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Effect of rare earth on microstructure and properties of niobiumizing layer on GCr15 steel for pin shaft

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Abstract

The powder pack cementation was used for niobiumizing treatment of GCr15 pin steel, and the effects of different rare earth types and contents on microstructure and properties of niobiumizing layer were investigated. Optical microscope, x-ray diffractometer, scanning electron microscope, electrochemical workstation and ball-disk friction wear machine were used to observe the structure and evaluate the properties of the niobiumizing layer. And the kinetics and mechanism of niobiumizing layer with rare earths was explored. The results show that a dense and continuous niobiumizing layer formed under different rare earth types and contents condition. The layer is 3 μm-15 μm in average thickness, 1800 HV_{0.2}-2500 HV_{0.2} in average microhardness and is composed of NbCx compound and α-Fe. Comprehensive comparison, La_{2}O_{3} can significantly improve the wear and corrosion resistance of the niobiumizing layer. The self-corrosion potential of niobiumizing layer is ~0.5759 V, the corrosion current density is 5.2365 \times 10^{-7} \text{A cm}^{-2}, and the average friction coefficient is 0.385 when La_{2}O_{3} is added at 2%.

1. Preface

GCr15 steel is widely used in bearings [1], die tools [2] and drive chains [3]. For transmission chains, the pins are prone to surface failure due to wear, fracture and fatigue during the chain drive, so surface strengthening of the pins to meet their increasing hardness and wear resistance technical requirements is an effective way to improve the service life of transmission chains [4, 5]. Metal carbide coating, such as chromium carbide, vanadium carbide and niobium carbide with high hardness and low coefficient of friction, has been applied for surface strengthening of die steel [6–9]. Researchers have used PVD (physical vapor deposition) or TRD (thermal reactive diffusion) methods to obtain metal carbide coating. Comparatively, the layer obtained by TRD method has higher bonding with the substrate than the PVD method and has excellent wear resistance. However, TRD is a diffusion process and requires higher temperature and longer holding conditions to obtain carbide layer. High temperature and long time will reduce compactness and increase brittleness of layer.

Studies have shown that rare earths in carburizing, nitriding and boriding can effectively improve properties of the layer [10–12]. Tao [13] et al studied the microstructure and mechanical properties of boron-vanadium co-diffusion layer by adding CeCl_{3} into the powder, and found that the addition of rare earth increased the diffusion rate by 40% and greatly improved the hardness and wear resistance of the coating. X.J. Liu [14] et al studied the effect of rare earth on the microstructure and properties of vanadium carbide coating by adding different content of FeSiRe23 in borax salt bath. And it was found that the addition of rare earths promoted the growth rate, reduced the grain size, and improved brittleness of prepared coating. Shuai Li [15] et al found that niobium carbide coatings prepared under 1.5 wt% La_{2}O_{3} conditions had the best wear resistance and the wear volume was substantially reduced.

In summary, there are few studies on the wear and corrosion behavior of the metal carbide diffusion layer with rare earth addition prepared by powder pack cementation method. And the effects of rare earth types and contents on wear and corrosion resistance of the layers are not deep enough. The surface of the workpiece after
the powder pack cementation metallizing treatment has less adherent powder particles and is convenient for subsequent processing, which is suitable for the surface treatment of small pin parts. Therefore, the powder pack cementation method is used for niobiumizing treatment on GCr15 steel in this paper. The microstructure and properties of niobiumizing layer are studied with different rare earth types and contents addition. The kinetics and influence mechanism of rare earths are explored. The study can provide instruction for the application of niobiumizing layer on pin shafts prepared with GCr15 steel.

2. Experimental materials and methods

The substrate material is Φ20 × 4 mm GCr15 steel. Pre-treatment of niobiumizing: The specimens were first spheroidized and annealed, then polished with 120#–800# sandpaper until the surface was bright, and finally dried after ultrasonic cleaning in anhydrous ethanol. Niobiumizing treatment: Niobium supply agent (Nb-Fe powder), activator (NH₄Cl), catalyst (La₂O₃, CeO₂, Nd₂O₃, Y₂O₃) and bulking agent (Al₂O₃) are dried and mixed according to the proportion in Table 1 by weighing the corresponding weight. The diffusion agent was mixed evenly and loaded into stainless-steel tank, and the treated GCr15 specimens were buried in the diffusion agent, and the water glass (Na₂O-SiO₂) and refractory clay were mixed and sealed to the tank lid, as shown in Figure 1. The sealed stainless-steel tank was put into the box resistance furnace for heating, and the temperature was set at 950 °C for 6 h. After niobiumizing, the stainless-steel tank was cooled to room temperature, the sample was removed and the surface of the sample was cleaned up.

