Preparation and dynamic behavior of W-Mo-Y co infiltrated layer on the surface of 45 steel parts

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Abstract—In this paper, W-Mo-Y co infiltration were carried out on the surface of 45 steel wedge components by plasma solid-state surface metallurgy technology. The phase, hardness, friction and wear properties before and after W-Mo co infiltration and W-Mo-Y co infiltration were systematically studied. The diffusion kinetics such as diffusion coefficient and diffusion activation energy were calculated by Fick's second diffusion law, and the effect of Y on the diffusion of W and Mo atoms in the infiltrated layer was obtained. It is found that the addition of rare earth Y element increases the diffusion coefficient of W and Mo atoms and reduces the diffusion activation energy, which has a certain catalytic effect. And the W-Mo-Y co infiltration significantly improves the surface hardness and wears resistance of the parts and prolongs the service life of the parts.

1. Introduction
In the field of mechanical manufacturing, ordinary steel is often used to make working parts, when the machine works, these parts are often affected by impact force, friction and wear, fatigue corrosion, making the working parts fail first[1]. The wedge-shaped component of the splitting machine is made of 45 steel, which is an important component of the splitting machine. In the process of rock splitting, the wedge-shaped component is the main component of the working component of the splitting machine, Therefore, the wedge-shaped component is most prone to failure in the form of wear, deformation and fracture.

One or more high-performance metal materials are infiltrated on the surface of ordinary steel or parts by ion implantation or coating preparation, to make the surface of parts have better performance[2]. This method is an important subject to improve the service performance of parts[3]. Plasma solid state surface metallurgy technology is by using the low-temperature plasma produced by
double glow discharge under vacuum\(^{[4,5]}\). And forming a variety of alloy layers with special physical and chemical properties which can successfully prepare high-performance surface high-speed steel, surface stainless steel, surface die steel and surface high alloy steel\(^{[6-10]}\).

The alloy W, Mo and Y elements are infiltrated into the surface of 45 steel wedge-shaped components by using plasma solid state surface metallurgy technology to form a certain thickness of metallurgical combined alloy layer containing W, Mo and Y. The surface hardness, friction and wear properties reach or exceed the properties of 45 steel, and improve the service performance and service life of wedge components of splitting machine. Through the calculation of diffusion kinetics such as diffusion coefficient and diffusion activation energy, the influence law of Y on the diffusion of W and Mo atoms in the infiltration layer is obtained, and the phase, hardness, friction and wear properties before and after W-Mo co infiltration and W-Mo-Y co infiltration are systematically studied.

2. Materials and methods

W-Mo and W-Mo-Y co infiltration tests were carried out on the surface of 45 steel wedge components by plasma solid state surface metallurgy technology to obtain a certain thickness of alloy layer containing W, Mo and Y. W-Mo co infiltration test, with 45 steel wedge component material as the base material, intercept the experimental sample (size:70mm×20mm×3mm), the source material is W-Mo (W: Mo = 1:1) alloy plate, the purity is 99.9%, and the size of W-Mo plate is 80 mm×50mm×5mm. The working gas is high-purity argon (≥ 99.99%), the working pressure is 28~35 Pa, the temperature during W and Mo co infiltration is (1200±20) ℃, and the holding time is 4 h. After the co infiltration, it is cooled to room temperature with the furnace. W-Mo-Y co infiltration test: the base material is the same as W-Mo co infiltration. The source material is W-Mo (W: Mo = 1:1) alloy plate + rare earth Y plate, with purity of 99.9% and size of 80mm×40mm×8mm, using the same experimental equipment and process parameters as W-Mo co infiltration.

AX10 metallographic microscope was used to measure the thickness of infiltrated layer and observe the microstructure; The microstructure of the infiltrated layer was analyzed by d8-advance X-ray diffractometer; DHL-1250 field emission scanning electron microscope (with EDS) for component analysis; HV-1000 microhardness tester is used for microhardness measurement. Each sample was tested 5 times to ensure the reliability of the experimental results. The friction and wear properties were tested by hsr-2m high-speed reciprocating friction and wear tester. The applied load mass is 230g, the grinding material is φ6mm SiC ball, and the wear time is 10min.

