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Formation and growth model of B-Al permeation layer of Steel 45①

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[Abstract] The B-Al permeation layers of Steel 45 were studied by means of SEM, TEM and XRD. The formation and growth model of permeation layer was proposed. The layer formation, growth and the migration behaviors of B were discussed. It is suggested that the diffusion of Al is deferred when the surface was covered by borides and aluminize compounds are surrounded by borides with the further growing of borides.

[Key words] Steel 45; B-Al permeation; formation and growth model
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1 INTRODUCTION

As B-Al permeation effectively deters the formation of FeB, the brittleness[1~4], hardness, thermal stability and wearing ability of the layers are therefore improved[5~7]. The growth kinetics and phase constructions of such layers were studied and had been reported in our previous works[8~14]. However, the model of the layer formation and growth, the migration law of B, and the formation behaviors of aluminize compounds have not been studied yet. In this paper the model of layer formation and growth was proposed and the proper analysis was made.

2 EXPERIMENTAL

The specimens of Steel 45 were 5 mm in thickness with a diameter 15 mm, and the surface finish was 1.6 μm. The specimens were heated in pipe-furnace with the protective gases of N_2 and Ar. The control accuracy of furnace temperature was within ±5 ℃. The specimens were coated with a layer of paste for 3~5 mm after degreasing. When the specimens were dried, once again they were coated with a layer of protective dope and dried again. The specimens was cooled after heated at 930 ℃ for 4 h. Microstructures of the specimens were observed by using SEM of Model S-570.

3 EXPERIMENTAL RESULTS

3.1 Observation results of SEM

Fig. 1 shows the SEM photograph and the corresponding Al-elemental area scanning after B-Al permeating for 4 h. It can be seen that the layer of B-Al permeation has the similar tooth-like shapes to that of B permeation. The teeth grow up vertically to the specimen surface, and some of them have fork teeth. The Al element distributes in black areas of secondary electron image. The quantitative analysis of EPMA showed that the amounts of Al element in the enriching zones were different. The analysis of TEM showed that complex compounds, such as Fe_3Al, $Al_3B_{48}C_2$ and $AlFe_3C_x$ ($x = 4\%$) were formed.

3.2 Analysis results of XRD

Analysis of metallography[8] and XRD showed that Fe_2B which is of about 10 μm in thickness, tooth-like shape, tidy, regular, comes to form after permeating for 8 min. The dimensions of the layer that is mainly composed of Fe_2B have grown to rather large after 32 min. When the time of permeation is up to 4 h, there is a little FeB, and other compounds are not detected because their diffraction peaks are submerged (as shown in Fig. 2).

4 LAYER FORMATION AND GROWTH MODEL

According to the microstructures and growth kinetics curves of the layer[8,11,12], the process of permeation and growth is described as follows (Fig. 3).

At stage Ⅰ, the active atoms [B] and [Al], which are decomposed from the paste, are absorbed on the surface of specimens. The solubility of B in γ-Fe is very low and it will reach saturation rapidly. The amount of active atoms [B] on the surface are rapidly up to 8.1% (mass fraction), which can make Fe_2B form.

At stage Ⅱ, the active atoms [B] form nuclei of

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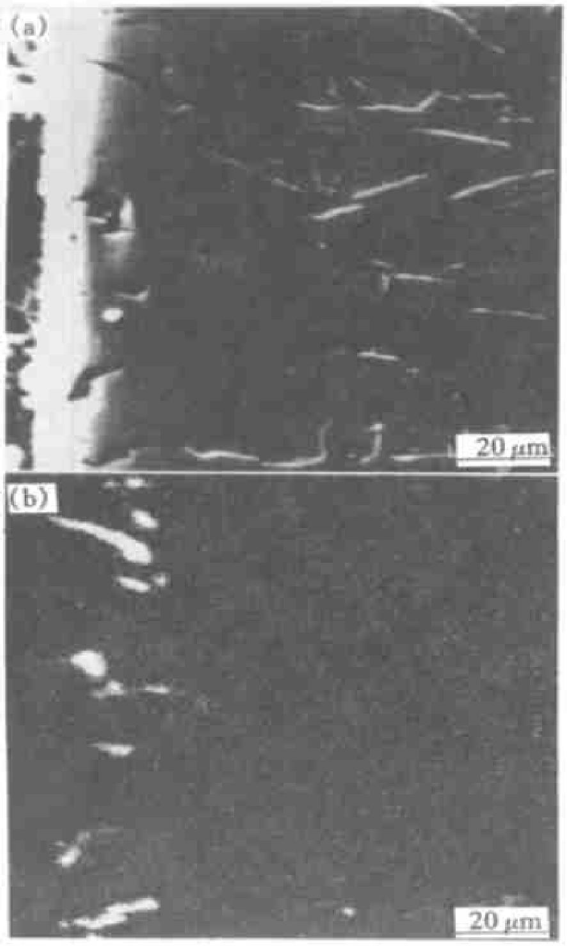

