Study on the microstructure and properties of 35Mn2V steel used in oil pipe by salt bath nitriding

Shuai Liu[1, a *]

[1]Shandong Science and Technology Service Development and Promotion Center, China.

[a]295400868@qq.com

Abstract. Oil pipe is easy to fail due to wear and corrosion during its service, which seriously affects the normal oil production and causes some unnecessary losses，while salt bath nitriding can form a composite infiltration layer through the composite technology on the surface of the workpiece, which can realize the combination of nitriding and oxidation, to achieve the effect of surface strengthening and modification. In this paper, salt bath nitriding is carried out on oil pipe (35Mn2V steel) with different temperature and time, and metallographic test, loose layer grade evaluation, XRD analysis, SEM observation, corrosion wear test, etc. are conducted to study the effect of salt bath nitriding process on the structure and properties of the permeating layer, comprehensively evaluate the quality of the permeating layer, and explore the wear resistance mechanism. The results show that when 35Mn2V is nitrided at 580℃, the infiltration layer mainly consists of oxide film, porous layer, compound layer and diffusion layer, while when it is nitrided at 630℃, the infiltration layer consists of an additional nitrogenous austenite layer. The thickness of 35Mn2V compound layer increases with the increase of nitriding temperature and the extension of nitriding time, and the influence of changing nitriding temperature on the thickness is greater than that of changing nitriding time. After a short time and low temperature nitriding, the phase composition of the infiltration layer is mainly ε-Fe3N and ε-Fe3O4, after a long time and high temperature nitriding, the phase composition is mainly ε-Fe2N and Fe3O4, in which Fe3O4 is formed in the subsequent oxidation process. The degree of loose layer of the infiltration layer increases with the increase of nitriding temperature and the extension of nitriding time. Most of the loose layer grades of the infiltration layer are level 3, and a few are level 2. The degree of loose layer of the infiltration layer is determined by the process of salt bath nitriding, and the subsequent oxidation, ion stabilization and other processes have little influence on it. When 35Mn2V is subjected to corrosion wear test under small load, the friction coefficient of oxide film is small. When the loose layer is worn, the friction coefficient increases obviously. The compound layer is mainly composed of iron-nitrogen compounds, and its friction coefficient is minimal and relatively stable. When the compound layer is worn through, the friction coefficient of the diffusion layer increases.

Keywords: 35Mn2V steel, salt bath nitriding, microstructure and properties.

1. Introduction

After years of development of oil field, the comprehensive water cut is increasing and the oil well is rich in strong corrosive media (H_2S, CO_2, Cl^-, etc.)[1-3], and the well condition is becoming more complicated, which makes the oil pipe, sucker rod, pump, packer and so on used in oil and water well under high temperature and high pressure condition suffer relatively serious wear and corrosion problems.

Oil pipe is a seamless steel pipe, its main role is to control the flow of crude oil in the casing. Oil pipe can not only form a channel for oil and gas transport from the bottom of the well to the surface, but also serve as a flow channel for fluid injection into the reservoir and internal circulation of the well. The average length of the tubing is about 9.6 meters, and the length of the individual tubing is short compared to the depth of the well, so hundreds of tubing connections are required to connect the tubing together. The working environment of the oil pipe is poor, and the oil well contains a variety of corrosive media, which is easy to produce hydrogen sulfide corrosion, carbon dioxide corrosion and oxygen corrosion, etc. In addition, the oil pipe have been subjected to alternating load, fluid flow and abrasive wear during use, which is easy to produce rod and tubing partial wear, resulting in wear and corrosion problems of the oil pipe[4]. 35Mn2V steel is one of the main materials of tubing.

In view of the comprehensive performance of salt bath nitriding technology to improve the wear and corrosion resistance of metal, its application to the surface modification of oil pipes, improve its life and cost performance, prolong the production cycle of oil wells, reduce the number of production wells, has an important role and great significance in the field of oil exploration and development.

In this paper, salt bath nitriding tests of 35Mn2V steel at different temperature and time are carried out, and metallographic tests, brittleness tests, hardness tests and friction and wear tests are conducted to comprehensively evaluate the quality of nitriding layer.

