

MECHANISM OF Re-B-V CO-PERMEATION^①

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ABSTRACT The influence factors and the kinetic conditions of the Re-B-V co-permeation by pasty agent were studied. It is shown that the Re elements in the pasty agent have obvious catalytic effects on the permeation under suitable technical conditions; KBF_4 has an important effect on the permeation of the activated atoms. The formation of the permeated layer was analyzed both theoretically and experimentally, and based on the analysis, the mechanism of the Re-B-V co-permeation was revealed.

Key words Re-B-V co-permeation mechanism kinetics rare earth pasty agent

1 INTRODUCTION

The aim of multiple co-permeation is to increase the hardness and wear resistance of the surface of a workpiece, and elongate its service life. It is shown that higher surface hardness and wear resistance can be obtained by Re-B-V co-permeating than by any other permeating. At present, the studies of the mechanism of the Re-B-V co-permeation, the hardness, and the structure of the permeated layer are very few. So it is important to research in this area to provide reasonable technical parameters for production.

2 EXPERIMENTAL

The pasty agent consisted of rare earth, B_4C , V_2O_5 , Al and KBF_4 . The experimental material was steel 45. The dimensions of permeated specimens were $7 \text{ mm} \times 10 \text{ mm} \times 15 \text{ mm}$, and the surface finish was $3.2 \mu\text{m}$.

Having been degreased, the surface of the specimen was coated with 3~5 mm thick pasty agent. After being baked, the specimen was packed into a sealed iron pot filled up with SiC stuff. The technical curve of the permeation is shown in Fig. 1.

The thickness of the permeated layer was investigated and tested under a magnification of 400 times with an optical microscope, and five

representative peak figures of the permeated teeth were measured to obtain the average thickness of the permeated layer:

$$\delta = (\sum_{i=1}^5 \delta_i) / 5$$

where δ is the thickness of the permeated layer, δ_i is the height of the peak tooth.

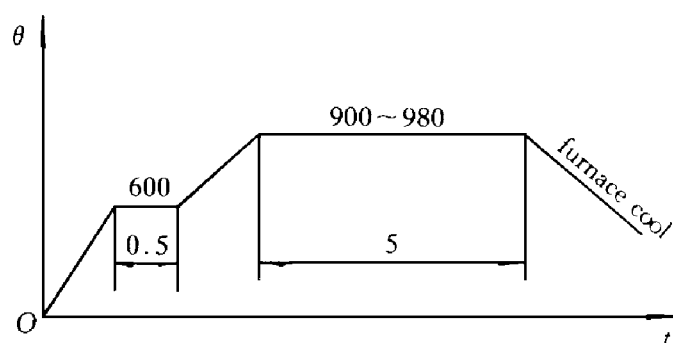


Fig. 1 Technical curve of permeation

The hardness of specimens was tested with a 71H-type hardness tester. And the phases of the permeated layer were analyzed with D/max-YB rotatory positive pole X-ray diffractometer.

3 EXPERIMENTAL RESULTS

3.1 Catalytic effect of Re

It is shown that the rare earth in the pasty agent is able to increase the thickness of the per-

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meated layer and change the kinetic process of the permeation.

As shown in Fig. 2 and Fig. 3, it can be deduced that in the initial stage of permeation, the addition of rare earth increases the decomposability of the pasty agent and the concentration of the active atoms on the surface of the specimen. Therefore, the diffusing speed of the active atoms and the thickness of the permeated layer increase. But after the content of the rare earth has reached the extreme value, there are too many excessive active atoms which

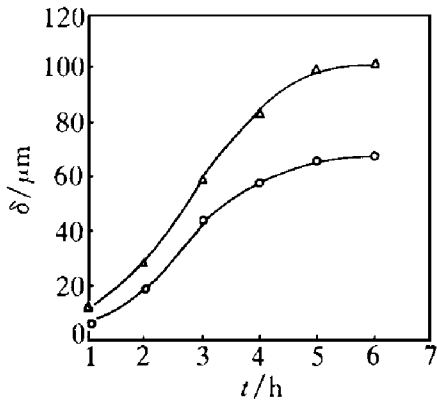


Fig.2 Relation between thickness of permeated layer(δ) and time(t)
 Δ —with Re; \circ —without Re

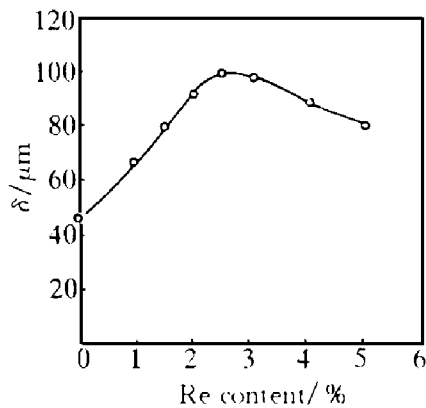


Fig. 3 Relations between thickness of permeated layer(δ) and content of rare earth

make the surface of the specimen supersaturated. These unabsorbed excessive active atoms may deposit on the surface of the specimen and form a layer of deposits or dissipate very quickly, which will decrease the concentration of the active

atoms, weaken the supplies of the active atoms, reduce the diffusing speed, and restrain the thickening of the permeated layer^[1].