The niobiumizing layer was analyzed according to JB/T 5069–2007 metallographic inspection method for steel parts. Axio Vert.A1 metallographic microscope was used to observe the morphology and measure the thickness of the diffusion layer at 500x; HVS-1000 micro hardness tester was used to test the diffusion layer specimens 7 times under the condition of 2 N load and 10s holding pressure, and the average value was taken as the hardness of the diffusion layer; D/MAX-2500 x-ray diffractometer was used to analyze the material phase of the diffusion layer under the condition of Cu target, scanning speed 8°/min and scanning angle 30–90°; Electrochemical corrosivity test of niobiumizing layer in 3.5% NaCl solution using IviumStat.Xri electrochemical workstation; the friction performance of the niobiumizing layer was evaluated by using the UMT-2 friction and wear tester with a ball-disk contact method, and the friction substrate was a Φ 6.35mm Al₂O₃ ball with a load of 10 N and a sliding speed of 0.48 m s⁻¹. The surface morphology of the diffusion layer and the surface morphology after wear were characterized by Sigma-500 scanning electron microscope.

Table 1. Diffusion agent composition.

| No. | Diffusion agent composition |
|-----|---------------------------|
| 1   | (49%) Al₂O₃ + (45%) Nb-Fe + (5%) NH₄Cl + (0.5%, 1%, 2%, 4%) La₂O₃ |
| 2   | (49%) Al₂O₃ + (45%) Nb-Fe + (5%) NH₄Cl + 1% CeO₂ |
| 3   | (49%) Al₂O₃ + (45%) Nb-Fe + (5%) NH₄Cl + 1% Y₂O₃ |
| 4   | (49%) Al₂O₃ + (45%) Nb-Fe + (5%) NH₄Cl + 1% Nd₂O₃ |
3. Experimental results and analysis

3.1. Diffusion layer sectional microstructure and surface morphology

Figures 2 and 3 show the metallographic microstructure and surface morphology of the section of the niobiumizing layer under the conditions of adding different types of rare earths (1% CeO$_2$, 1% Nd$_2$O$_3$, 1% Y$_2$O$_3$, 1% La$_2$O$_3$) and different contents of rare earth La$_2$O$_3$ (0.5%, 1%, 2%, 4%) to GCr15 steel. From the metallographic photographs in figure 2, it is obvious that a bright white layer of different thicknesses is formed on the surface of the substrate, and there is no obvious transition area between this layer and the substrate. From the electron micrographs of the surface of the diffusion layer, it can be seen that the diffusion layer had mainly presented a granular morphology with different particle morphology. Compared with the addition of other rare earth oxides, when Y$_2$O$_3$ was added, the thickness of the diffusion layer was thin and uneven, and the surface of the diffusion layer did not show obvious granular morphology and appeared more black holes, which indicated that the addition of Y$_2$O$_3$ was not effective in improving the quality of the niobiumizing layer. Figure 3 shows the sectional metallographic microstructure and surface morphology of the niobiumizing layer prepared by adding different La$_2$O$_3$ contents, from which it can be seen that at 1% of rare earth addition, the surface particle size of diffusion layer is clear and the particle size is smaller than that of the other three contents, indicating that this content of rare earth plays a role in refining the grain. With the increase of rare earth content, the thickness of the prepared diffusion layer also increases, but the surface quality of the diffusion layer deteriorates and the thickness does not change significantly when the rare earth content is increased from 2% to 4%. This shows that there is a critical value for the addition of rare earths, and the addition of more than the critical value will affect the quality of the diffusion layer.