2. Experimental

2.1 Test material

In this paper, 35Mn2V steel, which is widely used in oil pipelines, is selected as the test material. MnV steel has excellent comprehensive mechanical properties and is widely used in the manufacture of various important structural components. The main chemical components are shown in Table 1.

Table1 The components of 35Mn2V steel

element	C	Si	Mn	V	P
content[%]	0.35	0.2	1.6	0.11	0.26

35Mn2V steel is cut into the size of 10mm×10mm×5mm for metallographic observation, corrosion and wear test, scanning electron microscope observation, XRD analysis. All samples are polished prior to salt bath nitriding so that they had the same roughness of 0.8μm. The nitride salt in this test is mainly cyanate. In the process of salt bath nitriding, the concentration of cyanate should be controlled at about 31%, and the concentration of cyanate should be checked frequently. If the concentration is low, it should be timely supplemented to ensure the quality of infiltration layer.

2.2 Treatment technology of salt bath nitriding

The process route of salt bath nitriding technology is: loading card → pre-cleaning → preheating → salt bath nitriding → salt bath oxidation → cooling → post-cleaning → drying → ion stabilization → oil bath. In this study, the temperature and time of salt bath nitriding are mainly changed. The temperature of salt bath nitriding is 580℃ and 630℃, and the nitriding time is 30min, 60min, 90min, 120min and 150min, and the obtained samples are stored for tissue analysis and performance study.

3. Result and discussion

3.1 **Cross section analysis of infiltration layer**

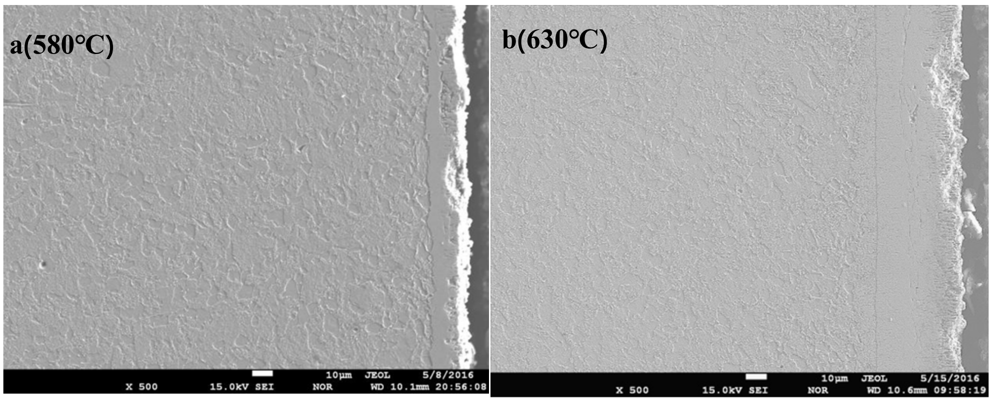


Fig. 1 SEM morphology of 35Mn2V nitrided for 90min at different nitriding temperatures

The structure composition of the infiltration layer is shown in Fig. 1. It can be seen from the figure that when nitriding at 580℃, the infiltration layer is mainly composed of oxide film, loose layer, compound layer and diffusion layer. When nitriding at 630℃, the composition of the nitriding layer is more than that at 580℃, there is one more intermediate layer[5], namely nitrogen-containing austenite layer.

According to the Fe-N phase diagram in Fig. 2, nitrogen-containing austenite will be formed when the temperature of salt bath nitriding is higher than 590℃ and the nitrogen content reaches 2.35%. Therefore, when nitriding is carried out at 630℃, a nitrogen-containing austenite layer will be formed between the diffusion layer and the compound layer.

