

## Preparation of aluminide coatings at relatively low temperatures

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**Abstract:** A method was presented to prepare aluminide coatings on metals by combining the pack aluminizing with the ball impact process. This technique applied mechanical vibration to a retort, which was loaded with pack-aluminizing powder, specimens and alloy balls. Pack aluminizing was carried out with repeated ball impact, which accelerated chemical reactions and atomic diffusion. Aluminide coatings were formed at a relatively lower temperature (below 600 °C) and in a shorter treatment time, compared with the conventional pack aluminizing. The effects of the operation temperature and the treatment time on the formation of the coatings were analysed. The SEM, EDS and XRD analysis results show that the aluminide coatings appear to be homogeneous, with a high density and free of porosity, and have excellent adherence to the substrate. The coatings mainly consist of Al-rich phases such as  $\eta$ -Fe<sub>2</sub>Al<sub>5</sub>,  $\theta$ -FeAl<sub>3</sub> and CrAl<sub>5</sub>. Oxidation resistance was studied by high-temperature tests. The formation mechanism of the Al-coatings was also investigated. This technique provides a new approach for industrial diffusion coatings with great energy and time savings.

**Key words:** low-temperature pack aluminizing; aluminide coating; ball impact; oxidation resistance

### 1 Introduction

Protective coatings by pack aluminizing are frequently applied to metals to protect them from high temperature oxidation and hot corrosion attack [1, 2]. Pack aluminizing consists of heating the parts to be coated in a closed or vented pack to a high temperature for a period of time, during which a diffusion coating of desired composition and thickness is produced on the metal. This process can be divided into four interrelated steps[3]: 1) a thermodynamic equilibrium state between the activator and the master alloy, which determines the vapor pressures of the active gaseous species in the pack; 2) the gaseous diffusions of the metal halides from the pack to the substrate surface, driven by the chemical potential gradients in the gaseous phase; 3) surface reactions at the substrate to deposit the coating elements and form the vapor products; 4) solid-state diffusion of the coating elements into the substrate.

Pack aluminizing is usually carried out above 900 °C for several dozens hours, while the process is

lattice-diffusion dominant because of the coarse-grains of substrate. Previous studies[3–8] concentrated on the chemical reactions, the products of reactions, the diffusion in gas and solid phases, and the microstructures of the aluminide coatings under thermodynamic equilibrium conditions. The pack processes for simultaneous depositions of Al and Cr[8–13], Al and Si[14,15] on either steels or superalloys have been studied using a mixture of alloy powder as the pack component. However, there were few reports on the effects of the surface conditions on the pack aluminizing.

Surface micro- or nano-crystallization was reported to promote the atomic diffusion and chemical reaction effectively[16], due to the amount of grain boundaries acting as the fast atomic diffusion channels. For example, it was reported[17] that pure iron nitriding was completed in flowing ammonia gas (NH<sub>3</sub>) at a relatively low temperature (300 °C) for 9 h, due to the surface nano-crystallization enhancing the atomic diffusion rate along grain boundaries. Surface micro- or nano-crystallization could be achieved by many ways such as ultrasonic shot peening[18–20] and mechanical attrition

treatment[21, 22]. However, as the grain growth of the surface micro- or nano-crystallization occurs at a relative high temperature, the atomic diffusion along grain boundaries would transform to the crystal lattice diffusion. So it is hardly to utilize the advantages of the surface micro- or nano-crystallization in pack aluminizing.

A new processing technique was developed[23], in which pack aluminizing was combined with ball impact generated by mechanical vibration, producing an aluminide coating on carbon steel at relatively low temperature. In this paper, we applied this technique to produce aluminide coatings on carbon steel, Cr13, Cr18-Ni9-Ti and Cr5Mo alloys.

## 2 Experimental

A schematic diagram of the experimental apparatus is shown in Fig.1. A retort, loaded with specimens, alloy balls and pack powder, was vibrated by a mechanical vibrator in a furnace. The retort was heated to 440–600 °C, vibrated with a frequency of 25 Hz for 15–240 min. The pack aluminizing was carried out with repeated impact of balls.

