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Effect of diffusion on coating microstructure and oxidation resistance of aluminizing steel①

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[Abstract] The effect of diffuse treatment on coating microstructure and oxidation resistance at high-temperature of hot-dip aluminum were studied by means of TEM, SEM and XRD. The results show that, the diffusion temperature has significant effect on structure of coatings and its oxidation resistance. After diffusion at 750 ℃, the coating consists of thick outer surface layer (Fe_2Al_5+ $FeAl_2$), thin internal layer (FeAl+ stripe $FeAl_2$), and its oxidation resistance is poor. After diffusion at 950 ℃, the outer surface layer is composed of single $FeAl_2$ phase, the internal layer is composed of FeAl phase, and its oxidation resistance declines due to the occurrence of early stage internal oxidation cracks in the coating. After diffusion at 850 ℃, the outer surface layer becomes thinner and consists of $FeAl_2$+ Fe_2Al_5(small amount), the internal layer becomes thicker and consists of FeAl+ spherical $FeAl_2$, and the spheroidized $FeAl_2$ phase in the internal layer and its existing in FeAl phase steadily improve the oxidation resistance of the coating.

[Key words] hot-dip aluminium; dip diffusion aluminum; oxidation resistance at high-temperature; surface coating; microstructure
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1 INTRODUCTION

Hot dip aluminizing (HDA) process is a surface coating technology developed in this century. After HDA process, steel turned into a new type of composite material with the strength of steel, the appearance and anti-corrosion performance of aluminum and enhanced oxidation resistance at high-temperature[1~3]. In recent years, hot dip aluminized steel (HDA-steel) was applied widely in such fields as petrochemical industry, building engineering, communication, transportation and oceanographic engineering.

In studies on HDA, more attention was paid on technology and anti-corrosion performance but less on oxidation resistance at high-temperature[4~,6]. It was generally accepted that HDA provided steel with both corrosion and heat resistance. But results of high temperature oxidation tests showed that, when the HAD coatings were applied at high temperature directly, its oxidation resistance was not good enough. In the view of solid diffusion, it was believed that for high-temperature oxidation resistance, HDA-steel products must undergo 4~ 6 h diffusion treatment at 950 ℃ in order to form continuous compact films on HDA-steel surface. But the microstructure evolution of hot-dip aluminum coating was ignored[7~9]. In the present paper, the effect of diffusion treatment on coating microstructure of aluminizing steel is studied by TEM and XRD. The aim is to establish theoretical basis for both enhancing high-temperature oxidation resistance and the further application of HDA-steel.

2 EXPERIMENTAL

The specimen were Q235 steel plates (10 mm × 10 mm × 1.5 mm) and cylinders (d 10 mm × 15 mm) respectively. The HDA procedure is as follows. Degreasing → Rinse → Pickling → Rinse → Activating → Rinse → Fluxing → Drying → Hot Dip Aluminizing. HDA was processed at 720 ℃ for 6 min. The surface coating was 70 μm thick. Diffusion treatments were processed at 750 ℃, 850 ℃ and 950 ℃ for 2 h or 5 h.

High-temperature oxidation tests were conducted in a self-made oxidation oven. Firstly, HDA-Q235 steel specimens were put into silica crucible; then the silica crucible was heated to 800 ℃; finally the specimens in silica crucible were oxidized in air at 800 ℃ for 300 h. Slices for TEM observation were prepared by peeling off the coated film from the surface, and 0.3 mm thick slices were obtained. Such slices were polished to 0.03 mm thick, cleaned in acetone solution, then further thinned by means of double-spray-electrolysis. Electrolyte was mixture of methanol and nitric acid, which was held at - 20 ℃. Electrolysis voltage was 12 V. TEM analysis was conducted on

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Philips CM 800/STEM at 120 kV voltage. XRD analysis was carried out on Japanese D/Max-rB XRD instrument. Graphite monochromatic wave filter and Cu target were employed at 40 kW and 120 mA.

