

EFFECT OF ALUMINIUM AND BORON ON SURFACE MODIFICATION OF SOME MATERIALS^①

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ABSTRACT The surface modification of some materials (45, T8, 5CrMnMo, 3Cr2W8V) in fused borax bath added with aluminium oxide powders and reductant was probed. The results showed that with proper salt composition and technical parameters, and B/Al ratio 1.3~3.2 in salt bath, the boron atoms and aluminium atoms can co-diffuse in steels, thus an ideal B-Al co-diffusion layer can be obtained which contains ferro-boron phases and ferro-aluminium phases and ensues surface modification in steels.

Key words: Al-B co-diffusion microstructure co-diffusion layer surface modification

1 INTRODUCTION

Boron-diffusion has been applied early in industrial departments of metallurgy and machine manufacture, but the boron-diffusion layer is brittle and its densification is poor, so its application range has been restricted. The brittleness of itself, depends mainly on the difference of the specific volume between boride and basal-body. The work by Liliental and others indicates that not only the brittleness of the two-phase boride-layer is great, but also the anti-wear property is not so good, besides, when loaded, it is easy to be bited^[1]. Generally considering, one-phase layer of Fe₂B is more ideal, because it not only has better wearability, but also bears certain rushing load. On the diffusion-layer of Fe₂B (chemical compound layer) whose thickness is about 75 μm , when the diffusion-layer of 250 μm (both ferrites and carburization-body bearing boron) is added on, it would produce the best property². The densification of boron-diffusion among the borides would be evident which would ensue the reducing of the antioxidization capability and would not be suitable for the condition of heat work. So, some persons at home and abroad have carried out the research work on B-Al co-diffusion so as to

improve the brittleness and densification of the diffusion layers and have also obtained a great deal of progress in their works^[3~6].

Up to now, under the laboratory condition, they have approached powder-method, melt-salt electroanalysis method, gaseity method, electrolytic method and so on, which are all co-diffusion methods. But they are relatively complex in technology, the differential property of co-diffusion structures is great, and difficult for use in production.

The purpose of this article is to probe the law of surface modification owing to Al-B atom diffusion among some materials most in use when added with aluminium oxide and reductant in borax fusion bath.

2 EXPERIMENTAL

2.1 Sample Preparation

After being annealed, the bars of 45, T8, 5CrMnMo, 3Cr2W8V were processed into the samples of $d22\text{ mm} \times 4\text{ mm}$. The rust and detergent oil were eliminated with one tenth oxalic acid solution and acetone.

2.2 Salt Bath Composition and Technic

The co-diffusion agent consists of borax,

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aluminium oxide, silicoiron, fluorate, and rare-earth, the solvate of above elements can compose the salt bath according to right proportion, and at 850 °C, it would have excellent flowability.

The samples of co-diffusion were heated separately to 850, 900, 950 and 1000 °C, and each kind of temperature was kept separately for 2, 3, 4, 5, 6 h, after diffusion. Then the samples were air-cooled.

2.3 Structure and Components of Diffusion layer

The diffusion layer structure was displayed with p. p. p. reagent, and then observed and photographed with Nikon (Japan) microscopes, the diffusion-layer structure was also analyzed with Mode D-9C diffractometer, the shape and face was observed with X-650 scanning electron microscope, and the aluminium in the diffusion layer was scanned to its energy spectrum and wave pattern.

3 RESULTS AND DISCUSSION

3.1 Structure of Diffusion Layer

The structures of the co-diffusion layer of 45, T8, 5Cr2W8V are shown in Fig. 1.

Fig. 1 indicates that shape and face of the co-diffusion layer structure appear mostly in the shape of comb-tooth, the top surface layer presents some irregular circle blocks, just like boriding layer, there are distributions of fine-strip shape and grain-shape phases within tooth and among teeth.

The analysis result by X-ray diffractometer shows that the thin surface layers present the phases of Fe_2B , Fe_3Al or Fe_2Al_5 , as shown in Fig. 2. The comb-tooth shape phase of the secondary-surface layer has been immersed with p. p. p reagent and measured to be Fe_2B by microhardness.