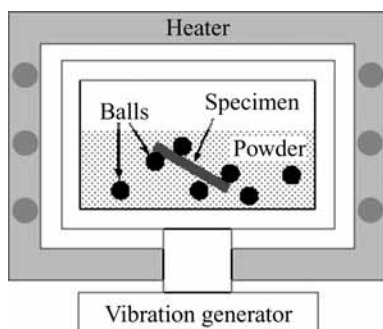


Fig.1 Schematic diagram of experimental apparatus

The pack powder consisted of pure Al powder, filler  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and activator (NH<sub>4</sub>Cl), which were mixed with FeCrAl balls (4 mm in diameter) at a ball-to-powder mass ratio of 4/1 to 6/1. The retort was loaded to 2/3 volumes with the pack powder, the alloy balls and the specimens.

Plate specimens of low-carbon steel (C: 0.21%, Si: 0.17%, Mn: 0.68%, Fe: 98.83%), Cr13 (C: 0.11%, Cr: 12.63%, Si: 0.84%, Mn: 0.92%, Fe: 85.4%), Cr18-Ni9-Ti (C: 0.10%, Si: 0.54%, Mn: 1.32%, Cr: 17.55%, Ni: 9.51%, Ti: 0.45%, Fe: 70.48%) and Cr5-Mo (C: 0.12%, Si: 0.49%, Mn: 0.74%, Cr: 5.13%, Mo: 0.33%, Fe: 93.08%) (mass fraction, the same below) were used in these experiments. The surface of the specimens was polished with SiC papers to 600-grade, and washed with acetone in an ultrasonic bath.

High-temperature oxidation tests were carried out in

a horizontal tub furnace with flowing dry air at 600 and 900 °C respectively. The mass changes and the spallation of the specimens were measured by a Mettler AE240 electronic balance with accuracy of 0.02 mg.

Cross-sectional observations of the aluminide coatings were performed on a scanning electron microscope(SEM). The composition was analyzed by energy dispersive X-ray spectroscopy(EDS). Surface phases were identified by X-ray diffraction(XRD).

## 3 Results

### 3.1 Formation of aluminide coatings

Aluminide coatings (Al-coatings) were successfully produced on carbon steel, Cr13, Cr18-Ni9-Ti and Cr5-Mo alloys at a lower temperature for a shorter treatment duration, compared with the conventional pack aluminizing. Fig.2 shows the relationship between the coating thicknesses and the operation temperatures for 120 min treatment. It can be observed that they follow an approximately linear relation. An Al-coating is produced on the carbon steel at a much low temperature of 440 °C. And over 520 °C is needed to produce over 10  $\mu$ m Al-coatings on the Cr13, the Cr18-Ni9-Ti and the Cr5-Mo alloys. The coating thickness increases with the increase of the operation temperatures.

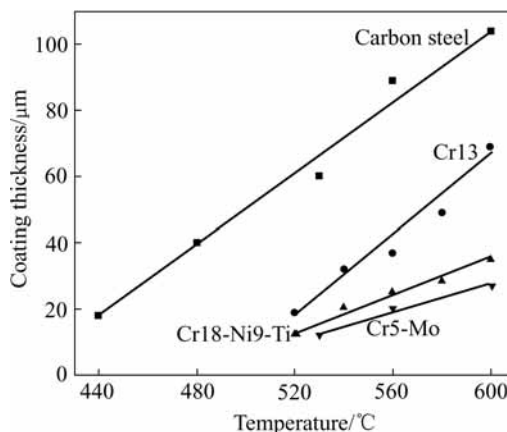


Fig.2 Relationship between coating thickness and temperature for 120 min treatment

Fig.3 shows the relationship between the coating thickness and the treatment time at 560 °C. It is interesting that the coatings are rapidly formed at 560 °C in ball peening process. About 27  $\mu$ m Al-coating in thickness is formed on the carbon steel after only 15 min vibration. Over 10  $\mu$ m Al-coatings in thickness are also formed at the Cr13, Cr18-Ni9-Ti and the Cr5-Mo substrates after 30 min treatment. The coating thickness increases with the extending vibrating time. They follow an approximately parabolic relation, suggesting that the process is diffusion controlled.

