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Growth kinetics and wear resistance of vanadium carbide on AISI D2 steel produced by TRD process

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Abstract

Vanadium carbide coating was obtained on the surface of AISI D2 steel by thermal reactive diffusion process using molten borax as based salt and vanadium pentoxide as vanadium donor. The process was performed at 900 \degree C, 940 \degree C, 980 \degree C and 1020 \degree C for 3 h, 4 h, 5 h and 6 h. The Optical Microscopy was used to observe the morphology of cross section of coating layer. Energy Dispersive Spectroscopy was used to analyse the element content of the matrix and the coating layer by spot scanning and line scanning. X-ray Diffraction was used to obtained the phase composition of the coating layer. Microhardness Tester was used to measure the Vickers hardness of the coating layer and matrix. Friction and wear tester were used to explore wear resistance of the coated and uncoated specimens. The results show that the thickness of vanadium carbide coating ranges from 7.54 \mu m to 19.1 \mu m under different treatment time and temperatures. The V\textsubscript{6}C\textsubscript{7} and VC\textsubscript{x} are the main phases contained in the vanadium coating layer. A thickness of about 3 \mu m transition layer is between the matrix and coating layer and the transition layer has a block effect on the diffusion of iron. The growth rate constants of vanadium carbide coating layer at 900 \degree C, 940 \degree C, 980 \degree C and 1020 \degree C were obtained as (5.20 \pm 0.116) \times 10^{-11} \text{cm}^{2}\text{s}^{-1}, (8.91 \pm 0.253) \times 10^{-11} \text{cm}^{2}\text{s}^{-1}, (1.26 \pm 0.020) \times 10^{-10} \text{cm}^{2}\text{s}^{-1}, and (1.70 \pm 0.036) \times 10^{-10} \text{cm}^{2}\text{s}^{-1} respectively. The activation energy for vanadium carbide layer is 123.3 \pm 10.1 \text{KJ mol}^{-1} and the diffusion constant is (2.58 \pm 1.96) \times 10^{-5} \text{cm}^{2}\text{s}^{-1}. The maximum hardness of vanadium carbide coating layer on the surface of AISI D2 steel can reach 2594HV. The wear rate of untreated and treated specimens was evaluated as 15.58 \times 10^{-13} \text{m}^{3}/(\text{N}\cdot\text{m}), 5.63 \times 10^{-13} \text{m}^{3}/(\text{N}\cdot\text{m}) respectively and the wear resistance of treated specimens by TRD process was about 3 times than untreated specimens.

1. Introduction

The hardness and wear resistance of cold working die have great influence on its service life and the quality of products. Once the surface of punch is seriously worn, the shear effect of cutting edge is not good, which leads to the poor appearance of the products, and even directly makes the production and processing unable to continue. In order to improve the hardness and wear resistance of the punch, reduce wear and extend the service life of the punch, surface strengthening treatment is necessary for the punches and other important components. The surface strengthening technologies mainly include surface induction quenching, thermal reaction diffusion(TRD), physical vapor deposition(PVD), chemical vapor deposition (CVD), Quench-Polish-Quench (QPQ), boronizing. The induction quenching can not meet the parts with complex shape. However, other technologies such as QPQ, CVD, PVD also have their own shortcomings. Therefore, TRD method is a very excellent surface treatment technology for industrial production due to its simple process, good fluidity of salt bath, good surface strengthening effect, pollution-free treatment process, and less equipment investment. It has been widely used in tools surface strengthening [5–15].
Since the carbide generated by chemical reaction between metal atoms such as vanadium, chromium and niobium and carbon atoms in steel has very high hardness and wear resistance, TRD process can be used to generate a thickness of $4 \sim 20 \mu m$ carbide coating layer on the surface of tools, which can significantly improve the surface hardness and wear resistance of cold working die [6]. The principle of chemical reaction diffusion is used by TRD process at high temperature of $800^\circ C$ to $1200^\circ C$ for 2 to 8 h to generate carbides coating on the surface of steel [7, 8]. Therefore, many researchers have been investigating the TRD process of different steels from different point of view. Shirinbayan et al [1] obtained the vanadium carbide on AISI D2 steel by immersion in a borax liquid bath at $900^\circ C$ to $1000^\circ C$ for 3 to 6 h and surface hardness of the coated specimen was evaluated as 2300–3200 HV while the hardness of the matrix was measured as 670–720 HV. Castillejo et al [13] have studied the corrosion resistance of Nb–Cr complex carbide coatings on the AISI D2 steel and the coating growth rates were evaluated, and a model of the layer thickness as a function of the treatment time and temperature was established. Aghaie-Khafri et al [14] have investigated the wear resistance and growth kinetics of vanadium carbide produced by TRD process on DIN1.2367 steel and the results showed that the coating layer had a superior wear properties.

