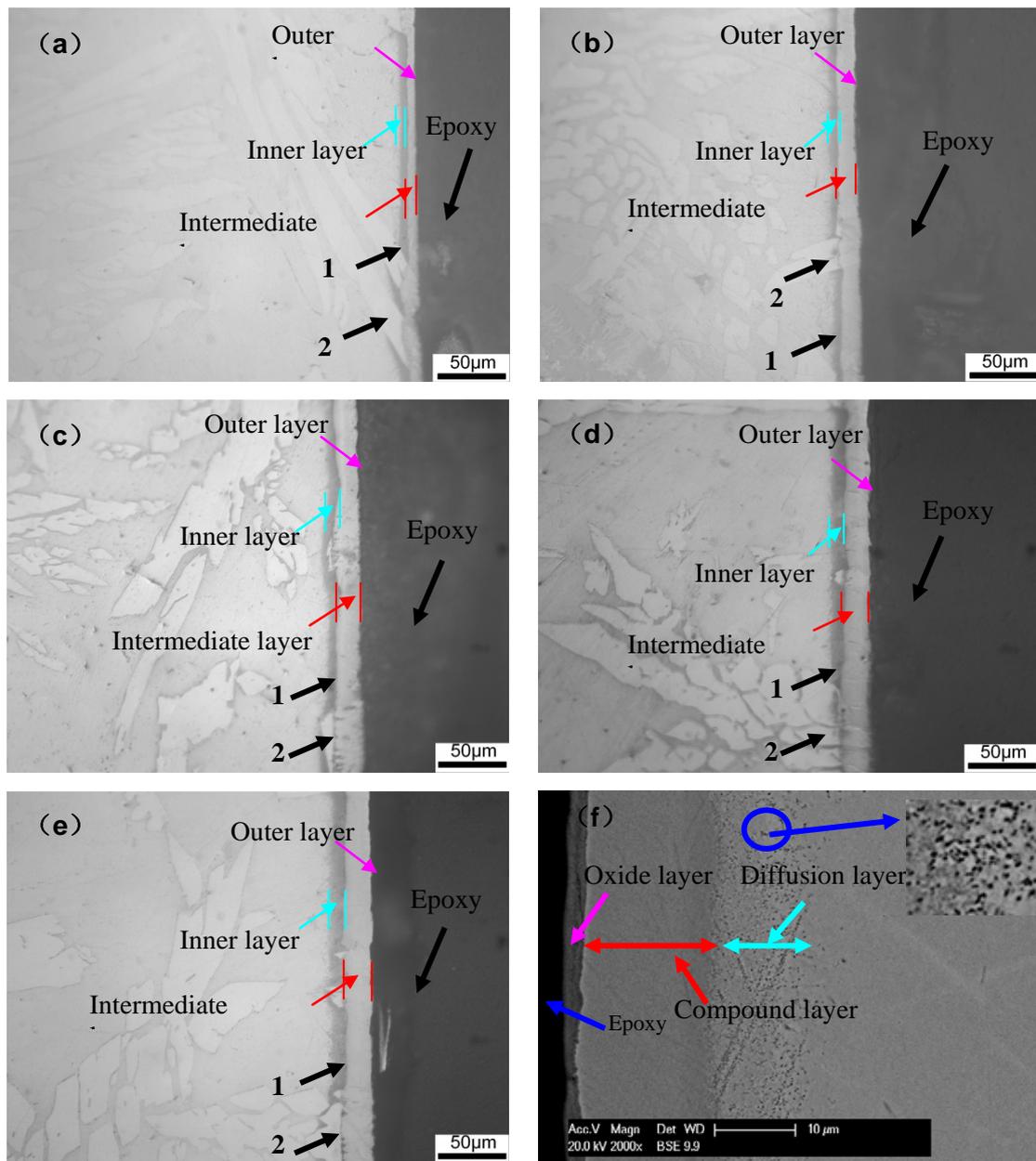


Figure 1. Cross-sectional metallographic microstructure of 2906 duplex stainless steel treated at 570 °C for different time.
(a)60min (b)90min (c)120min (d)150min (e)180min (f)150min.