The experimental results demonstrate that the

composition of the alloys has a significant effect on the formation of the Al-coatings (Fig.2 and Fig.3). The coating thickness of carbon steel is apparently thicker than that of other alloys, being around 100  $\mu\text{m}$  after vibrating at 600 for 120 min. With the increasing content of alloy elements, the coating thickness decreases. However, the coating thickness of Cr5-Mo is the thinnest. It is reported[24] that molybdenum is a barrier-forming element, which increases the tendency to form diffusion barrier, due to a low solubility of molybdenum in Al-rich phases. Molybdenum and chromium in Cr5-Mo form extremely compact CrMo-barrier at the interface between coating and substrate, which hinders the atomic diffusion, resulting in the thinnest Al-coating.

### 3.2 Characterization of Al-coatings

Fig.4 shows the cross-sectional microstructures of the Al-coatings on the various alloys respectively. It can be seen that all the Al-coatings exhibit the same features, being one layer structure with high density, free of porosity, homogeneous, and having a good adherence to the substrate. Coarse grains and inclusions, which are usually observed in the pack Al-coatings, are not identified in these Al-coatings. The concentrations of aluminium, iron, chromium and nickel are almost constant across the Al-coatings within the accuracy of microprobe analysis (listed in Table 1). The Al contents in all the Al-coatings are high level of about 45%–50%,

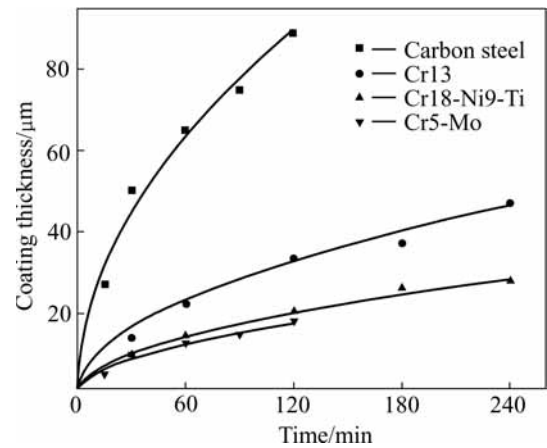


Fig.3 Relationship between coating thickness and treatment time at 560

which indicates that the Al-coatings are composed of Al-rich phases. The XRD patterns identify that the Al-coatings consist mainly of  $\eta\text{-Fe}_2\text{Al}_5$ ,  $\theta\text{-FeAl}_3$  and  $\text{CrAl}_5$  (shown in Fig.5).

Fig.6 shows the surface micrograph of a coating on the carbon steel treated at 560 for 30 min. The indents induced by ball impact are apparently observed, a round shape dent in one shot with a diameter of 50  $\mu\text{m}$ . The coarse grains are refined by the ball impact. The Al content in the ball impact areas is 90% measured by EDS, indicating pure Al adherence to the surface. On the other hand, 5  $\mu\text{m}$  nodules are clearly observed in foothill