3 RESULTS AND DICUSSION

3.1 Effect of diffusion at 750 ℃ on microstructure of HDA coating

Fig. 1 shows the TEM images of diffusion layers at different places treated at 750 ℃ for different times. It can be seen that all the phases in surface layer exhibit strip and block shape after diffusion treatment for 2 h, as shown in Fig. 1(a). Spectroscopy analysis shows that white region is Fe_2Al_5 phase in which Al content is 71.4% (mole fraction) and the black strip region is $FeAl_2$ phase in which Al content is 66.3%.

TEM images of layer at 100~ 150 μm from the surface indicate that strip and block shape phases disappeared, while narrow strips parallel to each other appeared (as shown in Fig. 1(b)). Spectroscopy analysis presents that the white region is FeAl phase with 45.7% Al and the narrow strips are $FeAl_2$ phase with 66.3% Al. That is to say, after diffusion treatment at 750 ℃ for 2 h, the surface layer is composed of Fe_2Al_5 + $FeAl_2$ phases and internal layer is composed of FeAl + $FeAl_2$ phases. All of those indicate that Al content changes obviously during diffusion treatment and such mixture of phases are easy to appear when cooling down.

When diffusion time is increased to 5 h, black $FeAl_2$ strips become larger in outer surface layer, and trends to gather gradually, as illustrated in Fig. 1(c). Analysis shows that the surface layers is still made up of Fe_2Al_5 + $FeAl_2$ phases and the internal layers (140 ~ 150 μm from surface) are narrow strips and blocks nearly parallel-arranged, as shown in Fig. 1(d). Dark field image and electron diffraction pattern of Fig. 1(d) are shown in Fig. 2. It can be seen that $FeAl_2$ phases arrange regularly in shape of narrow strips under diffusion treatment at 750 ℃. The composition of the coating doesn't change, but the phase morphologies are changed with increasing the diffusion time.

3.2 Effect of diffusion at 850 ℃ on microstructure of HDA coating

Fig. 3 shows TEM images of diffusion layers at different places treated at 850 ℃ for different times. $FeAl_2$ in shape of strip and block is dominant phase on the outer surface layer after diffusion treatment for 2 h (as shown in Fig. 3(a)). Spectroscopy analysis finds that there exist a few Fe_2Al_5 phases (region