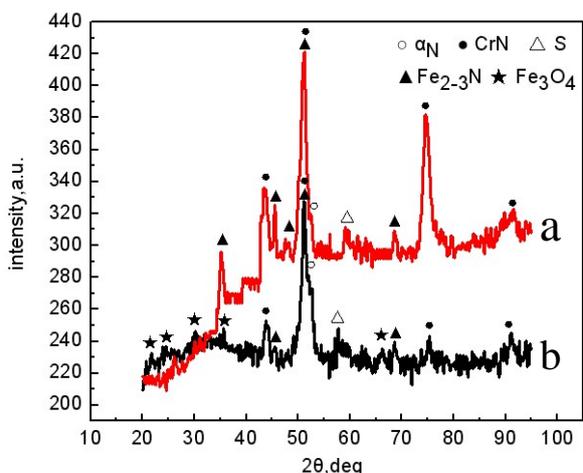


Figure 2. X-ray diffraction patterns of the QPQ treated sample and nitrided only sample. (a) nitrided only sample (b) QPQ treated sample.

3.2. Adhesion strength analysis

Indentation method is one of the commonly used for evaluating the adhesion strength of hard layer by using large loading, and make layer-substrate system occur significant plastic deformation, thereby qualitatively evaluating adhesion strength of layer-substrate system [12]. Figure 3 shows indent morphologies of the treated samples under the action of 150 kgf. It can be obtained from the figure 3 that the treated samples have favorable adhesion strength of HF-1 level as compared with criteria morphologies of evaluating adhesion strength, which is due to distribution characteristics of nitrogen in the surface layer displays a continuous gradient variation, making the hardness of the surface layer gradually decline from the outmost surface to the core and the surface layer exhibits good ability of coordination deformation, thus greatly guaranteeing the treated samples have excellent adhesion strength of surface layer-substrate. Moreover, nitrogen atoms combine with Mo、Cr and Ti, etc., to form stable nitrides, which distribute dispersely in surface layer- substrate interface, thus forming a certain thickness of transition layer between the surface layer and substrate, which is beneficial to improve adhesion strength of layer- substrate. It is also found that there is no cracks occurred on the surface layer of the treated samples with nitriding times of 60 min, 90 min and 120 min. Yet when nitriding time is 150 min and 180 min, there is some cracks appeared on the surface layer of the treated samples, and the longer the nitriding time is, the more the cracks are. This indicates when nitriding time is over 120 min, the adhesion strength of surface layer-substrate declines, and the longer the nitriding time is, the more obvious the decline is. This may be attributed to that the brittle phase of CrN increases and coarsens with nitriding time increasing, which causes a decrease in toughness of the surface layer. Besides, the structural differences of the phases increase the residual stress in the surface layer.