Among the phases of 45, T8 there are Fe_3Al with strip-shape and block-shape, and $\text{Fe}_3(\text{C},\text{B})$ of which the dissolvability could be variable^[2], as shown in Fig. 1(a) and (b). In

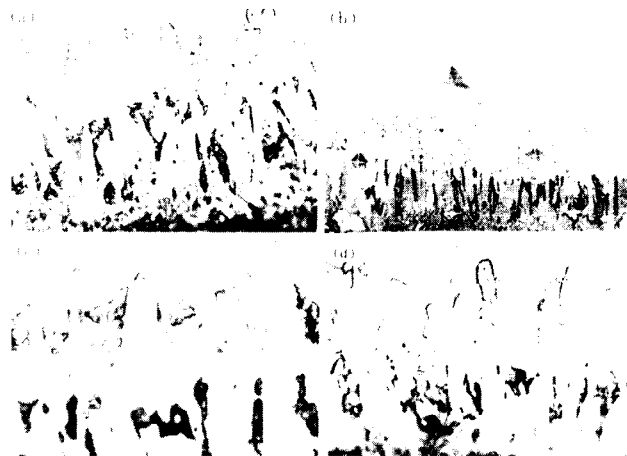


Fig. 1 The air-cooled structures of co-diffusion at 900 °C for 4 h of (a) 45; (b) T8; (c) 5CrMnMo; (d) 3Cr2W8V

Fe₃B phase of 3Cr2W8V, VC^[7] distributed in dissemination, as shown in Fig. 1(d).

The measured results with probes on the phase of iron-aluminium in 5CrMnMo co-diffusion-layer are shown in Table 1. From Table 1, we can see, Al-content is quite high.

Table 1 The results of measurement on Fe-Al phase with probes in 5CrMnMo co-diffusion-layer

Elements	Weight specific (%)	Atom specific (%)
Al	34.82	50.10
Fe	41.03	26.87
others	omitted	omitted

Fig. 3 shows the energy spectrum of 5CrMnMo co-diffusion layer. Fig. 4 and Fig. 5 show Al-surface distribution and Al-line distribution of 5CrMnMo co-diffusion layer.

Among the co-diffusion layer, immersed with p. p. p reagent and measured by micro-hardness, the boride types are relevant with technical parameters, as shown in Table 2.

3.2 Formation of Diffusion-layer Phase

In the four-components of Fe-Al-B-C, the temperature at which aluminium and boron form chemical compound is higher than melting-point of iron^[8], therefore, in the salt

bath, there is no interreaction occurring, and the carbon in Fe-C alloy would not form any carbide. So in the iron-sosoloid, action of the atom diffusion of Al-B would depend entirely on the properties of their interreaction separately with iron^[8].

The diffusion of boron in iron sosoloid would be fast, but its solubility is minor, and would form easily Fe-B chemical compound; the solubility of Al in iron sosoloid would be great, and aluminium could form both phases of α , β_1 (Fe₃Al), β_2 (FeAl), and phases of ζ

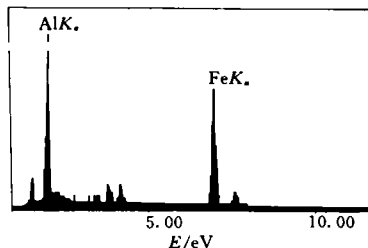


Fig. 3 Energy spectrum of 5CrMnMo diffusion layer

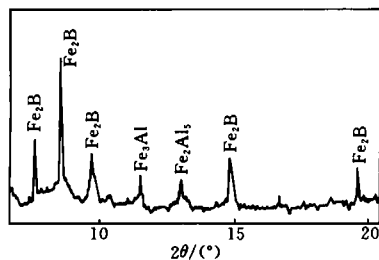


Fig. 2 Analysis spectrum (Fe₂B-Fe₃Al) of the surface structure of 5CrMnMo diffusion-layer



Fig. 4 Al-surface distribution of 5CrMnMo co-diffusion layer

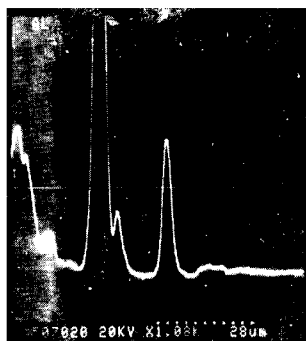


Fig. 5 Al-line distribution of 5CrMnMo co-diffusion layer

(FeAl_2), η (Fe_2Al_3) and θ (FeAl_3). When the atoms of aluminium and boron diffuse jointly in iron solid, the thinnest surface layer of the sample would form Fe-B chemical compound and α -phase which would affect the continuous diffusion and permeance of the atoms of aluminium and boron. Fe-B compound would obstruct the diffusion of Al-atom, in the process of its growth, it would repel aluminium to make the adjacent α -phase interface increase aluminium, when the dissolvability is at limit, it would form β -phase and η -phase, thus the structure of the

thinnest layer should be Fe-B chemical compound presenting irregular block-shape, being fine-strip phase, η -phase and block-shape α -phase, and HV1600~1680 of Fe_2B compound presents hard-phase; HV675~790 of η -phase and HV280~430 of β -phase present soft-phases^[7].