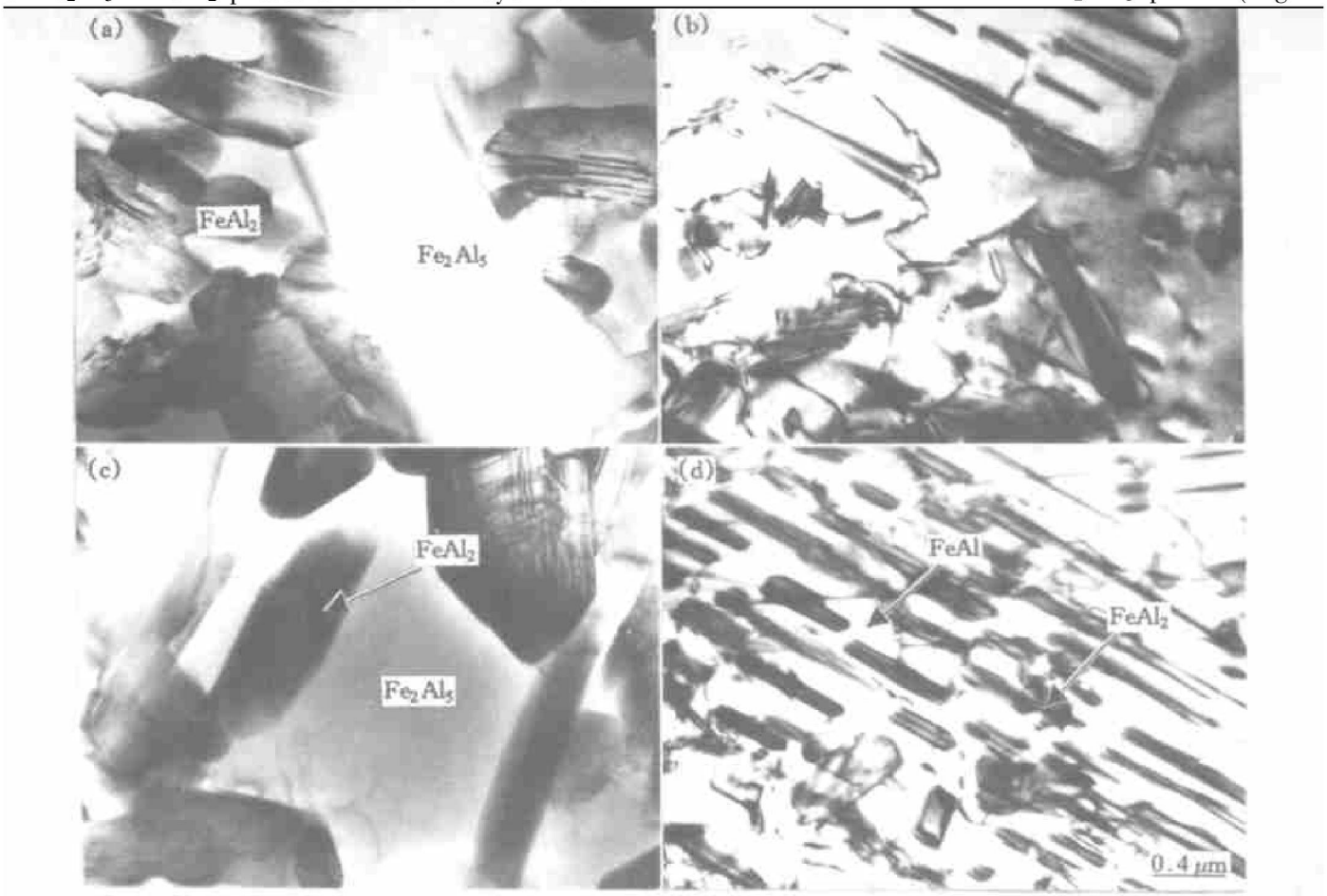

Fig. 1 TEM images of transition layers diffused at 750 ℃ for different times
(a) —2 h, surface; (b) —2 h, 100~ 150 μm from surface; (c) —5 h, surface; (d) —5 h, 140~ 150 μm from surface