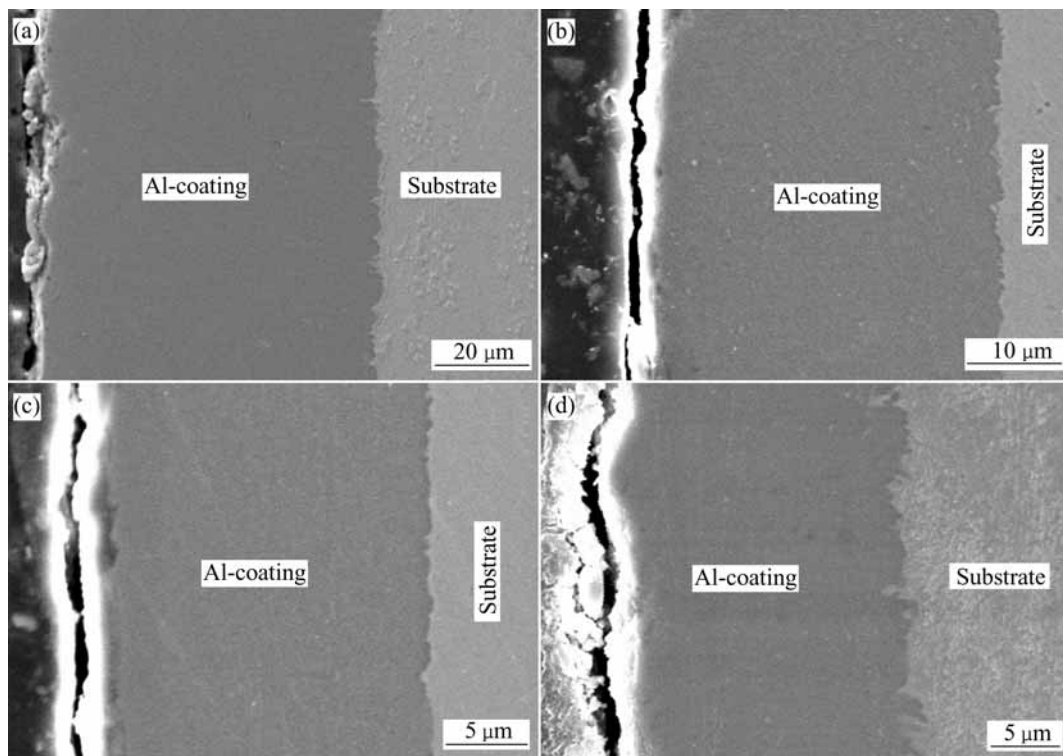
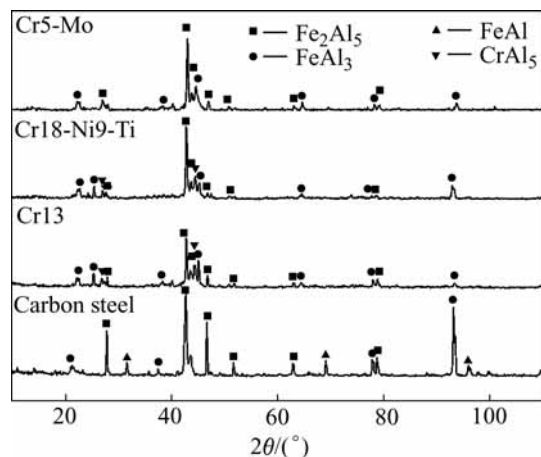
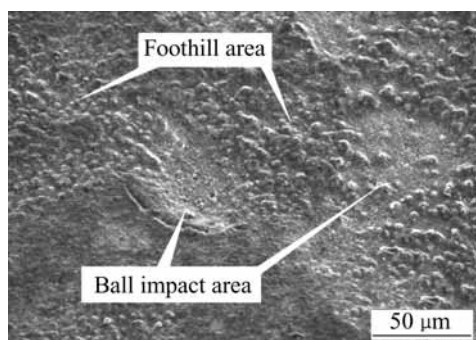


Fig.4 Cross-sections of Al-coating on carbon steel(a), Cr13(b), Cr18-Ni9-Ti(c) and Cr5-Mo (d)

**Table 1** Compositions of aluminide coatings on alloy (mass fraction, %)

Alloy	Al	Fe	Cr	Ni	Mo	Ti	Phases of coating
Carbon steel	51.8	48.2	—	—	—	—	FeAl <sub>3</sub> , Fe <sub>2</sub> Al <sub>5</sub> , FeAl
Cr13	46.7	49.4	3.90	—	—	—	FeAl <sub>3</sub> , Fe <sub>2</sub> Al <sub>5</sub> , Cr-solution
Cr18-Ni9-Ti	45.5	38.8	12.0	3.7	—	< 0.1	FeAl <sub>3</sub> , Fe <sub>2</sub> Al <sub>5</sub> , CrAl <sub>3</sub> , Ni-solution
Cr5-Mo	51.3	47.6	1.1	—	< 0.1	—	FeAl <sub>3</sub> , Fe <sub>2</sub> Al <sub>5</sub> , Cr-solution