3.2. Diffusion layer phase composition

The x-ray diffraction analysis of the diffusion layers prepared with different types of rare earths and different contents of La$_2$O$_3$ is shown in figure 4. It can be seen that the main phases composing the diffusion layer are the
NbCx phase and a small amount of α-Fe phase. α-Fe phase is the matrix phase, and the GCr15 steel matrix is detected by the rays penetrating the seep due to the local thinness of the seep. After the addition of rare earths, no formation of new phases was detected in the diffusion layer. On the one hand, it is assumed that the rare earths are involved in the reaction to form the compound, but due to the small amount of addition, there is no obvious peak signal in the XRD spectrum; on the other hand, it is assumed that the rare earths are not involved in the reaction and the rare earths remained in the permeating agent, so there is no peak signal in the XRD spectrum. Comparing the x-ray diffraction patterns, it can be found that the ratio of the diffraction intensities I(111) and I(200) corresponding to the two main peaks in the NbCx diffraction line will change with the change of rare earth species and rare earth La2O3 content, as shown in figure 5. It is found that different kinds of rare earth and different contents of rare earth have a certain influence on the preferential orientation of the grain of the diffusion layer. When rare earth Nd2O3 is added, the diffusion layer has a preferential orientation on the (111) crystal face, and when rare earth CeO2, Y2O3 and La2O3 are added, the diffusion layer has a preferential orientation on the (200) crystal face. When 0.5% and 4% La2O3 were added, the diffusion layer had preferred orientation on (111) crystal plane, and the diffusion layer prepared with 1% and 2% La2O3 content had preferred orientation on (200) crystal plane. In this paper, the texture coefficient was obtained according to the Harris algorithm and its ratio reflects the degree of grain preferred orientation. For the relationship between the texture coefficient and the properties of the diffusion layer in this paper, we think the adsorption energy and packing density difference maybe affect the hardness and compactness of the layer, as well as the wear resistance and corrosion resistance.

3.3. Diffusion layer thickness and hardness
The thickness and hardness variation of the niobium diffusion layer prepared by adding different types of rare earths and different La2O3 contents to GCr15 steel are shown in figures 6 and 7. From figures 5(a) and 6(a), it can...
be seen that compared to the other three rare earths, the thickness of the diffusion layer is 3.1 um and the hardness is 1750 HV0.2 when the rare earth type Y2O3 is added, the diffusion layer is the thinnest and the hardness is the lowest, and the addition of Y2O3 does not promote the growth of the seep layer. From figures 6(b) and 7(b), it can be seen that the maximum thickness of the diffusion layer is 15.1 um and the hardness reaches 2000 HV0.2 when the addition of rare earth La2O3 is 4% in the permeating agent, which is about 8.7 times of the hardness of the substrate. However, the thickness of the diffusion layer did not change significantly when the addition of La2O3 was increased from 2% to 4%, indicating that there is a certain critical value for the addition of rare earths, which corresponds to figure 3. The effect of rare earth CeO2 on the niobiumizing layer is the thickness and hardness of the layer. This is probably due to the fact that when the rare earth addition is CeO2, the grains on the surface of the diffusion layer are evenly distributed, and the grain size is small and no holes or cracks are seen. It is indicating that the addition of CeO2 inhibits the growth of grains in the niobiumizing layer and improve the strength and hardness of the layer.

3.4. Diffusion layer corrosion resistance
The corrosion resistance polarization curves of niobiumizing layer with different rare earth types and different La2O3 content are shown in figure 8, and the corrosion potential and corrosion current density are listed in tables 2 and 3. The corrosion potential and corrosion current density can accurately determine the corrosion resistance of the layer, the corrosion potential can determine the ease of corrosion, and the corrosion current density can determine the speed of corrosion. It can be seen from the graphs that the corrosion potential of niobiumizing layer is La2O3 > Y2O3 > Nd2O3 > CeO2, and the corrosion current density is La2O3 < CeO2 < Nd2O3 < Y2O3. From small to large, i.e., the niobiumizing layer prepared under the catalytic environment of rare earth La2O3 has the best corrosion resistance. From figure 8(b) and table 3, it is clear that the corrosion resistance of niobiumizing layers prepared by adding different contents of La2O3 increases and then decreases with the...
increase of La₂O₃ content, reaching the highest level at 2% addition. This rule also confirms the idea that there is a certain critical value for the addition of rare earths.