Fig. 1 SEM photographs of B-Al permeating for 4 h
(a) —Secondary electron image; (b) —Al area scanning

Fe_2B at grain boundaries, vacancies and dislocations first by chemical reaction. But the atoms [Al] have not nucleated yet because its solubility in γ-Fe is higher.

At stage Ⅲ, the boride nuclei appear inside the grains if the conditions of composition and energy are satisfied. Since borides grow up in their preferred orientation[15], the borides at boundaries have become rather big and Al also begins to segregate and form compound nuclei at this stage. The small nuclei that are formed latter are gobbled up by borides that are growing up continuously. Because of random nucleation and preferred growing orientation, a portion of nuclei grow up horizontally at a very high rate, collide with each other and then stop growing. The rest of them grow up toward inside and expand along the horizontal direction and the layer becomes tooth-like shape. The borides grow up further and will cover the surfaces of the specimen, and aluminize compounds become rather large. The stage Ⅳ is finished.

When the process gets to stage Ⅴ, borides covering the specimen surface will defer the diffusion of Al. The density gradient of Al becomes smooth, and the nuclei of aluminize compounds grow slowly or no longer grow at all, so they can not grow toward inside at this stage. At stage Ⅵ, the nuclei of borides

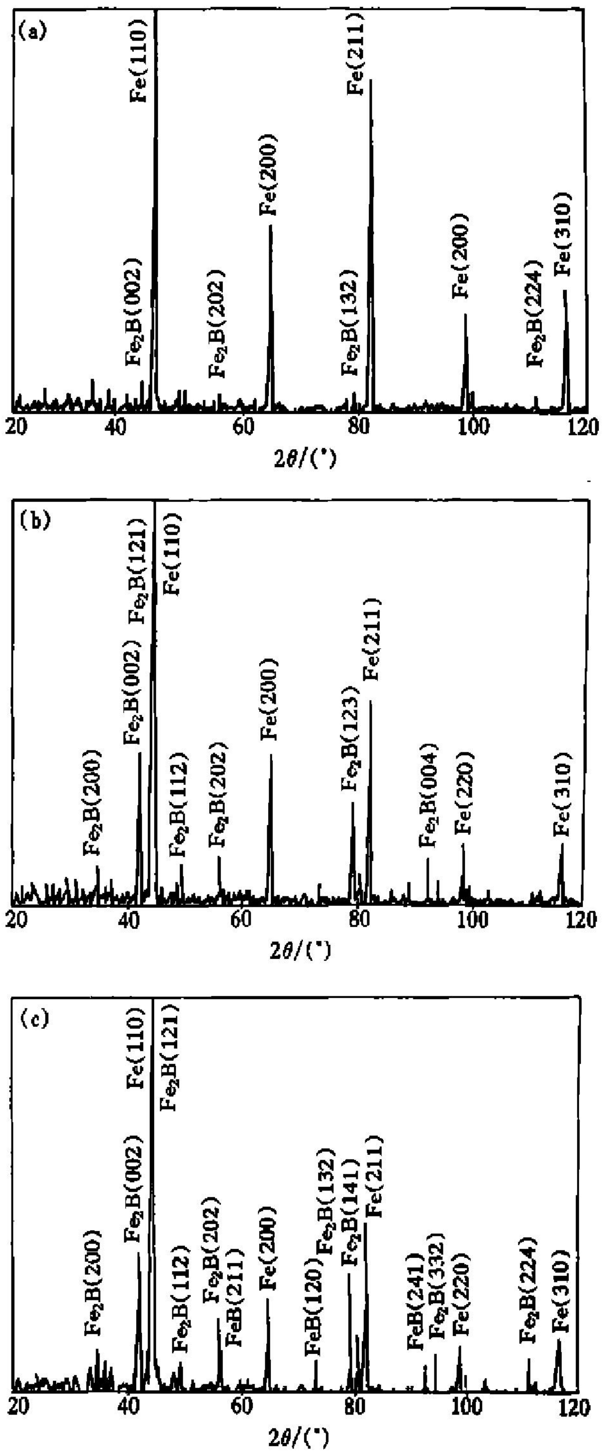

Fig. 2 X-ray diffraction patterns
(a) —Permeating for 8 min; (b) —Permeating for 32 min;
(c) —Permeating for 4 h