AISI D2 steel is a common cold working die material and the growth kinetics of vanadium carbide on AISI D2 steel have been investigated by some researchers for a long time [21–24]. However, the quantitative relation of wear resistance between the coated and uncoated specimens was studied less to the present. Therefore, on the base of growth kinetics, further study of obtaining the wear resistance of vanadium carbide and diffusing elements such as C, V, Cr and Fe in TRD process is essential.

With the aim to investigate the effect of TRD process parameters on coating morphology, the formation principle of coating layer and the quantitative relation of wear resistance between the coated and uncoated specimens, borax was used as the base salt and $V_2O_5$ was added as the vanadium feed agent to conduct TRD process for 3–6 h at $900^\circ C$ to $1020^\circ C$ for AISI D2 steel in the present work. Then the effects of TRD temperature and treatment time on the vanadium carbide coating thickness were studied. point scanning and line scanning were carried out on the cross section of the coating layer to study the diffusion mechanism of elements in the TRD process. X-ray Diffraction was used to obtained the phase composition of the coating layer. Meanwhile, the growth kinetic mechanism of the coating was studied to obtain the growth rate and the diffusion activation energy during the formation of vanadium carbide. The relationship between the hardness and thickness of the vanadium carbide coating was analyzed, and the wear resistance of the vanadium carbide coating was investigated by the wear test.

2. Materials and methods

2.1. Materials preparation and pre-treatment

The AISI D2 steel was used in this experiment and its chemical composition was shown in table 1. As shown in figure 1, specimens were processed into cylindrical punch with a working diameter of 13 mm, total length of 85 mm. Then the surface was burnished with sand paper and polished to mirror by polishing machine. The adherent oil on the specimens was removed by washing in alcohol, and then the specimens were soaked in 5%
hydrochloric acid solution for 5 min to remove the rust. Impurities such as oil and rust could decrease the surface activity of specimens and hinder the growth of carbide coating layer. After that, the specimens were immersed in 5% nitric acid solution for 2 min to activate the surface, and then cleaned and dried with alcohol. All the pretreatment of specimens must be completed half an hour before TRD process. If the activation of the treated surface was completed too early, it was easy to be oxidized in contact with the air, making the surface rusted or passivated and unable to achieve the pretreatment effect.

2.2. Formulation of salt and TRD process
83% sodium borate (Na₂B₄O₇), 8% vanadium donor (V₂O₅), 4% reducing agent (Al powder) and 5% activator (NaF) were contained in formulation of salt. After the completion of salt preparation, the salt was raised to TRD process temperature kept for one hour. Before the TRD process, the specimens were put into the well type tempering furnace and preheated at 520 °C for half an hour. Preheating finished, the specimens were put into the salt bath furnace for heat preservation. Specimens were treated at 900 °C, 940 °C, 980 °C and 1020 °C for 3, 4, 5 and 6 h respectively. During the stage of heat preservation, the molten salt was stirred every one hour to prevent salt bath segregation. After the salt bath, the specimens were quenched in oil, and then tempered at 220 °C for 1.5 h twice. Finally, the specimens were boiled in boiling water for one hour to clean the residual borax.