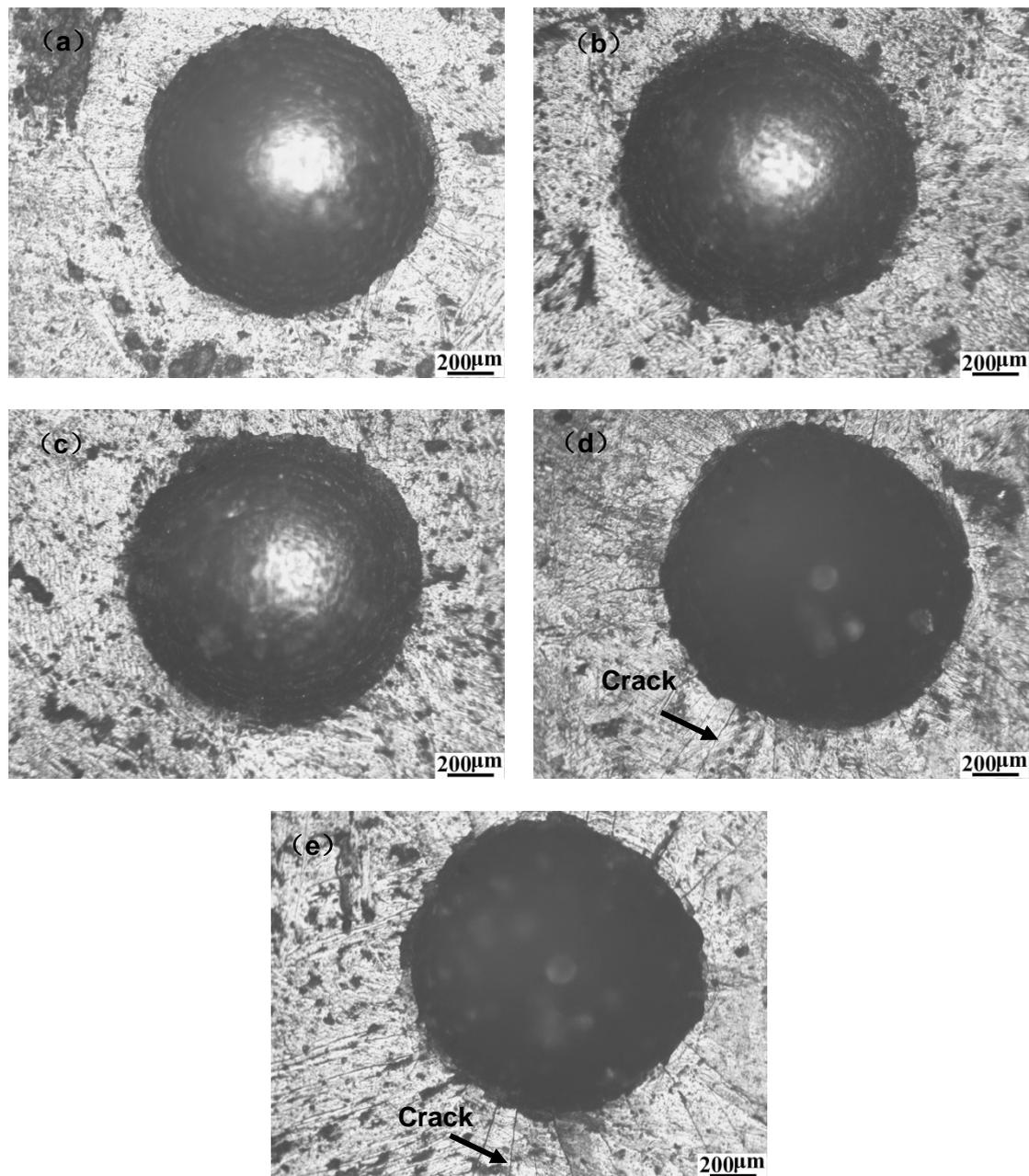


Figure 3. Indent morphologies of the QPQ treated samples by indentation method.
(a) 60min (b)90min (c)120min (d)150min (e)180min.

3.3. Hardness analysis

Figure 4 shows the relationship between the surface hardness of the treated samples and nitriding time. It can be obtained that the surface hardness of the samples after QPQ treatment has a significant increase and is over 3 times of the substrate. The significant increase in hardness is due to the surface microstructure of the substrate changes from low-hardness phases of α and γ into high-hardness phases of CrN, Fe₂₋₃N and α N etc, which makes the surface hardness notably reinforce. It can be also obtained from the figure that with the increase of nitriding time, the surface hardness of the treated samples gradually increases, when nitriding time is 150 min, its hardness reaches the maximum of 1283 HV_{0.2}. To furtherly increase nitriding time, the surface hardness of the treated samples decreases, which is related to the change of surface microstructure of SAF2906 duplex stainless steel. At an

initial stage of nitriding treatment, nitrogen atoms is dissolve into the substrate of α and γ , causing its lattice expansion, which improves the surface hardness of SAF2906 duplex stainless steel to some extent. Besides, nitrogen atoms combines with alloy elements or carbides to form nitrides (e.g. CrN and Fe₂₋₃N), which significantly enhances its surface hardness. When the surface layer reaches a certain thickness, the diffusion resistance of nitrogen atoms increases, and the degree of lattice distortion and the amount of nitrides have un conspicuous increase, the surface hardness of the treated sample reaches the maximum. With prolonged nitriding time, nitrides grow and coarsen, which causes the decrease of surface hardness instead.

3.4. Wear resistance analysis

Figure 5 shows the mass loss of the samples nitrided at 570 °C for different time. It can be seen from the figure that the mass loss of the substrate is about 36.5 mg, that of the treated samples is below 1.5 mg, that is, the wear resistance of the latter is over 20 times of the former. Besides, the surface hardness of the treated samples fist increased and then decreased with nitriding time increasing. When nitriding time is 60 min, its mass loss has a maximum of 1.5 mg, with nitriding time extended to 150 min, its mass loss reaches the minimum value of 0.8 mg, indicating that the optimum nitriding time to obtain the best wear resistance is 150 min, which is in good agreement with the surface hardness changing regularity.