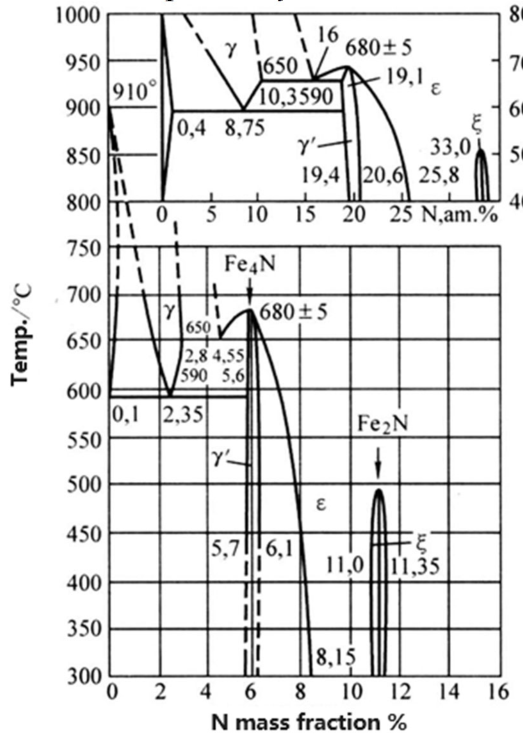


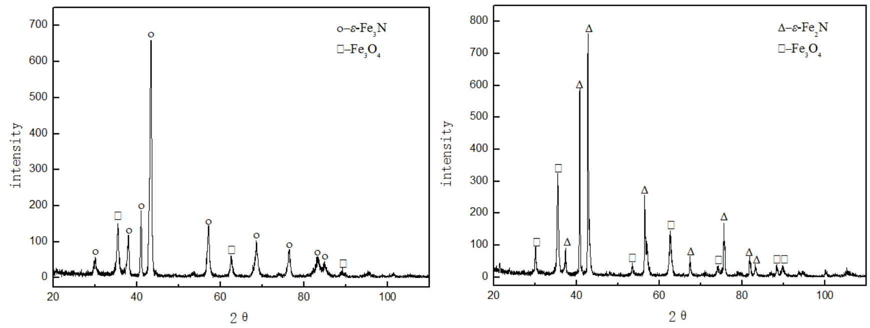
Fig. 2 Fe-N phase diagram

Compared with Figure 1, it can be seen that while the nitriding time is the same, the higher the nitriding temperature, the greater the thickness of the nitriding layer and the greater the thickness of the compound layer, and the increase of the thickness is more significant than the change of the nitriding time. The diffusion law can be used to explain: the concentration of nitrogen atoms in the salt bath environment and the sample surface are different, and more nitrogen atoms will migrate from the side of the high concentration to the side of the low concentration, that is, diffusion is caused by the concentration gradient. The process of salt bath nitriding is an unsteady diffusion process, that is, the concentration of nitrogen atoms at a certain point in the infiltration layer changes with time, and the diffusion rate of nitrogen atoms is related to the concentration of nitriding salt on the surface of the sample.

The diffusion coefficient of nitrogen atom increases exponentially with the increase of temperature, and the diffusion coefficient increases faster with the gradual increase of temperature. The increase of nitriding temperature will increase the activity of nitrogen atoms. Therefore, the higher the nitriding temperature is in the same time, the more active nitrogen atoms will penetrate into the sample, resulting in an increase in the thickness of the infiltration layer.

XRD analysis of infiltration layer

Fig 3 shows the XRD pattern of 35Mn2V nitriding after 580℃/30min and 630℃/150min. It can be seen from the analysis of the spectrum that the phase of 35Mn2V is mainly composed of ε-Fe_3N and Fe_3O_4 after the salt bath nitriding at a lower temperature for a shorter time, while the phase of 35Mn2V is mainly composed of ε-Fe_2N and Fe_3O_4 after the salt bath nitriding at a higher temperature for a longer time. According to the Fe-N phase diagram, γ 'phase (Fe_4N) is formed when the nitrogen concentration exceeds 0.1%, and ε phase ($Fe_{2\sim3}N$) is formed when the nitrogen concentration exceeds 6.1%. It can be seen that in the process of salt bath nitriding, with the increase of nitriding temperature and the extension of nitriding time, the nitrogen concentration increases, and the surface of the infiltration layer will successively form Fe_4N, ε-Fe_3N and ε-Fe_2N. Therefore, ε-Fe_3N is mainly formed during nitriding at 580℃/30min, while ε-Fe_2N gradually replaces ε-Fe_3N during nitriding at 580℃/150min and 630℃/150min. At this time, ε-Fe_2N is the most important phase on the surface of the infiltration layer.