Because of the permeation of the atoms of the rare earth, the teeth of borides of the permeated layer become regular, and wedge into the structure, which makes the pattern of the metal distort and form a directional stress field of distortion. At the same time, the rare earth forms specific compounds, which gather around crystal defects such as grain boundaries and dislocations and increases the concentration of the permeated layer. Therefore the addition of Re not only changes the kinetic factors, but also improves the morphology and the hardness of the permeated layer, as shown in Fig. 4 and Fig. 5.



Fig. 4 Morphology of permeated layer without Re

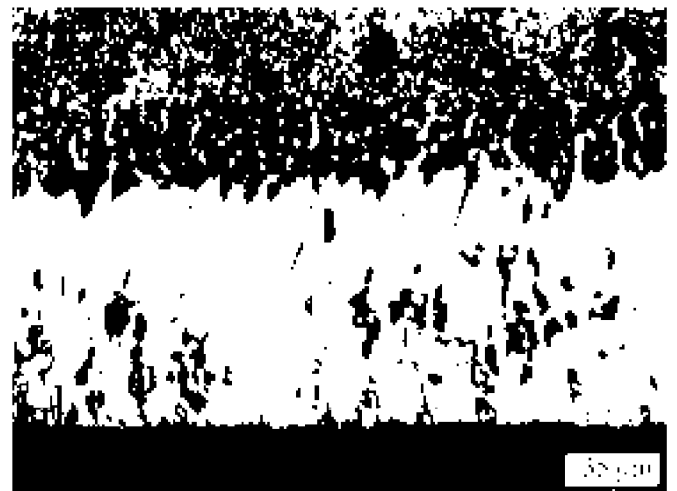


Fig. 5 Morphology of permeated layer with Re

3.2 Permeation accelerating function of KBF_4

The addition of moderate content of KBF_4 in the permeating agent accelerates the permeation, as shown in Fig. 6. It can be deduced that when it is heated, KBF_4 decomposes into two gases, namely KF and BF_3 , which can accelerate the atomic movement and make the effective active atoms, such as $[\text{V}]$, $[\text{B}]$, $[\text{Al}]$, move rapidly to the permeated surface, and therefore accelerate the permeating process^[2].

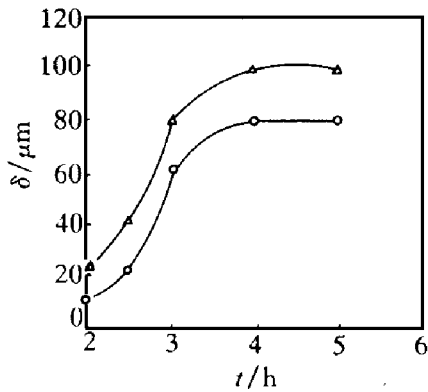


Fig. 6 Relations between thickness of permeated layer(δ) and time(t)
 Δ —with KBF_4 ; \circ —without KBF_4

3.3 Effects of technical parameters on co-permeating speed

The curve of relationship between thickness of the permeated layer and the co-permeating temperature of steel 45 is shown in Fig. 7. It is shown that the relationship between the thickness of the permeated layer and the co-permeating temperature is in the index change and coincides with the second law of diffusion. When the co-permeating temperature increases, the decomposability of permeating agent, and the diffusibility of the atoms become stronger, and a great number of the active atoms which are absorbed on the surface diffuse rapidly into the inner and form a thick permeated layer. Within the range of the temperature where the slope of the curve of the relationship is the biggest, the decomposing velocity of permeating agent, the absorbing and diffusing velocity of the active atoms are in the best harmony. Because of the increasing of the active atoms, the original balance is broken and some active atoms decomposed from the permeated agent are lost. So the slope of the

curve drops sharply and the velocity of the co-permeation becomes mild. When the permeating temperature is above 960°C , the velocity of the co-permeation has no change.