further grow up in preferred orientation and aluminize compounds are surrounded by borides and stay in subsurface layer. If once the amount of surface borides is up to 16.2%, FeB will be formed. In the process of FeB nuclei formation and growth, the dimension and number of aluminize compounds vary not obviously.

5 DISCUSSION

5.1 Kinetics process

As mentioned above, the nucleation and growth

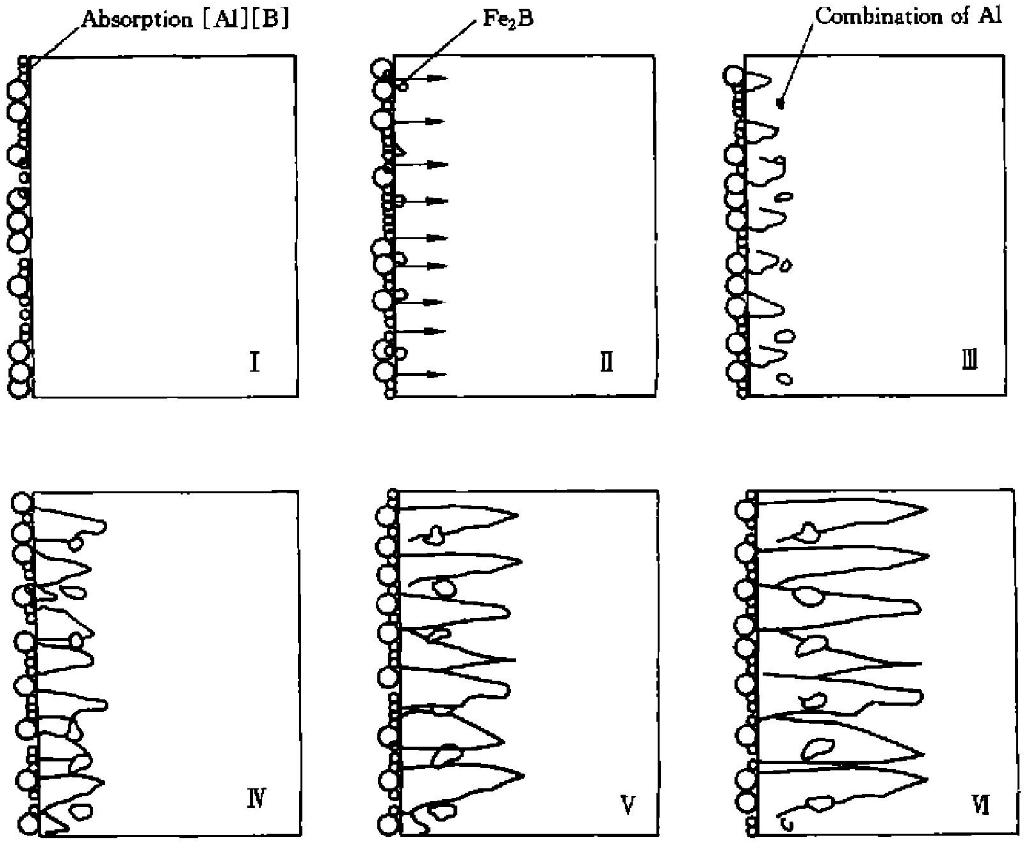

Fig. 3 Formation and growth model of layer

of borides are divided into three stages, that is, nucleation and equiaxial growth, growth in preferred orientation, formation and growth of FeB. The whole kinetics process depends on the speed of each stage. It is difficult to precisely measure and distinguish the speeds of every stage. The speed of the first stage is determined by chemical reaction, and the second stage by diffusion. Observation shows that the nucleation and growth of borides are mainly related to the permeation conditions and the compositions of matrix material. The layer thickness of specific steel is determined by the permeation conditions, especially by the permeation temperature and time.