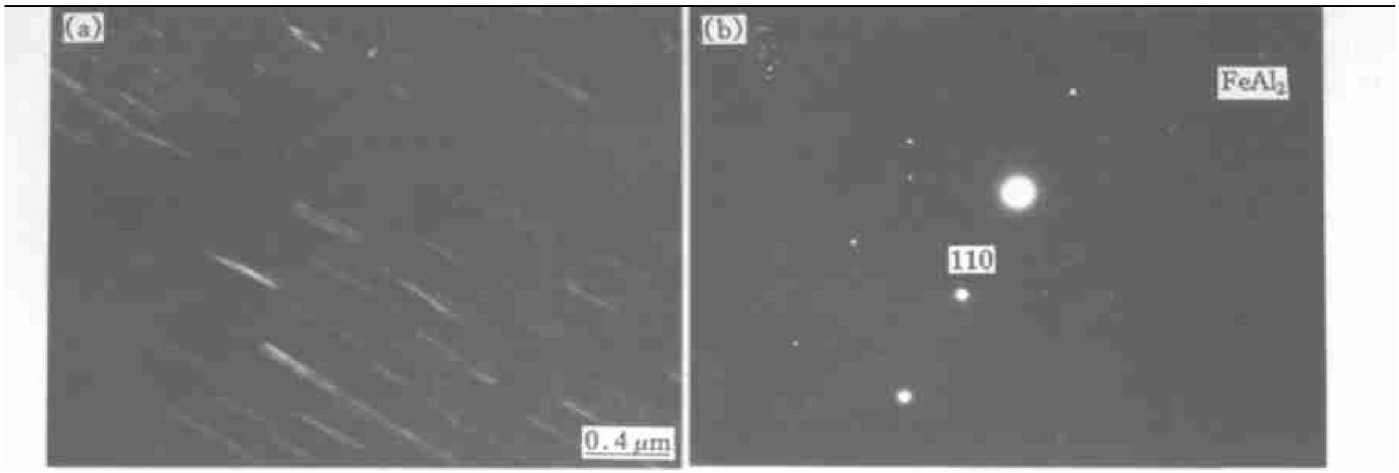

Fig. 2 Dark field image (a) and diffraction pattern (b) of Fig. 1(d)