2.3. Characterization
Before microstructure observation, the specimens were sectioned by wire cutting, ground to 2000 mesh emery paper, polished and then the specimens were etched with 2% Nital. The morphology of cross section of coating layer was observed by Optical Microscopy (OM). Energy Dispersive Spectroscopy (EDS) was used to analyse the element content of the matrix and the coating layer by spot scanning and line scanning. The phase composition of vanadium carbide was analysed by x-ray Diffraction (XRD) on the surface of specimens treated at different temperatures for 4 h with the angular range of 20°–100° and step size of 0.02°. Then the growth kinetics of vanadium carbide were studied according to the classical kinetic theory. The Vickers hardness (HV) of the surface of coating layer and matrix was measured by HX-1000TM Microhardness Tester and 9.8 N force, 4.9 N force was loaded on the surface of coating layer, matrix of cross section respectively. The all values of hardness were the average results of five times measurement.

Figure 2. Morphology of coating at different temperatures for 4 h; (a) 900 °C; (b) 940 °C; (c) 980 °C; (d) 1020 °C.
2.4. Wear test
The wear test was carried on the specimens coated by TRD process and uncoated respectively. The specimens were cut into a round piece specimen with a diameter of 13 mm and thickness of 10 mm. After polished, the surface of the specimen was cleaned, dried and weighed with a balance. The wear test was carried out by friction and wear tester at 150°C. The ball disc pair of the friction and wear tester was made of AISI 52100, and the rotational speed of 1000 r min⁻¹, the rotation radius of 2 mm, load of 10 N. After the wear test, the oxide scale and stickies on the surface of the specimen were cleaned. Finally, the specimens were weighed with an electronic balance.

3. Results and discussion

3.1. Morphology of vanadium carbide coating layer
The cross-sectional morphology of the coating layer produced at 900°C, 940°C, 980°C and 1020°C for 4 h were shown in figure 2. It was observed from the figure that with the TDR process temperature raised from 900°C to 1020°C, the thickness of the vanadium carbide coating increases continuously, from 8.9 ± 1.6 μm to 15.6 ± 0.16 μm. As the treatment temperature increased, the uniformity of the thickness coating layer was more pronounced and better. The cross-section morphology quality and density of the coating layer was obviously enhanced, and the voids and defects were less. When the temperature was 900°C, the thickness of the coating layer was very small and the surface uniformity was very bad. In some areas, there was almost no carbide coating generated, and the honeycomb holes was mixed in the cross section. When the temperature was 1020°C, the thickness of the coating increased a lot up to maximum value, and the uniformity was very good, and the density was also significantly enhanced.

The cross-sectional morphology of the coating layer treated at 980°C for 3, 4, 5 and 6 h were shown in figure 3. When the temperature kept on 980°C, with the increasing of treatment time, the thickness of vanadium carbide coating layer increased continuously, the defect inside the coating layer was less and the density was higher. It was found that the thickness of coating layer was very small at treatment time of 3 h, but it was double thickness at treatment time of 6 h. The coating layer thickness ranged from 11.3 ± 0.4 μm to 16.1 ± 0.5 μm. The treatment time for 4 h, there were lots of defects in the cross section and the defects decreased at treatment time.

Figure 3. The morphology of coating under different treatment times of 980°C; (a) 3 h (b) 4 h (c) 5 h (d) 6 h.
time of 5 h. The treatment time of 6 h, the thickness of coating layer was the best quality. Therefore, the increase in the process temperature of temperature also has an obvious improvement for quality of coating layer.

3.2. Element analysis of coating layer

The spot scanning of specimens treated at temperature of 1020 °C for 4 h was analysed by Energy Dispersive Spectroscopy (EDS), and the location of eight spots scanned was shown in figure 4. The eight spots were distributed on the substrate, the interface between the matrix and the coating layer, the inner surface of the coating layer, the outer surface of the coating layer respectively. The spot scanning result of the eight spots was shown in figure 5, and the spectra obtained by EDS spot scanning from 5 to 8 were shown in figure 6.