The formations of Fe-Al phase and Fe-B phase restrain the atom diffusion of aluminium and boron to varying degrees, so that they would affect the structure of the secondary surface layer. The aluminium atoms could only diffuse through α -phase, when they reach the limited dissolvability, they would form β , ζ , η , or θ -phases, the diffusion resistance would increase strikingly, but the boron atom diffusion would be different. Moreover and so forth pointed out after researching that boron diffused into iron, Fe-B compounds would grow by presenting finger-shape, and express preferred orientation so that boron could diffuse and pass through easily its lattice^[9], that is, the Fe-B compounds would be considered without evident influence to B-atom diffusion. From this, we could see that the increment component of the diffusion resistance of boron-atoms within the diffusion layer comes mainly from the appearance of β , η , θ phases. So, at the secondary surface layer, B-atom diffusion still precedes strikingly the Al-atom diffusion, and the growth of Fe-B compound preferred orientation would present comb-tooth shape. Fe-Al phases distribute on them

Table 2 Relations between boride-type in co-diffusion layer and technical parameters

Co-diffusion technology	Boride-type in co-diffusion layer			
	45	T8	5CrMnMo	3Cr2W8V
850 °C, 6 h	Fe_2B	Fe_2B	Fe_2B	Fe_2B
900 °C, 4 h	Fe_2B	Fe_2B	Fe_2B	Fe_2B
900 °C, 5~6 h	FeB(a little) + Fe_2B	Fe_2B	FeB(a little) + Fe_2B	Fe_2B
950 °C, 4 h	FeB + Fe_2B	FeB(a little) + Fe_2B	FeB(a little) + Fe_2B	Fe_2B
950 °C, 5~6 h	FeB + Fe_2B	FeB + Fe_2B	FeB + Fe_2B	FeB(a little) + Fe_2B
1000 °C, 4 h	FeB + Fe_2B	FeB + Fe_2B	FeB + Fe_2B	FeB + Fe_2B

or among the teeth.

To sum up, it is not difficult to see that the atom diffusion of aluminium and boron in diffusion layer would restrain each other, and structures of the diffusion layer would be controlled by the Al-potential and B-potential. 5CrMnMo in salt-bath of different values of B/Al through the same parameter co-diffusion air-cooled would display in structure that when Al-potential is weak, but B-potential is strong ($B/Al \geq 3.2$), the Al-atom diffusion would be restrained and its structure of diffusion-layer would be like the usual B-diffusion one; on the contrary, when the Al-potential is quite higher than B-potential ($B/Al \leq 1.3$), the B-atom diffusion would be restrained, the surface structure of diffusion-layer would present phases of β , η and secondary surface layer would present α -phase, as shown in Fig. 6, only when $B/Al = 1.3 \sim 3.2$, atoms of Al and B within the diffusion-layer would diffuse in parity, we could obtain the diffusion-layer which consists of Fe-Al phase Fe-B phase, as shown in Fig. 1.

Of course, the carbon and alloy elements in basal body could have nonegligible effect to Al/B atom diffusion. In the periodic table of elements, carbon and boron are close, that's to say, they are alike, both of carbon atom is smaller, and easy to keep gaps in Fe-soloid, which would obstruct B-atom diffusion. The diffusion and solating in of boron should repel carbon entering the soloid around (γ -Fe). The higher the carbon content in basal body

is, the greater the resistance of boron atom diffusion would be; owing to the diffusion and solating in of aluminium, γ -Fe would continue transforming into α , β , η phases could not solvate carbon generally, the Al-atom diffusion and solating in should also repel the carbon entering the soloid around (γ -Fe), which would lead to the appearance of high carbon area at the diffusion layer and the interface of basal body, thus there would exist high carbon area and carburet in interfaces of Fe-B phase and Fe-Al phase.