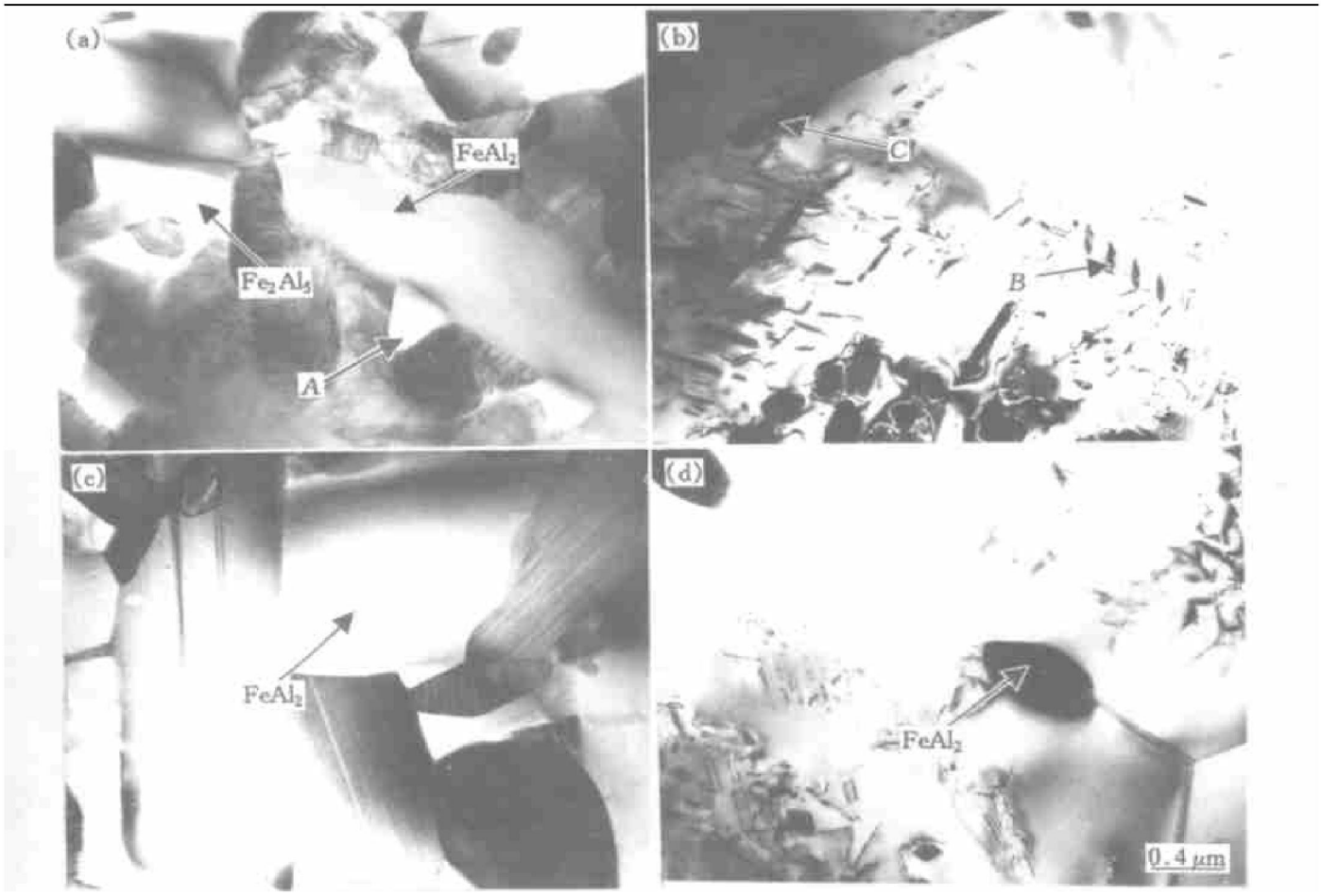

Fig. 3 TEM images of transition layers diffused at 850 ℃ for different times
(a) —2 h, surface; (b) —2 h, 80~ 130 μm from surface; (c) —5 h, surface; (d) —5 h, 60~ 110 μm from surface

A). TEM images of layer (80~ 130 μm from surface) shows that $FeAl_2$ parallel strips are reduced (Fig. 3(b)), and arrange in small flakes (region *B*) and exhibit elliptic at the crystal border with FeAl phases (region *C*). Fig. 4(a) and 4(b) are bright field and dark field images for region *B* in Fig. 3(b) respectively. Composition analysis reveals that the small black elliptic phases are $FeAl_2$, which means when diffusion treatment temperature is increased from 750 ℃ to 850 ℃, $FeAl_2$ phases at internal layer changes into spherical shape and its arrangement is transferred from parallel strips to small ellipsoids.

When diffusion time is prolonged to 5 h at 850 ℃, it is found that $FeAl_2$ phases at outer surface layer grow and pack to form big blocks, as shown in Fig. 3(c). TEM images of layers (60~ 110 μm from surface) are shown in Fig. 3(d), which further confirms that $FeAl_2$ phase changes to spherical shape at

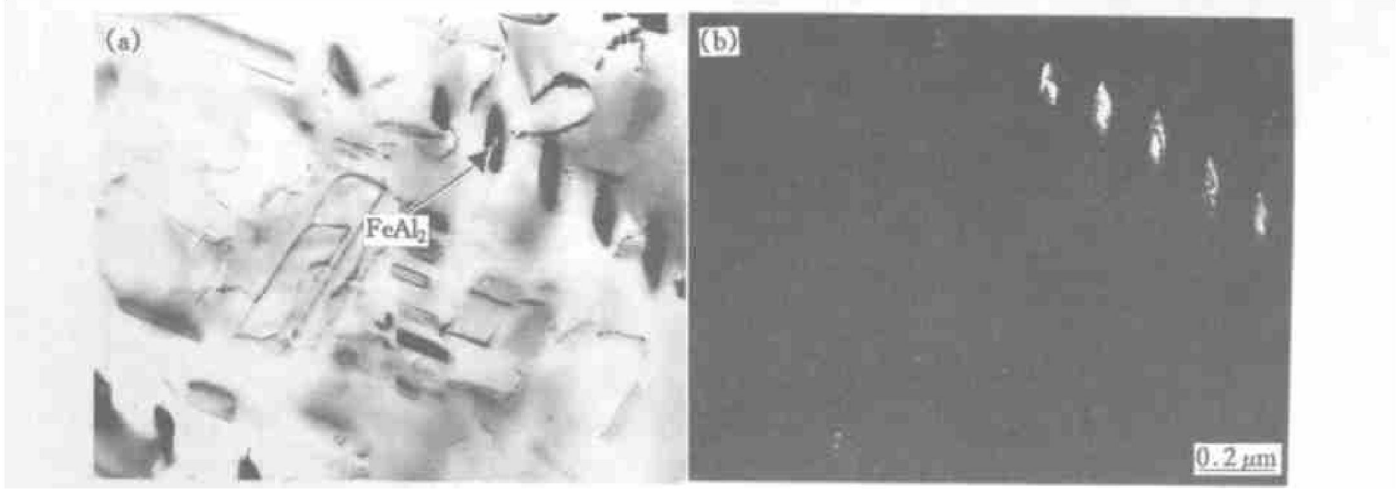

Fig. 4 Magnification bright field (a) and dark field (b) images of region *B* in Fig. 3

crystal-boundary and $FeAl_2$ phase doesn't arrange in parallel strips any more. It can be concluded that $FeAl_2$ changes its form after diffusion at 850 ℃ for 5 h.