It was observed that the content of Fe in the matrix was of 90.3%, and 78.05% in the interface between matrix and coating layer. But, the content of Fe in the inner surface of coating layer was decreased sharply and nearly of zero. However, the content of V in the matrix was nearly zero, but it changed sharply in the interface between matrix and coating layer, and it kept a high content of 95.62% in the coating layer. The content of C decreased from 2.23% of interface to 1.33% in the outer surface of coating layer. The spot scanning revealed that the coating layer had a high content of V, a low content of Fe, and a decreased tendency of C from the interface to the surface.
From the figure 6, in the spectrum 1 and spectrum 5, the carbon element was not detected in the spot scanning process, it was because Carbon element in D2 steel was mainly combined with strong carbide forming elements and exited in form of carbide reinforced phase, which leads to the uneven distribution of carbide reinforcement phase in the matrix. Therefore, it was difficult to ensure that the location of the scanning spot was on the carbide phase exactly, and a small amount of carbon existed in forming of graphite could not be detected. So, the C in the matrix cannot be detected.

3.3. Phase composition analysis of coating layer

The specimens treated at different temperatures for 4 h were analysed by XRD and the diffraction patterns were presented in figure 7. The V₈C₇ and VCₓ were detected in the specimens and it indicated that vanadium carbide was the main phase in the coating layer [3, 14]. It could be observed from the patterns that each peak line of VCₓ phase consists of many overlapped small peaks, so it existed more than one phase. And according to the different ratios of C/V atoms in the vanadium carbide coating layer, the VCₓ may consist of one or more phases of V₆C₅, V₄C₃ or VC [15]. Moreover, the Cr₀.₄V₀.₆C phase was detected in the specimens treated at 940 °C for 4 h, which proved the existence of a low content of Cr in the coating layer and it was consistent with the EDS analysis results. Then, it could be also found that the phase of Fe was detected on the surface of specimens treated at 900 °C for 4 h. This may be the reason that the thin coating layer have been penetrated by x-ray and the phase of Fe in the matrix has been detected [15].

In the process of TRD process, the vanadium carbide is produced by the chemical reaction between V atoms and C atoms. Firstly, the V₂O₅ was reduced by reductant (Al powder) to produce mass active V atoms through the following reduction reaction [11]:

\[
10\text{Al} + 3\text{V}_2\text{O}_5 = 6\text{[V]} + 5\text{Al}_2\text{O}_3
\]  

(1)

Then at a state of high temperature, carbon atoms on the surface of specimens were activated and reacted with vanadium atoms according to the following reaction [11, 16]:

\[
\text{V} + [\text{C}] \rightarrow \text{VC}
\]  

(2)

\[
4\text{V} + 3[\text{C}] \rightarrow \text{V}_6\text{C}_3
\]  

(3)

\[
8\text{V} + 7[\text{C}] \rightarrow \text{V}_6\text{C}_7
\]  

(4)
The vanadium carbide generated through above reaction deposit on the surface of specimens and the more C atoms diffusing from matrix, the thicker the vanadium carbide coating layer. With the different ratios of C/V atoms in the above reaction, the vanadium carbide coating layer may consist of single vanadium carbide phase, but may also the mixture of vanadium carbide multiphase.

3.4. Formation mechanism of coating layer

In order to explore the principle of element diffusion and coating layer formation, the line scanning of cross section of the coating layer was shown in figures 8 and 9. It was seen that at the x-axis value of 80 μm, the content of element started to change and at value larger than 83 μm, the variation of element content was not obvious.

\[ 6V + 5C \rightarrow V_{0.5}C \]  \hspace{1cm} (5)

Figure 7. The XRD patterns of specimens treated at different temperatures for 4 h: (a) 900 °C (b) 940 °C (c) 980 °C (d) 1020 °C.