In order to analyze the corrosion resistance of the diffusion layer more accurately, the diffusion layer was further determined by electrochemical impedance spectroscopy with consideration of the polarization curve. As shown in figure 9, the Nyquist plots (as shown in figures 9(a) and (b)) and Bode plots (as shown in figures 9(c)–(f)) were obtained from the electrochemical impedance spectroscopy tests of the diffusion layer samples prepared with different rare earth types and different La₂O₃ contents in 3.5 wt% NaCl solution. Observation of figures 9(a), (c) and (e) reveals that the impedance spectra of the diffusion layer prepared by adding different types of rare earths have similar shapes. Without considering the rare earth Y₂O₃, the diffusion layer prepared in the catalytic environment of Nd₂O₃ and La₂O₃ have a larger radius of capacitive resistance arc, and the phase angle and impedance modulus in the low frequency region are also larger than those of other rare earth types, indicating that the corrosion resistance of the percolation niobiumizing layers prepared by the rare earth CeO₂ is poor. As can be seen from figures 9(b), (d), (f), when the addition of rare-earth La₂O₃ is 2%, the capacitive arc resistance radius, phase angle and impedance mode values of the niobiumizing layer are larger than those of other La₂O₃ contents, which, like the above polarization curves, indicate a certain critical value for the addition of rare earths.

### 3.5. Frictional wear performance

The dynamic friction coefficient and the average friction coefficient of the diffusion layer and the alumina mating pair are shown in figures 10 and 12 when the friction wear experiment was carried out at room
Figure 9. Impedance map of niobiumizing layer with different rare earth types and different La$_2$O$_3$ contents: (a), (c), (e) rare earth types; (b), (d), (f) content of rare La$_2$O$_3$.

Figure 10. Dynamic and average friction coefficient of niobiumizing layer with different rare earth types.
temperature, load of 10 N and speed of 500 rmp min\(^{-1}\) for 900 s using ball-disk contact. It can be seen from the figures that the dynamic friction coefficient of the diffusion layer under different types of rare earths and different contents of La\(_2\)O\(_3\) are relatively smooth and fluctuate less; the influence of different rare earth types and contents on the average friction coefficient of the diffusion layer is small, and the average friction coefficient of the diffusion layer with the addition of La\(_2\)O\(_3\) is about 0.4, and the average friction coefficient decreases from 0.44 to 0.395 when the content of La\(_2\)O\(_3\) increases from 0.5% to 4%. As shown in figures 11 and 13, the wear surface morphology was observed: the wear surface of the La\(_2\)O\(_3\)-added diffusion layer was smooth and free of excess debris, while the wear surface of the Y\(_2\)O\(_3\)-added and Nd\(_2\)O\(_3\)-added diffusion layer was uneven and had more debris adhering to it. Combined with figure 3(c), it can be found that the surface of the diffusion layer is large, rugged and accompanied by the existence of many black holes, which may be the main reason. When La\(_2\)O\(_3\) is added at 2%, the surface morphology is still smooth and dense after friction, with less friction debris and the best wear resistance. However, at 4% addition, the surface of the diffusion layer after friction is obviously adhered to the abrasive debris, and it is easy to produce wear on the diffusion layer again. Thus, it can be seen that within the experimental range, the best wear resistance is achieved by adding 2% of rare earth La\(_2\)O\(_3\) niobiumizing layer.

4. Growth kinetics of diffusion layer

To better study the catalytic effect of rare earth oxides, niobiumizing layers were prepared by holding at three different heating temperatures of 1198K, 1223K and 1248K for 1h, 3h, 5h and 7h, respectively, and it was found...
that the thickness of niobiumizing layers showed a parabolic relationship with the holding time, satisfying:

\[ d^2 = Dt \]  

Where \( d \) represents the thickness of the diffusion layer, cm; \( t \) represents the holding time, s; and \( D \) represents the atomic diffusion coefficient, \( \text{cm}^2 \text{s}^{-1} \). A plot of the squared fit of the holding time versus the thickness of the diffusion layer for different heating temperatures is shown in figure 14. The linearity of the correlation between \( d^2 \) and \( t \) also demonstrates the parabolic nature of the diffusion layer growth. The value of the diffusion coefficient of the niobiumizing layer at different heating temperatures can be estimated from the slope of the plot, and it can be found that the diffusion coefficient of the niobiumizing layer is related to temperature and increases with the increase of temperature.