Above analyses reveal that the outer layer is $FeAl_2$+ Fe_2Al_5 (a little), and the internal layer is FeAl+ strips $FeAl_2$ after diffusion treatment for 2 h, while outer surface layer is $FeAl_2$+ Fe_2Al_5 (trace) and the internal layer is FeAl+ spherical $FeAl_2$ after diffusion at 850 ℃ for 5 h. It is thus evident that composition of the outer surface layer changes from Fe_2Al_5 to $FeAl_2$ which has relatively high hardness and is brittle[10]. But its thickness decreases to about 40 μm after diffusion at 850 ℃ for 5 h. With increasing the diffusion time, $FeAl_2$ phase at surface is changed into FeAl phase.

3.3 Effect of diffusion at 950 ℃ on microstructure of HDA coating

It was difficult to prepare TEM specimen from coatings after diffusion at 950 ℃ for 2 h because micro-cracks appeared in outer surface and internal layer. Therefore, the microstructure of the coating was determined just by means of XRD. XRD patterns of outer surface layer and the inner layer (30 μm from the surface) are shown in Fig. 5. It can be seen that the coating is composed of Al_2O_3, FeAl and $FeAl_2$ (as shown in Fig. 5(a)). Al_2O_3 is the main phase at the outer surface. At 30 μm from the surface, Al_2O_3 diffraction peaks disappeared, the peaks corresponding to FeAl (110) appeared and contained all the peaks marked in ASTM cards, that is to say, internal layer is composed of only FeAl phase after diffusion treated for 2 h at 950 ℃.

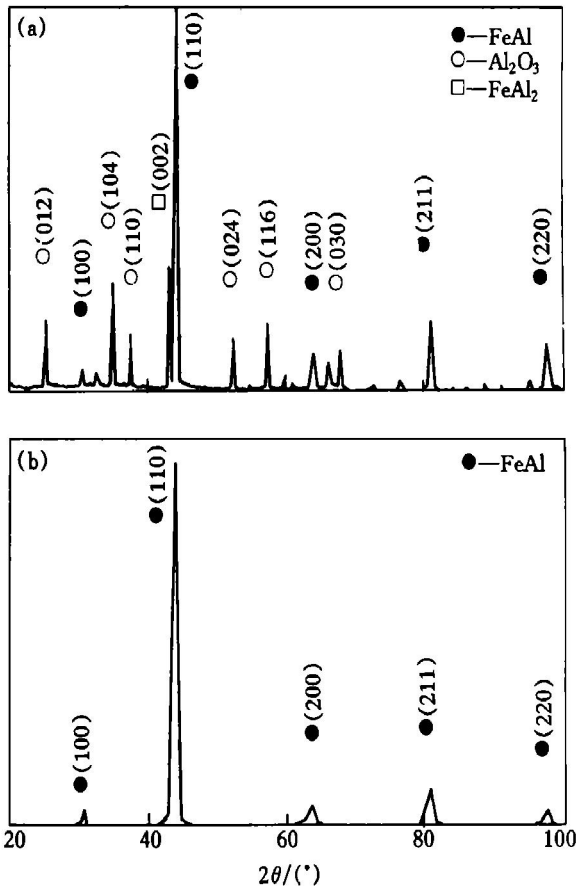

Fig. 5 XRD of HAD coating diffused at 950 ℃ for 2 h
(a) —Surface; (b) —30 μm from surface