Figure 8. Line scanning result of cross section.
Therefore, it revealed that it existed a wide of 3 \( \mu \text{m} \) diffusion transition layer between the matrix and coating layer. Due to the molten salt does not contain C, Fe, and Cr element, so the elements of C, Fe, and Cr in the transition layer was diffused form the matrix. Then, the content of V in the D2 steel was very low, so the V in the transition layer was diffused from the molten salt.

At the \( x \)-axis value between 83 \( \mu \text{m} \) and 95 \( \mu \text{m} \), the content of V in this coating layer was especially high and the content of Fe was extremely low, nearly zero. It indicated that the V in coating layer was diffused from the molten salt still, but the Fe couldn’t diffuse from the matrix to the coating layer because the block function of transition layer. However, C and Cr in the coating layer was in a certain content, so it also indicated that the transition layer not had block function for element of C and Cr, which could cross the transition layer and diffuse from the matrix to the coating layer.

As the partial enlargement of C content at figure 9, the decrease tendency of C content between the coating layer was observed. The composition of coating layer was mainly of vanadium carbide and the combining capacity of V with C was extremely strong. therefore, the dense vanadium carbide coating layer generated previously had impact on the diffusion of C. The treatment time of TDR process longer, the denser and thicker the coating layer, C had more difficulty to diffuse to the surface and combined with the V atoms.

Therefore, the principle of element diffusion at transition layer and coating layer D2 steel TRD process was concluded and it was described in the figure 10. The results of point scanning and line scanning on the cross section of the coating layer revealed that the formation process of the vanadium carbide coating was that the active carbon atoms diffuse to the surface of the matrix under the action of high temperature, and then combine...
with the reduced active vanadium atoms in the salt bath to form vanadium carbide, which adheres to the surface of the substrate. The transition layer has a strong impact on the diffusion of Fe from transition to the coating layer and Cr and C can diffuse from the transition layer to coating layer with less impacts of transition layer.

When the active vanadium atoms on the surface of the matrix were combined with carbon atoms and were consumed completely. The V was replenished by the flow of molten salt and reacted with carbon atoms continually. while the carbon atoms in the matrix will continue to move towards the surface of the matrix under the effect of carbon concentration gradient and defect concentration gradient. When the thickness of the coating layer reached a certain extent, the diffusion of carbon atoms could be hindered by the dense coating layer, and the diffusion of carbon atoms becomes more and more difficult with the thickness of the coating. Because the inner surface of the coating was bonded with the substrate through the formation of chemical bond, the bonding between the substrate and the coating is very good, and the coating quality is better than the traditional surface coating technologies such as electroplating, PVD, CVD, etc.

3.5. Process parameters analysis
The thickness of coating layer at different temperature and time were shown in the figure 11. The results showed that the thickness of vanadium carbide coating ranges from 7.54 μm to 19.1 μm. At a certain treatment time, the thickness of coating layer increases more and more slowly as the temperature rises. Due to the process of coating layer need enough V atmos diffusing from the molten salt combined with C atmos, the activity of molten salt was lower and the fluidity of borax salt was poor at a low temperature conditions, so the active vanadium atom near the coating layer surface cannot be supplemented in time. Therefore, under the same treatment time, the lower the temperature, the lower the thickness of coating and the metal atomic activity is small, which lead to severe segregation of molten salt and uneven coating thickness on the surface of parts.

When the temperature increased, the thermal vibration of the active carbon atoms in the matrix increased, and the number of carbon atoms in the high energy state increased, so the diffusion rate of the carbon atoms in the matrix to the surface of the substrate was accelerated, which makes the growth speed of the coating faster than that at low temperature, and the morphology quality and the thickness of the coating layer was improved obviously.