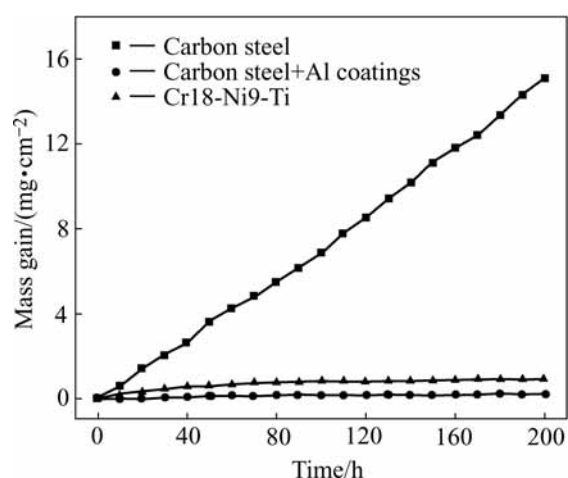
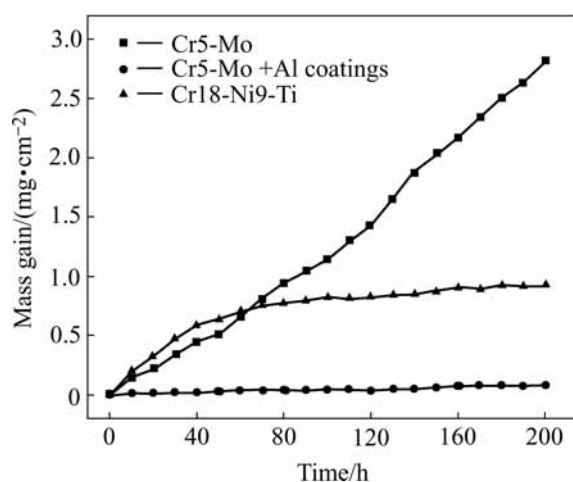
**Fig.5** XRD patterns of surfaces of Al-coatings formed on various substrates**Fig.6** SEM micrograph of Al-coating on carbon steel treated at 560 °C for 30 min

areas. The Al content of the nodules is 53%, consistent with  $\eta$ -Fe<sub>2</sub>Al<sub>5</sub> phase. The nodules are up-growth. The surface microstructures of the Al-coatings formed on other alloys exhibit the same features.

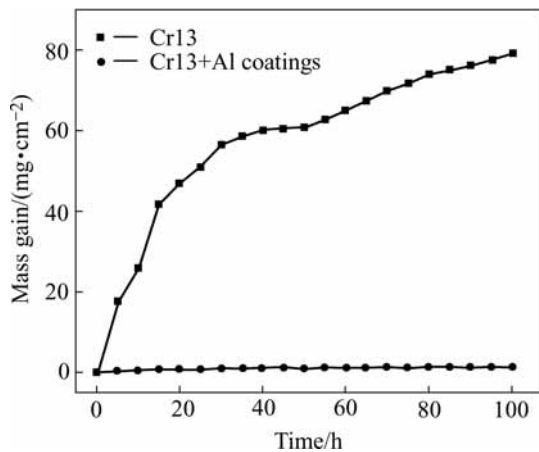
### 3.3 High-temperature oxidation resistance

Figs.7–10 show the oxidation kinetic curves of the coated and uncoated specimens of the carbon steel, the Cr13, the Cr18-Ni9-Ti and the Cr5-Mo respectively, exposed to air at 600 °C and 900 °C for 200 h. The Al-coatings show much lower mass gains compared with the uncoated specimens, greatly improve the oxidation resistance. The mass gains of the Al-coating on carbon steel and Cr5-Mo are only about 2% and 3% of that of the uncoated specimens, exposed to air at 600 °C for 200 h, even much lower than that of the Cr18-Ni9-Ti