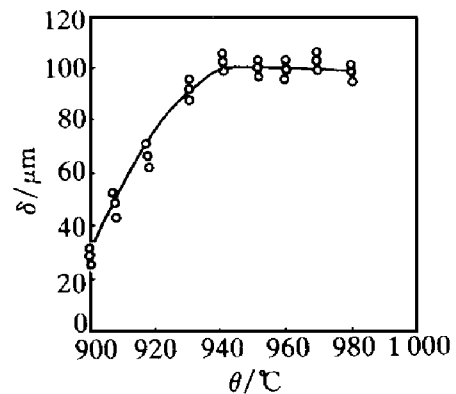


Fig. 7 Relation between thickness of permeated layer(δ) and temperature(θ)

The relationship between the thickness of the permeated layer and the holding time is in accordance with $X = Kt^{1/2}$, that is, the law of parabola and also accords with the second diffusing law. As shown in Fig. 8, in the original period of the co-permeation, the permeated layer hinders the movement of the diffusing elements, increases the diffusing resistance of the active atoms, such as $[\text{V}]$, $[\text{B}]$, $[\text{Al}]$, and restrains the development of the boundary of the new phase. The farther the spot is from the surface of the specimen, the weaker the potentials of the $[\text{V}]$, $[\text{B}]$, and $[\text{Al}]$ are. With increasing time

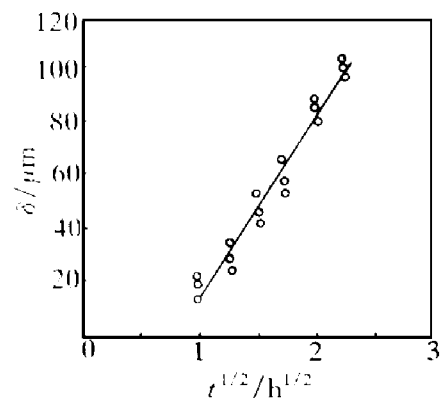


Fig. 8 Relation between thickness of permeated layer(δ) and time($t^{1/2}$)

the velocity of the co-permeation increases slowly, and when the holding time is above 6 h, the thickness of the permeated layer has little

change.

It is shown that the relation among the co-permeating temperature, the time of heat preservation and the hardness of permeated surface is also in accordance with the above regularity. The best technique of Re-V-B co-permeation is under the temperature of 940 ± 5 °C, 5 h heat holding. The hardness of the permeated surface is $H_{V0.1} 1800 \sim 2200$. The thickness of the permeated layer is $60 \sim 80$ μm. The teeth of the permeated layer are regular and embedded into the structure, as shown in Fig. 5.

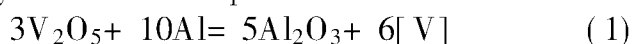
4 MECHANISM OF CO-PERMEATION

4.1 Formation conditions of permeated layer

The Re-V-B co-permeating process, just like other metals permeation, can be divided into three periods. The first period is the supply of the active atoms. The second period is the absorption of the active atoms. And the third period is the diffusion of the active atoms to the inner part of the metal. Besides the three periods, the principal condition of the permeated layer formation is that the permeated elements must be able to combine with the substrate metal and form solid solution or metallic compound^[5].

4.1.1 Kinetic condition of agent supplying active atoms of permeated elements

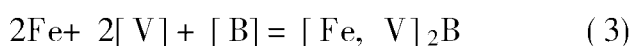
The generation of the active atom [V] is analyzed as an example.



The equilibrium constant of eq. (1) is K_I .

$$\lg K_I = \lg a([V]) + \lg a(Al_2O_3) - \lg a(Al) - \lg a(V_2O_5) \quad (2)$$

In eq. (2), a is the activity of the matter (when the matter is a gas, a is the differential pressure of it). The active atom [V], which is generated from eq. (1), combines with the substrate metal.



The equilibrium constant of eq. (3) is K_{II} .

$$\lg K_{II} = \lg a([Fe, V]_2B) - \lg a(Fe) - \lg a([V]) - \lg a([B]) \quad (4)$$

Eq. (2) and Eq. (4) merge into Eq. (5).

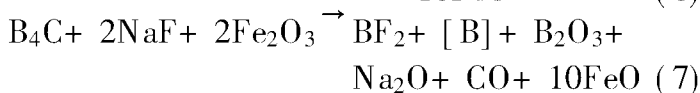
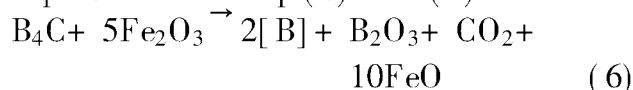
$$\lg K_I + \lg K_{II} = \lg a([Fe, V]_2B) + \lg a(Al_2O_3) + \lg a(V_2O_5) -$$

$$\lg a(Al) - \lg a(Fe) - \lg a([B]) \quad (5)$$

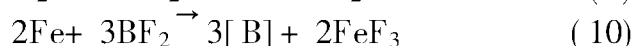
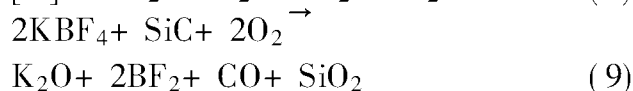
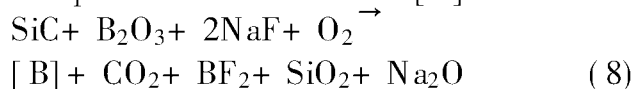
It is shown that only when the value of $(\lg K_I + \lg K_{II})$ is no less than -2 , that is the conversion amount of the value of $K_I \times K_{II}$ is no less than 1%, the permeated layer has practical value^[2].