3. Results and discussion

3.1 Microstructure analysis of infiltration layer

Metallographic photos of W-Mo and W-Mo-Y sections are shown in Fig. 1. In addition, it can be seen from the figure that the thickness of W-Mo co infiltration layer is 36um. The thickness of W-Mo-Y co infiltration layer is 42um. W-Mo-Y co infiltration layer is thick. In addition, there is an obvious interface between the infiltration layer and the matrix. The microstructure of the infiltrated layer is columnar crystal, and some columnar structures maintain a certain crystal degree relationship with the matrix grain. The formation process of the new phase of reaction diffusion is dependent on the nucleation and growth of the matrix. The alloy layer formed by solid-state metallurgy is well combined with the matrix\(^{[11]}\). In addition, comparing Fig. 1 (a) and Fig. 1 (b), it is found that the addition of Y element refines the grain of the alloying layer, so as to improve the performance of the alloying layer. According to the X-ray diffraction pattern of W-Mo and W-Mo-Y co infiltrated layer in Fig. 2, the W-Mo infiltrated layer is mainly composed of Fe\(_2\)Mo, Fe\(_2\)W, Fe\(_2\)W\(_2\) and other phases. The W-Mo-Y layer is mainly composed of Fe(W, Mo, Y), Fe\(_2\)Mo, Fe\(_2\)Y\(_2\), W, Y and other phases, which is due to the low electronegativity of rare earth Y and the large difference between ferroelectronegativity, forming complex intermetallic compounds\(^{[13]}\).
Fig. 1 Metallographic structure of cross section of infiltration layer: (a) W-Mo, (b) W-Mo-Y

Fig. 2 X-ray diffraction pattern of infiltration layer

The composition analysis of W-Mo co infiltration test is shown in Fig. 3(a). The contents of W and Mo on the surface of the infiltration layer are 2.21% and 3.67% respectively. For the W-Mo-Y co infiltration test, the component content is shown in Fig. 3(b), on the surface of the infiltration layer, the contents of W, Mo and Y are 2.56%, 5.17% and 4.62%. The content of W and Mo decreases gently with the increase of surface distance, but compared with the W-Mo co infiltration test, the content of W and Mo in the W-Mo-Y co infiltration test decreases more gently, which shows that the addition of Y has a certain effect on the content of W and Mo in the infiltrated layer. In the W-Mo-Y co infiltration test, the content distribution of Y in the infiltrated layer is relatively uneven. This is because when the content of Y exceeds its solid solubility in iron, Y is easy to produce segregation at the grain boundary with loose atomic arrangement, resulting in uneven component content[13].

Fig. 3 Distribution diagram of atomic content: (a) W-Mo, (b) W-Mo-Y

3.2 Calculation of diffusion coefficient

The diffusion coefficients of W and Mo atoms in W-Mo co infiltration and W-Mo-Y co infiltration are calculated by Fick’s second diffusion law[14], and the effect of the addition of rare earth Y element on the diffusion of W and Mo atoms is analyzed. The composition distribution of W and Mo elements in each diffusion layer is measured by energy spectrometer. The results are shown in Table 1 and 2.
Table 1 Composition distribution of W-Mo co infiltration layer

| Distance from the surface $x_i$(um) | 0   | 5   | 10  | 20  | 30  | 35  | 40  |
|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| W content $y_W$ (at%)             | 2.21| 1.94| 1.78| 1.33| 0.85| 0.26| 0.09|
| Mo content $y_{Mo}$ (at%)         | 3.67| 3.34| 2.94| 2.26| 1.23| 0.56| 0.22|

Table 2 Composition distribution of W-Mo-Y co infiltration layer

| Distance from the surface $x_i$(um) | 0   | 5   | 10  | 20  | 30  | 35  | 40  | 45  |
|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| W content $y_W$ (at%)             | 2.56| 2.39| 2.28| 1.86| 1.24| 1.02| 0.71| 0.13|
| Mo content $y_{Mo}$ (at%)         | 5.17| 4.81| 4.52| 3.54| 2.42| 1.93| 1.26| 0.32|

Table 1 and Table 2 show the composition distribution of W-Mo and W-Mo-Y co infiltration layer; The data are fitted by Matlab software\textsuperscript{[15]}. The fitting curve of W-Mo composition distribution in W-Mo co infiltration experiment is shown in Figure 4 (a) and (b), and the fitting curve of W-Mo co infiltration composition distribution in W-Mo-Y co infiltration experiment is shown in Figure 5 (a) and (b). Through comparison, it is found that the fitting degree of cubic function curve is the best, the error is the smallest. The coefficients of linear regression equation of W-Mo co infiltration are $R_w=0.9952$ and $R_{Mo}=0.9985$; The coefficients of linear regression equation of W-Mo-Y co infiltration are $R'_w=0.9967$ and $R'_{Mo}=0.9988$; Check the correlation coefficient checklist\textsuperscript{[14]}, its shows that the R value is greater than this value, so the linear fitting is meaningful. The equation of the relationship between the diffusion distance and the content of each element is as follows:

The relation equation between infiltration layer composition and diffusion distance in W-Mo and W-Mo-Y co infiltration experiment is as follows:

\[ y_W = -8.57 \times 10^{-6}x^3 - 1.42 \times 10^{-5}x^2 - 3.96 \times 10^{-2}x + 2.18 \]  

\[ y_{Mo} = 1.07 \times 10^{-5}x^3 - 1.32 \times 10^{-3}x^2 - 5.15 \times 10^{-2}x + 3.64 \]  

\[ y_W = -9.37 \times 10^{-6}x^3 - 8.45 \times 10^{-5}x^2 - 3.02 \times 10^{-2}x + 2.56 \]  

\[ y_{Mo} = -1.21 \times 10^{-5}x^3 - 2.68 \times 10^{-4}x^2 - 7.02 \times 10^{-2}x + 5.19 \]  

The relationship curve between diffusion distance and content of each element is shown in the Figure 4 and Figure 5 below.

![Fig. 4 Relationship between content and diffusion distance in W-Mo](image)

![Fig. 5 Relationship between content and diffusion distance in W-Mo-Y](image)

To calculate the diffusion coefficient of each element in the infiltration layer, according to Fick's second law of diffusion:

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \]  

Conversion expression:
The thickness of infiltration layer is within a certain range, so the integral is a definite integral, where $f^{-1}(y_i)$ is the inverse function of $y$. For the calculation of W element in Table 1, when $y_i$ is 0.09, $f^{-1}(y_i)$ is 40. Therefore, by substituting the values of $X$ in Table 1 and table 2 into the calculation, the relationship between the diffusion distance of each element in the co infiltration layer and the diffusion coefficient can be solved.  

Table 3 Diffusion coefficients of W and Mo at different positions in W-Mo co infiltration layer

| Distance from the surface $x_i$(um) | 0  | 5  | 10 | 20 | 30 | 40 | 70 |
|-------------------------------------|----|----|----|----|----|----|----|
| $D_W \times 10^{10}$(cm$^2$/s)      | 4.36 | 4.23 | 3.9 | 2.8 | 1.44 | 74310$^{-1}$ | 4.2010$^{-2}$ |
| $D_{Mo} \times 10^{10}$(cm$^2$/s)   | 5.59 | 4.47 | 3.7 | 2.54 | 1.45 | 86510$^{-1}$ | 1.9810$^{-1}$ |

Table 4 Diffusion coefficients of W and Mo at different positions in W-Mo-Y co infiltration layer

| Distance from the surface $x_i$(um) | 0  | 5  | 10 | 20 | 30 | 40 | 70 |
|-------------------------------------|----|----|----|----|----|----|----|
| $D_W \times 10^{10}$(cm$^2$/s)      | 8.34 | 7.89 | 7.10 | 5.03 | 2.97 | 2.02 | 1.14 | 2.9410$^{-1}$ |
| $D_{Mo} \times 10^{10}$(cm$^2$/s)   | 7.02 | 6.64 | 6.06 | 4.55 | 2.87 | 2.02 | 1.19 | 3.6110$^{-1}$ |

From the calculation results of diffusion coefficient in Table 3 and table 4, it can be seen that the W-Mo atomic diffusion coefficient in W-Mo-Y co infiltration is greater than that in W-Mo co infiltration. Therefore, it can be seen that the addition of Y atom increases the W-Mo atomic diffusion coefficient of the infiltration layer. At the same time, the diffusion coefficients of W-Mo atoms in W-Mo-Y and W-Mo are basically of the same order of magnitude. This is because the W-Mo atomic radius is similar, and the W-Mo atomic diffusion coefficient should be the same order of magnitude in alloying element Co infiltration.

3.3 Calculation of diffusion activation energy

In the process of metallization, ion splashing from one equilibrium position to another requires splashing energy, which is collectively referred to as diffusion activation energy. According to Arrhenius formula:

$$D_0 = \frac{D}{\exp \left(-\frac{Q}{RT}\right)}$$  \hspace{1cm} (7)

$Q$ is the activation energy during the diffusion of one vacancy mechanism per mole of atom, which can be found in table, $T$ is the thermodynamic temperature, and the diffusion coefficient of each element in iron can be found in table$^{[13]}$. $R$ is the molar gas constant, $R=8.314$J mol$^{-1}$·K$^{-1}$. The diffusion coefficient constants of each element $D_0$ can be obtained, Convert equation (7) into (8),

$$Q' = -RT \ln \frac{D}{D_0}$$  \hspace{1cm} (8)

The diffusion activation energy of each element is calculated by substituting the previously calculated diffusion coefficient constant $D_0$ into equation (8). By comparing the changes of diffusion activation energy of W and Mo before and after the addition of rare earth Y element at the same common infiltration layer, the table below shows.