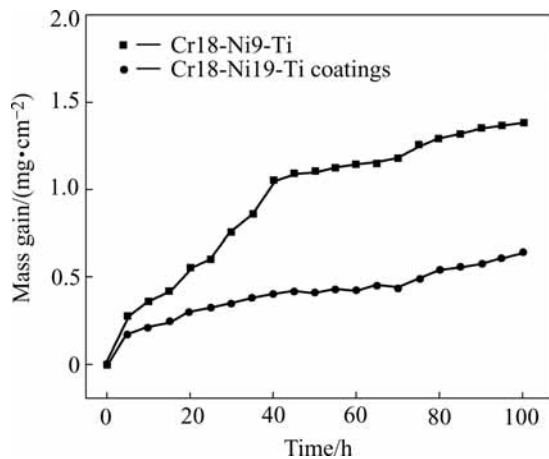
alloy (shown in Fig.7 and Fig.8). The mass gains of the Al-coating on the Cr13, and the Cr18-Ni9-Ti are about 1/55 and 1/2 of that of the uncoated specimens respectively, exposed to air at 900 °C for 200 h (shown in Fig.9 and Fig.10).

**Fig.7** Oxidation kinetics of specimens in air at 600 °C for 200 h**Fig.8** Oxidation kinetics of specimens in air at 600 °C for 200 h

The cross-section of oxide scales, formed on the coated specimen of the Cr13 and the Cr18-Ni9-Ti after oxidized in air at 900 °C for 200 h, are shown in Fig.11. In order to protect the oxide scale, Ni is plated on the surface of the oxidized specimens. As may be observed that a full, dense, and continuous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale is formed on the surface of the coated specimens. The oxide scale inserts in substrate, exhibiting a good adherence to the



**Fig.9** Oxidation kinetics of Cr13 specimens in air at 900 for 200 h



**Fig.10** Oxidation kinetics of Cr18-Ni9-Ti specimens in air at 900 for 200 h

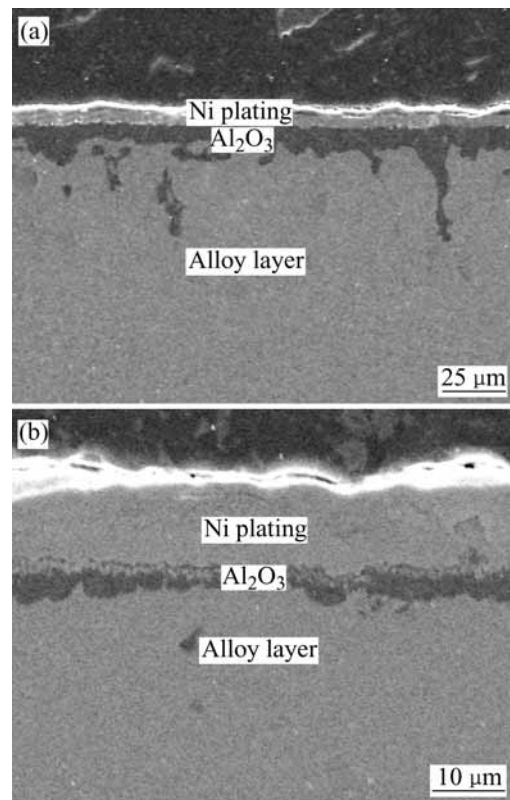
substrate. Therefore, the Al-coating has excellent protection to the alloys when oxidized in air at 900 .

#### 4 Discussion

The formation of the Al-coating at relatively low temperature and in short time can be attributed to the multi-reactions induced by ball impact. In conventional diffusion coating processes, the formation of Fe-Al intermetallic compound can only be realized at high temperature by lattice diffusion. It is well known that temperature as high as 1 000 is needed in pack-aluminizing and 720 for hot dipping. It was reported that over 100 h was needed when the Fe-Al phases started to nucleate at 500–600 in the Elphal process. Diffusion at 500 for 240 h only produced discontinuous alloy layers less than 20  $\mu\text{m}$  in thickness [26]. The formation of a continuous alloy layer needed 240 h treatment at 580 .