4.1.2 Supplying process of active atoms

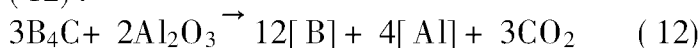
The active atom [V] in the co-permeation is provided from eq. (1). And the active atom [B] is provided from eq. (6) and (7):



And SiC and KBF₄ in the packing can combine and produce the active atom [B].



The active atom [Al] is obtained both directly from the aluminum powder and from eq. (12).



The full combination of the agent can generate a lot of active atoms [V], [B], and [Al] to provide the necessary conditions for the permeated layer formation.

4.2 Formation of phases in permeated layer

In the process of the co-permeation, the active atoms [V], [B], and [Al], which are produced in the combinations, can be absorbed by the surface of the specimen and combine with one another. Because the active atom [B] has a small atomic radius and a small atomic weight, and the active atom [V], which belongs to transition metal with valence bond, has an unfilled outer electronic layer d and a strong combining power to absorb the external atoms easily; when they meet in diffusion process, the combination $3[V] + 2[B] = V_3B_2$ is found in the X-ray diffraction figure, as shown in Fig. 9.

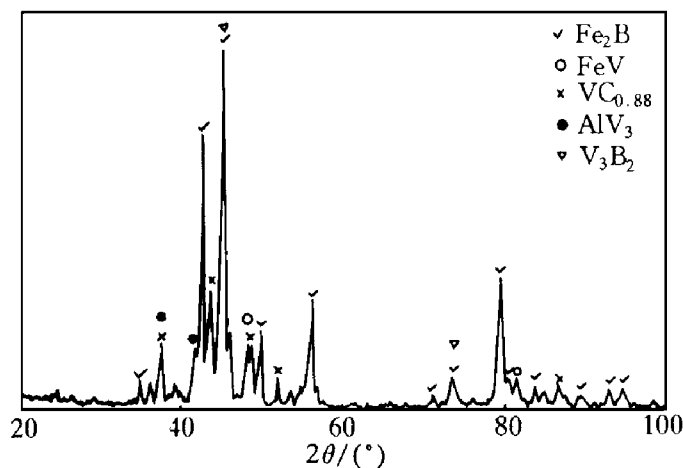


Fig. 9 X-ray diffraction of Re-B-V co-permeated layer

Since the radii of the vanadium and aluminum atoms are larger than that of the iron atom, their diffusion is difficult and there are many tiny areas which are rich in vanadium and aluminium atoms in the thin layer on the substrate surface. In those areas, the boron atom, because of its small atomic radius, can permeate through the tiny area into the substrate.

The relative dimensions of the atoms are shown in Table 1.

Table 1 Relative dimensions of atoms

Element	Radius of atom/ Å	Electronegativity
V	1.338	1.6
B	0.020	2.0
Fe	1.260	1.8
C	0.776	2.5
Al	1.429	1.5

According to the Fe-B phase diagram, the solubility of boron in the steel is very low. The active atom [B] can only form substitutional solid solution in α -Fe. But in γ -Fe, besides the substitutional solid solution, the active atom [B] can also form interstitial solid solution, the active atom [B] and [V] can dissolve into it^[6].

When the Re-B-V co-permeation time increases, the concentration of the active atom [B] will be much higher than the solubility of boron in the solid solution and the new phase formed in γ -Fe is Fe₂B which is tooth-shaped. With the

active atom [B] permeating, Fe₂B grows continuously and the second kind of boride FeB appears on the surface of Fe₂B. The active atoms [V] and [Al] dissolve into those new solid solutions. It makes the hardness of the permeated layer much higher than that of Fe₂B. Phases Fe₂B, VC, and Al₃V can be found in Fig. 9. And the increasing of the interval of the crystal planes indicates that the active atoms [V] and [Al] dissolve into Fe₂B. The other phases such as Fe₂B, (Fe, Al)₂B, Fe₂B, (Fe, V)₂B, are also found in the permeated structure.

5 CONCLUSIONS

(1) The composition of permeating agent and the permeating technique parameters have an obvious effect on the kinetics of Re-B-V co-permeation.

(2) The addition of the rare earth has changed the kinetic process of co-permeation and accelerates the permeation. The reasonable addition of KBF₄ can also accelerate the active atoms to permeate.

(3) The phases of the permeated layer are Fe₂B, VC, Al₃V, V₃B₂, (Fe, V)B etc, and the active atoms [V] and [Al] dissolve in phase Fe₂B.

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