$Q_{W-Y}$ and $Q_{Mo-Y}$—The diffusion activation energy of W/Mo in W-Mo-Y experiment is subtracted from the diffusion activation energy of W/Mo in W、 Mo co infiltration experiment.
It can be seen from the calculation results in Table 5 that with the inward diffusion of atoms, the more significant the promotion effect of Y atoms on the diffusion of W and Mo atoms, and the greater the decrease of diffusion activation energy of W and Mo atoms. The atomic radii of W and Mo are greater than those of Fe, so the inward diffusion mechanism of atoms is displacement diffusion. Ion bombardment causes more defects and vacancies on the surface of the workpiece, which makes it easier to transition, the easier the inward diffusion and the lower the diffusion activation energy. The vacancy concentration decreases gradually from the surface to the inside. Therefore, the more obvious the promotion effect of rare earth element Y, the more effective it is to reduce the diffusion activation energy of W and Mo atoms.

Table 5 Change of diffusion activation energy at different co infiltrated layer positions after adding rare earth Y element

| Distance from the surface $x_i$(um) | 0  | 5  | 10 | 20 | 30 | 35 | 40 |
|-------------------------------------|----|----|----|----|----|----|----|
| $Q_{W-Q_{W+Y}}$(KJ/mol)             | 7.94 | 7.64 | 7.34 | 7.17 | 8.87 | 12.25 | 40.32 |
| $Q_{Mo-Q_{Mo+Y}}$(KJ/mol)           | 2.79 | 4.85 | 6.04 | 7.14 | 8.36 | 10.52 | 21.96 |

3.4 Microhardness and friction and wear properties of carburized layer

The test data are shown in Table 6 below. It can be seen that W-Mo infiltration layer can significantly improve the microhardness of wedge-shaped component samples. The increase of microhardness is mainly due to the formation of an infiltration layer close to the composition of high-speed alloy steel on the substrate surface, which improves the hardness of the substrate surface under the transformation strengthening of carbides. After adding rare earth element Y, the microhardness of W-Mo-Y layer is further improved to achieve the purpose of surface strengthening. At the same time, Y element not only plays a certain solid solution strengthening effect, but also promotes the formation of carbides. A large number of fine carbides are dispersed and distributed in the carburizing layer, which hinders the growth of austenite grains, refines grains, strengthens grain boundaries, and improves microhardness.

Table 6 Microhardness values of different samples

| specimen | Wedge assembly specimen | W-Mo co infiltration specimen | W-Mo-Y co infiltration specimen |
|----------|-------------------------|--------------------------------|---------------------------------|
| Hardness(HV) | 216                     | 307                            | 445                             |

Fig. 6 Friction coefficient of infiltration layer

The friction coefficients of W-Mo and W-Mo-Y layer are shown in Fig. 6. Through comparison, it is found that the friction coefficient of W-Mo-Y layer is relatively stable and has been in a steady state stage, indicating that W-Mo-Y layer plays an effective role in antifriction and lubrication. The friction coefficient of W-Mo infiltration layer fluctuates little with time in 4min. After 4min, the friction coefficient fluctuates greatly, indicating that there is a serious adhesion shear behavior. This is because in the friction process, the infiltrated layer begins to wear and fracture, forming debris particles, and the unstable contact conditions lead to the increase of friction coefficient.

From the sliding wear morphology of W-Mo co infiltrated sample in Fig. 7(a), it can be seen that
there are obvious multiple furrows and a large amount of adhesion on the surface of W-Mo co infiltrated sample, and the wear mechanism is mainly abrasive wear and adhesion wear. During the friction process, the grinding ball is pressed into a large depth, and the infiltration layer produces serious plastic deformation, adhesion and tear. The stripped particles plough the infiltration layer continuously with the progress of the friction process, and finally become wear debris falling off or adhesion. In Fig.7 (b), the W-Mo-Y co infiltrated sample has no obvious peeling off, only a small amount of furrows and adhesion, which belongs to slight wear, and its wear resistance is significantly higher than that of W-Mo infiltrated layer.

Fig. 7 Sliding wear morphology of sample: (a)W-Mo,(b) W-Mo-Y.

4. conclusion
(1) According to Fick's second diffusion law, it is found that the addition of rare earth Y reduces the diffusion activation energy and increases the diffusion coefficient of W and Mo at the same common infiltration layer, indicating that Y atom has catalytic effect on W and Mo atoms, and the addition of rare earth Y makes W and Mo elements easier to penetrate and form w and Mo infiltration layers.

(2) After Plasma w, Mo and Y co infiltration, 42um deposition layer is formed on the surface of 45 steel wedge assembly, which further improves the hardness and wear resistance of 45 steel wedge assembly. The research and development of this technology is of great significance to the application and development of surface modification of mechanical parts.

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