When the temperature kept on a certain value, with the increasing of treatment time, the thickness of vanadium carbide coating layer increased continuously. However, it was observed that the coating layer thickness increased more and more slowly at any temperature when increasing the treatment time, and it increased not obviously when treatment time more than 5 h. Therefore, the holding time of TRD process exceed 5 h had little effect on the growth of the coating layer. The main reason was that the coating formed at the early stage had a blocking effect on the subsequent element diffusion, and the diffusion rate of carbon atoms decreases, resulting in the growth rate of the coating slowing down and the thickness increasing more and more slowly.

Figure 11. Thickness of coating layer at different temperature and treatment time.
3.6. Study on growth kinetics

The thickness of vanadium carbide coating layer has a great relationship with temperature and treatment time. It was assumed that the vanadium atom is the main factor affecting the thickness and growth of vanadium carbide coating. Therefore, under a certain treatment temperature, according to the diffusion kinetics theory, the relationship between the coating thickness and the diffusion time is as follow equation (6);

\[ d^2 = Kt \]  

Where \( d \) is diffusion layer thickness (cm), \( K \) is the growth rate constant (cm\(^2\) s\(^{-1}\)), \( t \) is the treatment time of TRD process (s). The relationship between the square of the layer thickness and the treatment time at different temperatures was shown in figure 12. It was obvious that there was a linear relationship between the square of coating layer thickness and treatment time, and the slope of the fitted curve represents the growth rate \( K \) of the coating layer. Therefore, the growth rate constant of vanadium carbide coating layer at 900 °C, 940 °C, 980 °C and 1020 °C were obtained of \((5.20\pm0.116)\times10^{-11}\) cm\(^2\) s\(^{-1}\), \((8.91\pm0.253)\times10^{-11}\) cm\(^2\) s\(^{-1}\), \((1.26\pm0.020)\times10^{-10}\) cm\(^2\) s\(^{-1}\), \((1.70\pm0.036)\times10^{-10}\) cm\(^2\) s\(^{-1}\) respectively.

To reveal the growth kinetics theory of TRD process and evaluate the energy barrier of the vanadium carbide layers growth. According to the Arrhenius equation, the growth rate constant can be expressed as follows equation [17–20, 14]:

\[ K = K_0 \exp \left( -\frac{Q}{RT} \right) \]  

Where \( K \) is the growth rate constant (cm\(^2\) s\(^{-1}\)), \( K_0 \) is the diffusion constant (cm\(^2\) s\(^{-1}\)), \( R \) is the gas constant (\( R = 8.314 \) J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the process temperature (K). The equation (7) can be also described as follows:

\[ \ln K = \ln(K_0) - \frac{Q}{RT} \]  

The equation (8) reveals the linear relationship between the \( \ln K \) and \( 1/T \), and it was depicted in figure 13. The slope and intercept of the straight line was used to calculate the activation energies \( Q \) for vanadium carbide layer of \((123.3\pm10.1)\) kJ mol\(^{-1}\) and the diffusion constant \( K_0 \) of \((2.58\pm1.96)\times10^{-5}\) cm\(^2\) s\(^{-1}\).

The activation energy \( Q \) and diffusion constant \( K_0 \) of vanadium carbide layer on AISI D2 and other steel by previous study was showed on table 2. The activation energy of AISI D2 steel calculated in the reference [1] is similar with present work, which indicates that the present work has a certain practical significance. But according to the literature [11], the activation energy \( Q \) can be only seen as a constant when the temperature changes in a small range. Moreover, compared with the literature, the diffusion constant is in a large range error, which suggests that more experiments and further studies should be performed to investigate the more factors on the thickness of coating layer. For example, a new growth kinetics mathematical model that defines the influence of the type of steel matrix, process temperature and treatment time on the thickness of coating layer should be established in the further study to reduce the error [15].
3.7. Coating layer hardness

The hardness of coating layer and matrix was shown in figure 14. It was observed that specimens treated by TRD process and low-temperature tempering process, the maximum hardness of vanadium carbide layer reached 2594HV. With the increased of TRD process temperature and treatment time, the coating layer thickness increased, the density of the coating layer increased, the voids and defects decreased, so the hardness of coating layer increased obviously. The high hardness of coating layer has enormous improvement of wear resistance.