Secondly, the relationship between diffusion activation energy, diffusion coefficient and treatment temperature can be expressed by the Arrhenius equation:

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]  

Where \( Q \) represents the diffusion activation energy, J \( \text{mol}^{-1} \); \( D_0 \) is the constant, \( \text{cm}^2 \text{s}^{-1} \); \( T \) is the treatment temperature, K; \( R \) is the gas constant \((8.314 \text{ J mol}^{-1} \text{K}^{-1})\), taking logarithms on both sides of Formula (2), we can get:

\[ \ln D = \ln D_0 - \frac{Q}{RT} \]  

By linear fitting \( \ln D \) and \( 1/T \) at 1198 K, 1223 K and 1248 K, the relationship between growth rate of niobiumizing layer and heating temperature can be obtained, as shown in figure 15. The slope of the fitted line is the diffusion
activation energy $Q = 171.22 \text{ KJ mol}^{-1}$ of the niobiumizing layer with the addition of rare earths, compared with the diffusion activation energy $Q = 91.257 \text{ KJ mol}^{-1}$ of the niobiumizing layer without the addition of rare earths, confirmed that the addition of rare earths does have the effect of activation and osmosis.

In this paper, we experimentally determined the best rare earth types and rare earth content for the powder pack cementation niobiumizing process of GCr15 steel, and explored the catalytic effect of rare earths, which was found to be mainly in the decomposition, adsorption and diffusion of the diffusion agent. Firstly, according to the literature [16], the rare earth atoms have strong reduced properties, which accelerate the decomposition of the percolator and enable the continuous production of Nb atoms. Secondly, due to the unique electronic structure of rare earth atoms ($4f$), rare earth atoms have a strong adsorption ability to the surrounding Nb atoms, and at the beginning of the experiment, part of the rare earth atoms on the surface of the steel part penetrated into the interior of the steel part, which made the material surface more attractive to Nb atoms and improved the penetration of Nb atoms; the other part reacted with the oxygen atoms on the surface and played the role of cleaning the surface. Finally, due to the large size of rare earth atoms, rare earth infiltration into the surface of steel parts causes large lattice distortion, which provides a channel for the diffusion of C atoms and accelerates the formation of diffusion layers. Based on the above experiments, it is clear that the diffusion activation energy of the niobiumizing layer generated when rare earths are added to the diffusion agent is $171.22 \text{ KJ mol}^{-1}$, and the diffusion activation energy of the niobiumizing layer without the addition of rare earths to the diffusion agent is $91.257 \text{ KJ mol}^{-1}$, so it is obvious that the addition of rare earths promotes the diffusion of the diffusion agent. As can be seen from figure 4, the presence of rare earths was not found on the surface of the diffusion layer, probably because the thickness of the diffusion layer increased with time, which prevented the diffusion of rare earth atoms to the interior due to their larger size. However, there is also a critical value for the addition of rare earths. When a small number of rare earths is added, its adsorption ability to Nb atoms is weak and the catalytic effect of rare earths is not obvious. When an excessive number of rare earths is added, a large number of rare earth atoms form a buildup on the surface of the steel parts, which hinders the combination of Nb atoms with C atoms and thus affects the formation of the diffusion layer. Experimental analysis shows that the addition of rare earth La$_2$O$_3$ directly affects the thickness, hardness and wear resistance of the diffusion layer, and with the addition of rare earth La$_2$O$_3$, a large number of C atoms and Nb atoms form a large number of aggregates on the surface of the substrate, probably because the attraction of rare earth La$_2$O$_3$ to Nb atoms is greater than that of the other three rare earths, which furthermore promoting the generation of high hardness ceramic coating NbC$_x$ and further improves the wear resistance of the diffusion layer. However, the effect of the addition of rare earth La$_2$O$_3$ on the corrosion resistance of the diffusion layer is not obvious, which may be related to the difference in the microstructure of rare earths or the different characteristics of different rare earths affecting the crystalline growth of the coating, and the specific mechanism needs further study.

5. Conclusion

(1) The rare earth niobiumizing layer prepared by the powder pack cementation is dense, homogeneous and continuous, with good bonding to the substrate, and the addition of different types and contents of rare earths has little effect on the phase composition of the diffusion layer, which mainly consists of NbC$_x$ and $\alpha$-Fe.

(2) Different types of rare earths have different effects on the improvement of niobiumizing layer, among which the rare earth CeO$_2$ has obvious improvement on the thickness and hardness of niobiumizing layer, with the hardness up to 2600 HV$_{0.2}$, and the rare earth La$_2$O$_3$ has better effect on improving the wear and corrosion resistance of niobiumizing layer.

(3) There is a critical value for the addition of rare earths, and excessive addition will directly affect the growth of the diffusion layer, considering factors such as the working environment of the material, the optimal addition of rare earth La$_2$O$_3$ is 2%.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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