3.4 Effect of diffusion on oxidation resistance of HDA coating

Fig. 6 shows the kinetic curves of the coating oxidized at 800 ℃. It can be seen that mass gain differs obviously under different diffusion treatment conditions, but all kinetic curves accord with parabola growth rule. Experiment results reveal that after 300 h static oxidation, mass grain of coating diffusion-treated at 850 ℃ for 5 h is 2.71 mg/cm^2, and the rate of mass gain is 9.04×10^{-5} kg/(m^2·h), which is the smallest among all diffusion conditions. For the samples diffusion-treated at 750 ℃, the coating becomes heavier with increasing diffusion time from 2 h to 5 h. This is because that when diffusion temperature is just a little higher than hot dip temper-

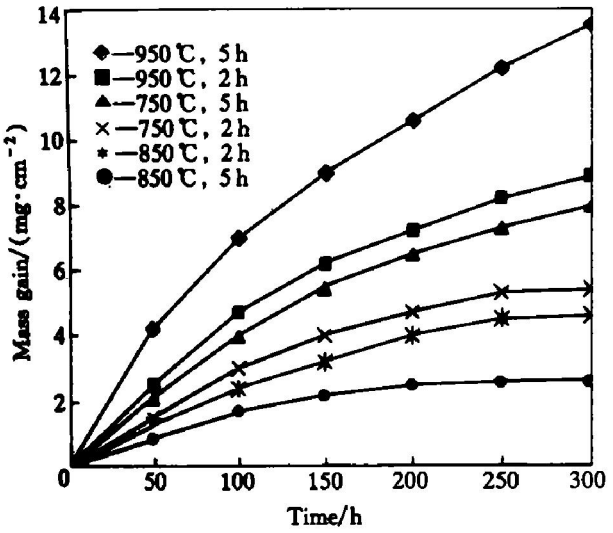

Fig. 6 Kinetic curves of aluminized steel heated in air at 800 ℃ for different times

ature, Fe_2Al_5 is the main phase in transitional coating, which is easy to crack during static oxidation. So oxidation resistance is poor. The mass gain is the biggest during oxidation for the sample diffused at 950 ℃. This is because internal-oxidation of HDA coating occurs during high temperature diffusion treatment. The inner oxidation corrosion spots develop further during static oxidation tests at 800 ℃ that results in mass gain.

It can be recognized that it is the internal metallic compound in transitional coating that acts on the high temperature oxidation resistance. The oxidation resistance changes with continuity, density, phase composition and crystal structure. So, to improve oxidation resistance of HDA coatings, suitable phase composition must be achieved through optimizing diffusion process.

4 CONCLUSIONS

1) The effect of diffusion temperature on phase structure of HDA coating is great. The rule is:

Surface layer:

$$Fe_2Al_5 + FeAl_2 \xrightarrow{(750\ ℃)} FeAl_2 + Fe_2Al_5(\text{a little}) \xrightarrow{(850\ ℃)} FeAl_2 \xrightarrow{(950\ ℃)}$$

Internal layer:

$$FeAl + FeAl_2(\text{strips}) \xrightarrow{(750\ ℃)} FeAl + FeAl_2(\text{spherical}) \xrightarrow{(850\ ℃)} FeAl \xrightarrow{(950\ ℃)}$$

The condition for $FeAl_2$ to change into spherical shape is determined to be diffused at 850 ℃ for 5 h.

2) Oxidation resistance tests at 800 ℃ indicates that high temperature oxidation resistance of HDA coating is related to diffusion condition. High resistance can be obtained for the sample diffused at 850 ℃ for 5 h, $FeAl_2$ among FeAl of internal layer can be changed into spherical shape totally.

3) TEM images of layers parallel to the surface show that after diffusion below 850 ℃, the coating consists of thick brittle phases (Fe_2Al_5 and $FeAl_2$) and parallel $FeAl_2$ strips. Thus accelerated oxygen transport inward occurs and its oxidation resistance is poor. After diffusion at 950 ℃, its oxidation resistance declines due to the occurrence of early stage internal oxidation cracks in the coating.

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