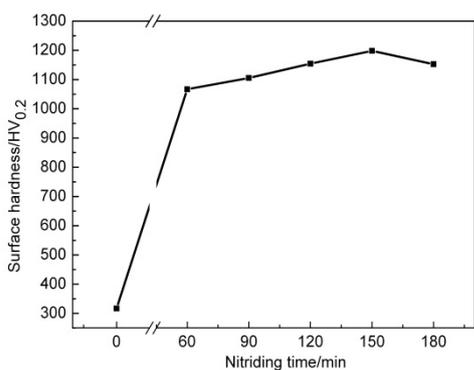


Figure 4. Variation of surface hardness versus nitriding time

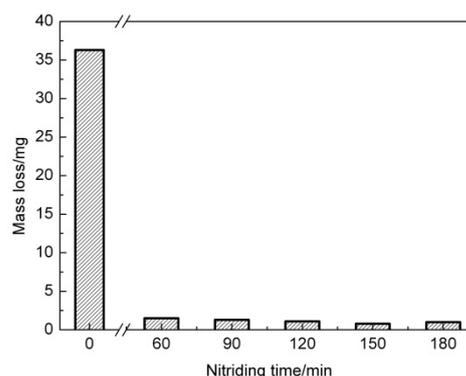


Figure 5. The mass loss of the samples nitrided at 570 °C for different time.

Figure 6 shows the surface SEM micrographs of the substrate and the sample nitrided for 150 min after wear test. It can be seen from figure 6a that a very rough metallic surface with severe abrasion grooves, peeling-off and plastic deformation is seen on the surface of the substrate. As for the sample nitrided for 150 min, a basically smooth appearance with very mild abrasion grooves is observed, nearly no peeling-off and plastic deformation occurred on the surface are found, and only some wear debris are seen from the surface. Therefore, plough wear is the main wear mechanism that causes the damage of the substrate, the main wear mechanism observed at the surface of the treated sample is micro-cutting. The reason why the substrate and the treated sample show different wear mechanism, which has a great relationship with the microstructure and property of material. This can be explained that due to the hardness of the substrate is far lower than that of mating material, its surface is prone to produce plastic deformation under the action of loads. In addition, some weak areas appear crack and fall off, then form tiny wear debris. In the wear process, wear debris have “plough” effect on the substrate surface, thus producing severe abrasion grooves on the surface. As for the treated sample, the surface of which consists of high-hardness and dispersed nitrides (e.g. CrN and Fe₂₋₃N), is not easy to produce wear debris compared with the substrate, and wear debris is also not easy to insert into the substrate. So only some shallow scratches occur on the treated sample surface.

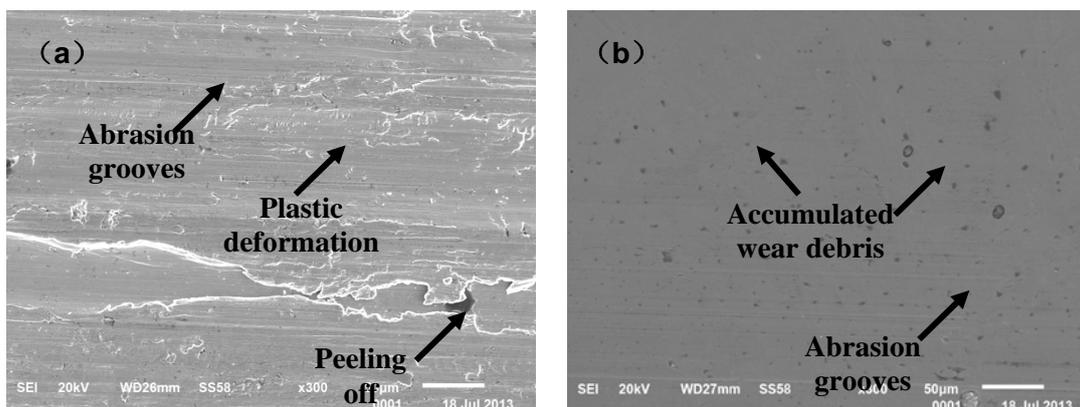


Figure 6. Worn surface morphology of the substrate and the sample treated at 570°C for 150min
(a) Substrate (b) QPQ treated sample

4. Conclusions

The surface layer of the samples after QPQ treatment was composed of outer layer, intermediate layer and inner layer from the outmost surface to the core. The outer layer was composed of Fe_3O_4 . The main phase of the intermediate layer was CrN, αN and Fe_{2-3}N . The main phase of the inner layer was CrN and S. The QPQ treated samples have favorable adhesion strength of HF-1 level. With the increase of nitriding time, the growth rate of the compound layer gradually slowed down and the surface hardness first increased and then decreased, and the maximum hardness was 1283 $\text{HV}_{0.2}$ at 150 min.

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Acknowledgements

This work was financially supported by the Key Project of Science and Technology Department of Fujian Province(No:2014H003); The Development of Science and Technology Fund of Fuzhou university(2014XQ13); Education Scientific Research Project Plan of Young and Middle-aged Teachers in Fujian Province(No.JAT160066).

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