With the present method, ball impact results in severe plastic deformation of the substrate. The

microstructure near the surface is refined by the plastic deformation, causing a large amount of grain boundaries and structure defects, and local high temperature in the impact zones. While the ball impact also caused an Al layer adhered onto the surface. Therefore the atomic diffusion occurs along the fast diffusion paths of the large amount of grain boundaries and structure defects. An initial Fe-Al alloy layer is produced. The  $\theta$ -FeAl<sub>3</sub> phase is first formed according to the thermodynamic equilibrium condition. But  $\theta$ -FeAl<sub>3</sub> has an orthorhombic structure with 70% lattice sites along the *c* axis occupied by Al atoms and 30% vacant. These vacancies provide easy diffusion paths in the *c* direction, contributing to the rapid growth of  $\eta$ -Fe<sub>2</sub>Al<sub>5</sub> phase [27]. This is why that the initial alloy layer on the specimens is dominant by  $\eta$ -phase.



**Fig.11** Cross-section of Al-coating on Cr13(a) and Cr18-Ni9-Ti (b) exposed to air at 900 for 200 h

The continuous ball impact may cause a series of reactions, including breaking the Al-rich layer on the surface, causing more homogeneous and denser microstructure. The grains are refined to the micro- or nano-levels. The large amount of grain boundaries and defects provide fast atomic diffusion paths on the surface layer. At the same time, new Al layer is continuously produced by ball impact. Fast diffusions of Al and Fe atoms occur at the interface of the alloy and the Al layer. However, the inward diffusion of Al atoms may be

restrained by the coarse-grain structure of the substrate. Therefore, the inward diffusion of Al is lattice controlled, which is much slower than the grain boundary diffusion. This effect will slow down the inward growth of Al-rich phases, leaving Fe atoms diffuse through the alloy layer along the high-density grain boundaries, and resulting in outward growth of the Al-rich phases.

Consequently, another alloy layer is produced. In order to verify this mechanism, carbon steel specimens with Pt markers on the surface were treated at 560 for 90 min. This test is often used to investigate the growth mechanism of diffusion layers. After annealing, the Pt marker is found to be located between the substrate and coating, indicating that the Al-Fe intermetallic compound coating grows from inside toward outside (shown in Fig.12). The intermetallic coatings grow outward by the repeated ball impact. With this mechanism, Fe-Al intermetallic coatings formed at a much lower temperature in a much shorter time compared with the conventional aluminizing process. This concept provides a new approach that can be used in other diffusion coating processes.

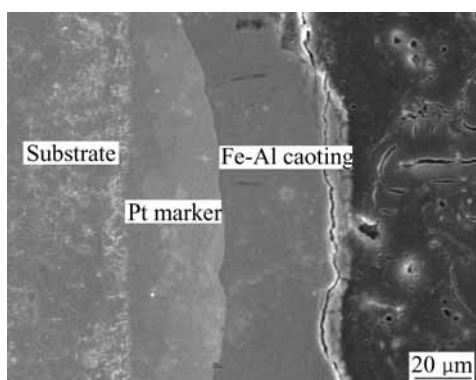


Fig.12 Location of Pt-marker in Al-coating

## 5 Conclusions

1) Aluminide coatings are successfully produced on carbon steel, Cr13, Cr18-Ni9-Ti and Cr5-Mo at a relatively lower temperature (440–600 °C) and in a shorter treatment time (15–240 min) in a modified pack-aluminizing process. In this process, chemical reaction and atomic diffusion are accelerated by ball impact, resulting in the formation of the Al-coating. The operation temperature, treatment time and composition of alloys have significant effects on formation of the Al-coatings. The formation of the Al-coating is diffusion controlled.

2) The Al-coating has one-layer structure, and exhibits high density, homogeneity and a good adherence to the substrate, showing different features with the Al-coating obtained by other aluminizing processes. The concentrations of aluminium, iron and chromium

almost uniformly distribute across the coatings. The Al-coating mainly consists of Al-rich phase.

3) The Al-coating obtained at relatively low temperature apparently improves the high-temperature oxidation resistance. After oxidized in air at high temperature, a full, dense, and continuous oxide scale is formed on the surface of the coated specimens, giving an effective protection to the alloys.

4) The formation of the Al-coating includes that the ball impact produces a thin layer of Al onto the substrate surface, and the mechanical deformation caused by ball impact produces local high temperature and ultrafine structure, promoting diffusion of Fe and the formation of Fe-Al compounds, resulting in formation of the Al-coatings by outward growth.

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