3.3 Factors Controlling Thickness of Diffusion Layer

The air-cooled diffusion-layer thickness of co-diffusion of T8, 5CrMnMo, 3Cr2W8V is shown in Fig. 7. It is clear the effecting laws of co-diffusion parameters on the diffusion layer thickness of three kinds of steels are basically identical, but the effecting degrees are different. The effect of high temperature, and long time would be great; when co-diffusion time is long, the effect of temperature is great, while the parameter is identical, the diffusion layer of T8 would be thick, the diffusion layer of 3Cr2W8V would be thin, the diffusion layer of 5CrMnMo would be medium. This is because the alloy-elements in 5CrMnMo and 3Cr2W8V could both form carburet and solvate into soloid, the obstruction of which to Al-B atom diffusion would be evident. But its properties and contents are different, so the obstruction degrees of Al-B atom diffusion are not alike. Among them, strong carburet would form the element vanadium, generally it would form interval phase VC (or V_3C) distributing with dispersion in the basal body, its stability is quite high, it couldn't solvate at co-diffusion temperature, its resistance to Al-B atom diffusion in diffusion layer is the greatest, the medium-strong carburet would form the elemental chromium, when its content in steel is not high, it would only form the alloy cementite $(Fe, Cr)_3C$, its stability is not high, when its content is high, it would form special carburet $(Cr, Fe)_3C$, the medium-strong carburet would form the



Fig. 6 Structure of diffusion-layer as $B/Al \leq 1.3$, $\times 600$

elements W and Mo, in steel, besides forming alloy cementites $(\text{Fe}, \text{W})_3\text{C}$, $(\text{Fe}, \text{Mo})_3\text{C}$, it would still form some special carburets $(\text{W}, \text{Fe})_{23}\text{C}_6$, $(\text{Mo}, \text{Fe})_{23}\text{C}_6$, WC , $(\text{Mo}, \text{Fe})_6\text{C}$, MoC , Mo_2C . Their resistance to Al/B atom diffusion is weaker than the elements formed by strong carburets, the affinity of Mn-element formed by weak carburet for Fe would

be slightly stronger than that of Fe for C, its dissolvability in γ -Fe is very high, and would form alloy cementite $(\text{Fe}, \text{Mn})_3\text{C}$ in general, its stability is not evidently different from that of Fe_3C , its resistance to Al-B atom diffusion would be alike to Fe_3C ^[10]. Generally, the alloy elements such as Cr, Mn, Mo, W and V within 5CrMnMo, 3Cr2W8V would hinder B-atom diffusion, so they would restrict the growth of Fe_2B phase. The rare-earth added in co-diffusion bath has striking action of hasten-diffusion which would weaken gradually as the co-diffusion time lasts, as shown by the dotted line in Fig. 7.

4 CONCLUSIONS

(1) In non-electrolyte salt bath of borax, aluminium-oxide, right amount of reductant and activator, Al/B co-diffusion of steelwork surface could be realized, and diffusion layer composed of Fe-B phases of high hardness and Fe-Al phases of good toughness could be obtained, the surface modification could also be completed.

(2) The structure of modification layer would mainly be controlled by ratio of B/Al and technical parameter in salt bath.

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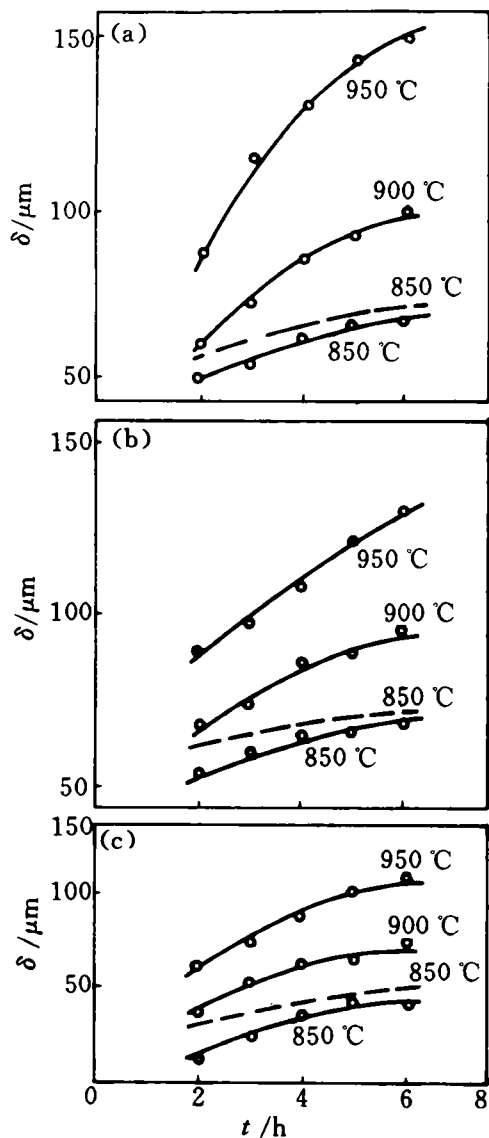


Fig. 7 Curve of temperature-time-thickness of diffusion-layer

(a)—T8; (b)—5CrMnMo; (c)—3Cr2W8V