Analysis of different kinetics curves shows that increasing the permeation temperature will reduce the time of nucleating and covering the surface layer. Therefore it is considered that the time of continuous layer formation depends on the permeation temperature. Increasing the permeation temperature can speed up the growth of the continuous layer. The growth speed obeys the parabolic law. It is concluded that the growth of layer thickness is controlled by diffusion, and the process of nucleation and growth of borides is rather fast compared with the growth of layer thickness.

According to chemical heat treatment, the process of atoms [B] migration can be divided into two stages, that is, the migration of atoms [B] before Fe_2B forming and the respective migration after Fe_2B and FeB forming. After Fe_2B has formed, the migration of atoms [B] can also be divided into two stages-one is controlled by surface reaction, and the other by chemical reaction.

5.2 Migration of B before Fe_2B forming

Since there are micro-inhomogeneities (vacancy, dislocation, grain boundary) in crystals, the atoms [B] inevitably segregate at these defects of the crystal. When the density of atoms [B] is over the solubility of B in γ-Fe, nuclei form at grain boundaries firstly. The SEM micrographs show that nuclei exist at grain boundaries. In RE-B-Al permeating and B-Al permeating, this migration appears in transition layers before Fe_2B nuclei forming and after layer forming.

5.3 Migration of atoms B as Fe_2B forming on surface

Since the solubility of B in γ-Fe is very low, after the surface absorbs [B] atoms, nuclei form at the defects of surface firstly and then grow up in the preferred orientation. At the same time the nuclei at other positions also begin to form and grow up. This process is called nucleation. But nuclei have not covered the metal surface completely yet. The migration of atoms [B] is controlled by surface reaction, and the reaction speed is not related to the layer thickness. The relation is as follows:

$$\frac{dy_1}{dt} = k \quad (1)$$

$$y_1 = kt \quad (2)$$

where y_1 is the layer thickness which is controlled by chemical reaction, and y is the coefficient which is related to the vibration frequency of atoms and the density of diffused elements.

5.4 Migration of atoms [B] after continuous Fe_2B forming

After continuous Fe_2B forming, the migration of atoms [B] is controlled by the interface chemical reaction speeds of Fe_2B and Fe, the migration speed of atoms [B] in Fe_2B as well. If only the diffusion of atoms is taken into account, the relationship between the growth speed and thickness of layer can be described as follows:

$$\frac{dy_2}{dt} = D_B \frac{C_B}{y_2} K' \quad (3)$$

$$y_2^2 = 2D_B C_B K' t \quad (4)$$

where D_B is the diffusion speed of atoms [B] in borides, C_B is the amount of atoms [B] on metal surface, K' is the coefficient which is related to the amount of atoms [B] in borides and the vibration frequency of atoms, and y_2 is the layer thickness when only diffusion of atoms is taken into account. If two factors are considered simultaneously, y is set as layer thickness, the kinetic equation of layer growth is then as follows:

$$y = k_1 t^2 + k_2 t \quad (5)$$

Eqn. (5) is the relation of the given kinetic layer thickness vs time in the test[5]. The time controlled by the surface chemical reaction is shorter than that controlled by the diffusion of atoms [B] in Fe_2B. The curve of layer thickness vs time is parabolic, and only the initial stage is linear.

5.5 Migration of atoms [B] after FeB forming

During permeating, when the amount of atoms [B] migrated is over the amount necessary to form Fe_2B, it will cause further concentration of atoms [B] on the surface, and when the amount of B is up to 16.2%, FeB will begin to form. The way of atom [B] migration is still diffusion, and the layer thickness increasing obeys the parabolic law. In order to prevent hard-breakable compounds from forming, the amount of atoms [B] of specimen surfaces should be controlled, the formation speed of atoms [B] should be suitable. The experiment shows that FeB formation can be controlled by reasonably selecting permeation temperature and adjusting material composition.

6 CONCLUSIONS

1) Al element mainly exists in the subsurface layers and distributes inhomogeneous, and there are enriching zones of Al element in the layers.

2) The migration of atoms [B] can be divided into two stages: the migration before Fe_2B forming, the migration after Fe_2B and FeB forming. After Fe_2B forms, the migration of atoms [B] is also divided into two stages that are respectively controlled by surface reaction, by chemical reaction and diffusion of atoms.

3) Aluminize compounds are formed by the diffusion of atoms [Al] before the surface of the layer are covered by the borides. Borides resist the diffusion of atoms [Al] after borides covering the surface of specimens, therefore Al element stays in the subsurface layers.

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