(a) (b)

Fig. 3 XRD spectra of 35Mn2V of different nitriding processes (a)580℃/30min; (b)630℃/150min

3.2 Analysis of loose layer of infiltration layer

The loose layer of nitriding layer is a kind of defect tissue produced in the process of nitriding, and its degree is divided into 5 levels. The loose layer level is mainly determined by the shape, number and density of micropores in the surface compound layer. The higher the loose layer level of the permeability layer, it means that there are more defects in the permeability layer, which will have an adverse impact on the performance of the permeability layer, so necessary measures should be taken to control the degree of loose layer at a small level.

Fig. 4 shows the degree of loose layer of 35Mn2V after nitriding at 580℃/30min, 580℃/90min, 630℃/90min and 630℃/150min. It can be seen from the figure that when the nitriding temperature is the same at 580℃, the loose layer of the nitriding layer becomes larger with the extension of the nitriding time. When the nitriding temperature is 630℃, the degree of loose layer of the nitriding layer is obviously greater than that when the nitriding temperature is 580℃.

Rating the loose layer of 35Mn2V nitriding layer, as shown in Table 2. As can be seen from the table, the loose layer grade of 35Mn2V infiltration layer is mostly level 3, and only a few of the loose layer at 580℃ is level 2, and the loose layer grade is higher at 630℃. The degree of loose layer of the infiltration layer is determined by the process of salt bath nitriding, and the subsequent oxidation, ion stabilization and other processes have little influence on it.

3.3 Corrosion wear test analysis

Fig 5 shows the corrosion wear friction coefficient curve of 35Mn2V nitriding at different times at 580℃. The friction coefficient of the pre-cleaned sample is larger than that of the nitriding sample and has little change, basically keeping at about 0.3 The friction coefficient of nitriding at 580℃/30min is large, which is due to the short nitriding time and the insufficient diffusion of nitrogen atoms, resulting in a large friction coefficient of the compound layer, and the thickness of the compound layer is small, and the compound layer is quickly worn through, resulting in an increase in the friction coefficient. The friction coefficient of the nitriding sample after 580℃/90min and 580℃/150min is larger in the early stage and decreases in the later stage, mainly because there are a loose layer on the surface of the infiltration layer. When the loose layer is worn through, the friction coefficient of the infiltration layer is reduced.

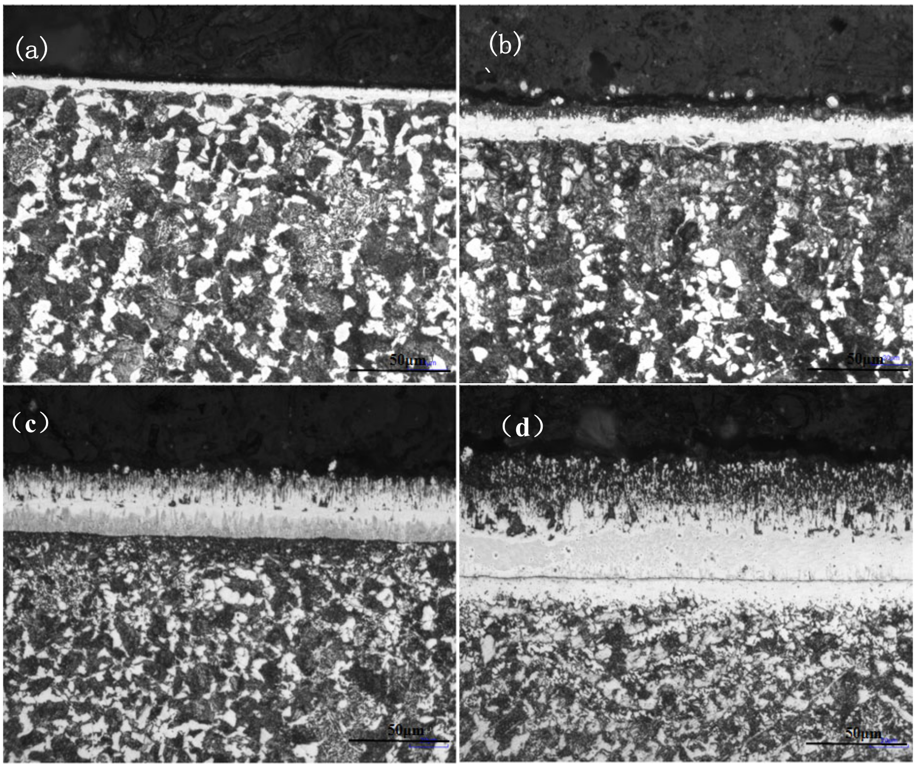


Fig. 4 The loose layer level of 35Mn2V of different nitriding processes (a)580°C/30min; (b)580°C/90min; (c)630°C/90min; (d)630°C/150min