| Steel   | Q (KJ mol⁻¹) | \(K_0\) (cm² s⁻¹) | References |
|---------|--------------|---------------------|------------|
| D2      | 113.2 ~ 133.4| (2.58 ± 1.96) × 10⁻³| Present work|
| D2      | 114.5        | —                   | [1]        |
| D2      | 137.69       | 3.88 × 10⁻³         | [21]       |
| DIN 1.2367 | 173.2    | 7.98 × 10⁻⁴         | [14]       |
| H13     | 199.3        | 4.16 × 10⁻³         | [15]       |
| H13     | 215.68       | 2.01 × 10⁻¹         | [11]       |
3.8. Wear resistance analysis

Wear rate is one of the important factors to measure the wear resistance of materials. Wear rate can directly reflect the wear condition of cold working die materials and evaluate the wear resistance of materials [25–27]. The wear rate is directly proportional to the wear volume and inversely proportional to the friction distance and positive pressure, which is described as follows [14]:

\[ W_r = \frac{V}{S \times L} \] (9)

Where \( V \) is worn volume, \( S \) is friction stroke, \( L \) is the value of positive pressure. Based on the given parameters of friction experiment above, friction sliding distance was calculated of 188.4 m, and the value of positive pressure 10 N. As shown in the table 3, according to the mass variation before and after the wear test, the wear rate of untreated specimens and treated specimens was evaluated of 15.58 \( \times 10^{-13} \) m\(^3\) / (N \( \cdot \) m), 5.63 \( \times 10^{-13} \) m\(^3\) / (N \( \cdot \) m).

Under the same experimental conditions, the wear rate of AISI D2 cold working steel untreated by TRD process was much higher than that of treated specimen, about three times. Therefore, after TRD treatment, the high hardness coating produced on the die surface can greatly improve the wear resistance, reduce the wear rate and prolong the service life of the tool.

4. Conclusions

(1) EDS line scanning showed that a thickness of 3 \( \mu \)m transition layer was between the matrix and coating layer. The transition layer has strong block effect on Fe and leading to the coating layer with no Fe element. The C atoms can diffuse across the transition layer from the matrix to coating layer and combined with V in the molten salt to generate the coating layer on the surface of specimens.

(2) The coating layer has a block effect on the diffusion of C to some extent, and the content of C was lower at the outer surface than inner surface. Therefore, the coating layer was thicker, the speed of layer increasing was slower.

(3) The \( V_8C_7 \) and \( VC_x \) are the main phases contained in the vanadium coating layer and the \( VC_x \) phase may consist of one or more phases of \( V_6C_3 \), \( V_4C_3 \) or VC with the different ratios of C/V atoms.

(4) The growth kinetics study shows that the growth rate constants of vanadium carbide coating layer at 900 °C, 940 °C, 980 °C and 1020 °C were \((5.20 \pm 0.116) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}\), \((8.91 \pm 0.253) \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}\), \((1.26 \pm 0.020) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}\), \((1.70 \pm 0.036) \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}\) respectively. The calculated activation energy Q for vanadium carbide layer was 123.3 ± 10.1KJ mol\(^{-1}\) and the diffusion constant \( K_0 \) was \((2.58 \pm 1.96) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}\).

(5) The hardness of vanadium carbide formed on the surface of D2 steel can reach 2594HV. As coating layer thickness increasing, the coating layer was denser and defects was less, so the hardness was higher.

(6) The wear test showed that the wear rates of untreated and treated specimens were 15.58 \( \times 10^{-13} \) m\(^3\) / (N \( \cdot \) m), 5.63 \( \times 10^{-13} \) m\(^3\) / (N \( \cdot \) m) respectively. The wear resistance of treated specimens by TRD process was 3 times than untreated specimens.

Data availability statement

No new data were created or analysed in this study.
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