Table 2 The loose level of nitrided layer of 35Mn2V

	580°C			630°C		
	nitriding	oxidation	oil bath	nitriding	oxidation	oil bath
30min	2	2	2	3	3	3
60min	2	2	3	3	3	3
90min	2	3	2	3	3	3
120min	3	3	3	3	3	3
150min	3	2	3	3	3	3

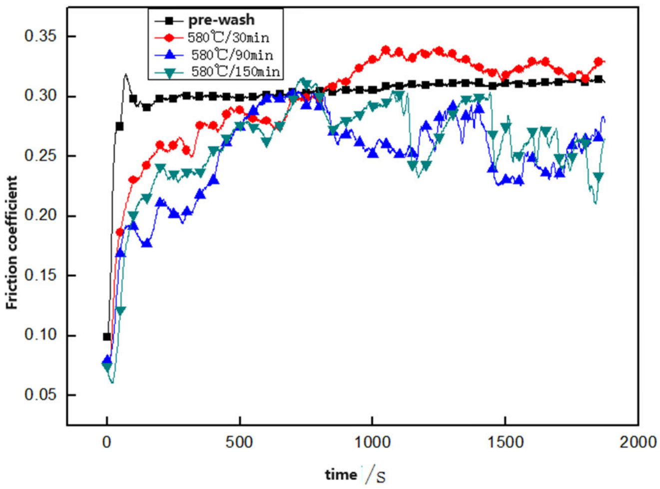


Fig. 5 The friction coefficient curve of corrosion wear of 35Mn2V with time

4. Summary

1. When 35Mn2V is nitrided at 580°C, the infiltration layer is mainly composed of oxide film, loose layer, compound layer and diffusion layer, while when it is nitrided at 630°C, the infiltration

layer is composed of an additional nitrogenous austenite layer. The thickness of 35Mn2V compound layer increases with the increase of nitriding temperature and the extension of nitriding time, and the influence of changing nitriding temperature on the thickness is greater than that of changing nitriding time.

2. 35Mn2V is mainly composed of ε-Fe_3N and Fe_3O_4 after the salt bath nitriding at a lower temperature for a shorter time, while the phase of 35Mn2V is mainly composed of ε-Fe_2N and Fe_3O_4 after the salt bath nitriding at a higher temperature for a longer time.

3. The loose layer degree of 35Mn2V infiltration layer increases with the increase of nitriding temperature and the extension of nitriding time. The loose layer grade of 35Mn2V infiltration layer is mostly level 3, and a few are level 2. The degree of loose layer of the infiltration layer is determined by the process of salt bath nitriding, and the subsequent oxidation, ion stabilization and other processes have little influence on it.

4. When 35Mn2V is subjected to corrosion wear test under small load, the friction coefficient of oxide film is small. When the loose layer is worn, the friction coefficient increases obviously. The compound layer is mainly composed of iron-nitrogen compounds, and its friction coefficient is minimal and relatively stable. When the compound layer is worn through, the friction coefficient of the diffusion layer increases.

References

[1] Wang Xinling, He Cheng, He Weidong. Research and application of oil pipe anti-corrosion technology [J]. Enterprise Technology Development, 2011, (18): 184.

[2] Cui Xindong. Corrosion and protection of Xianhe Oil Production Plant [J]. Petrochemical Corrosion and Protection, 2007, (04): 26-29.

[3] Yao Hongyan. Research on corrosion and protection measures of oil and water well tubing [D]. Qingdao: China University of Petroleum (East China), 2006.

[4] Liu Xiaoyong. Causes and prevention measures of off-wear of pipe rod in oil Wells [J]. Petrochemical Technology, 2016, (10): 231+224.

[5] Zhang Lei. Effect of oxidation process on wear resistance of deep QPQ Workpiece [D]. Chengdu: Xihua University, 2013.