Preparation and microstructure characterization of zinc coating prepared by pack cementation

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Abstract. The zinc coatings on Q235 steel substrate were prepared by pack cementation at 400 °C for different holding time. The microstructure, thickness and hardness of the coatings were investigated. The thickness and hardness of the coating increased gradually with increasing heating time. The coating was composed of two layers. The inner layer is composed of 60.67 at.% Fe and 39.33 at.% Zn, and the outet layer is composed of 10.30 at.% Fe and 89.70 at.% Zn. The coating was consist of Zn, $Fe_{11}Zn_{40}$, $FeZn_7$ and $FeZn_9$ phases.

1 Introduction

Due to its high strength, excellent ductility, easy machining and low cost, steel is widely used in aerospace, transportation, f architecture, military, shipbuilding and other fields [1]. Chronic constantly exposure to atmosphere or aqueous solution can result in the serious corrosion of steel. The corrosion strongly influences the normal operation and safety of steel equipments, which is a problem for the economic development. Hence, the demand for improving corrosion resistance is increasing constantly.

In recent years surface alloying treatment on steel is developing. Common elements for alloying treatment are Cr, Ni, Al, etc. A. Sheibani Aghdam et al. studied the Ni-Cr coating electrodeposited on low carbon steel [2]. With its complex process, high cost and environmental pollution, the application of electroplating process is limited. The Al coating prepared by pack cementation has been widely used in improving corrosion resistance of steel. T.L Hu et al. studied the microstructure of Al coating on 310 stainless steel prepared by pack cementation method, and the pack was heated in an argon atmosphere at the treating temperature of 900 °C for 5 h [3]. The high temperature oxidation behavior of Al diffusion coating on Fe-30Cr alloy was investigated by C. Houngniou et al [4]. The aluminizing treatments were carried out at 1000 °C for 5 h. The reason that the Al coating have been widely used is that the Al can form Al_2O_3 which is highly resistant to oxidation at elevated temperature and hostile environment [5]. Most of the Al coatings were fabricated at high temperature. Due to its high working temperature and serious waste of Al powder, the pack cementation calls for further development. The zinc (Zn) coating prepared by pack cementation at low temperature is developing.

In this work, the Zn coating on Q235 steel prepared by pack cementation at low temperature of 400 °C was investigated. Microstructure, thickness, vickers hardness and composition of the coating were analyzed. The effect of heating time on the kinetics in the formation of Zn coating was also analyzed in this paper.

2 Experimental

The substrate material for this study was commercial Q235 steel, consisting of C: ≤ 0.22 wt.%, Mn: ≤ 1.4 wt.%, Si: ≤ 0.35 wt.%, S: ≤ 0.050, P: ≤ 0.045 wt.%, balanced by Fe. Specimens having a size of 1.5×10×15mm were cut from the Q235 steel sheet. The Zn coatings on Q235 steel were prepared by pack cementation. Before the process, all specimens were ground with silicon-carbide papers down to 2000-grit followed by ultrasonic cleaning in acetone. Then the specimens were buried into the crucibles filled with mixed powders of Zn powder and NH_4Cl powder. The weight ratio of the Zn powder to NH_4Cl powder was 100:3. The crucibles were heated in a box resistance furnace, and the heating rate was 10 °C/min. The heating was a three-step process. The crucibles were first preheated at 200 °C for an hour, then held at 400 °C for different time (2 h, 4 h, 6 h, 8 h and 10 h), finally followed by furnace cooling. The specimens were removed from the pack and cleaned in distilled water.

The microstructure and thickness of the coating was observed by optical microscope (OM). A further observation and chemical composition of the coating were analyzed using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). X-ray diffractometry (XRD) analysis in 2θ range from 20 to 90° was conducted to determine phase compositions of the coating. The vickers hardness was measured by HV-1000 type micro-sclerometer.

3 Results and discussion

The cross-sectional micrographs of the specimens after different holding time of penetration are presented in Fig. 1. All the coatings are of compact and uniform structures. They are proved a good adherence with the steel substrate, and consist of two layers. In Fig. 1a, Fig. 1d and Fig. 1e, some tiny cracks are observed in the coatings. Some small drop-cuts are distributed at the edges of the coatings which cause the cracks extension. Few of cracks are observed in Fig. 1b and Fig. 1c. It illustrates that holding time too long or too short will lead to crack formation of the coating. With increasing of holding time, the coating quality is firstly improved and then decreased.

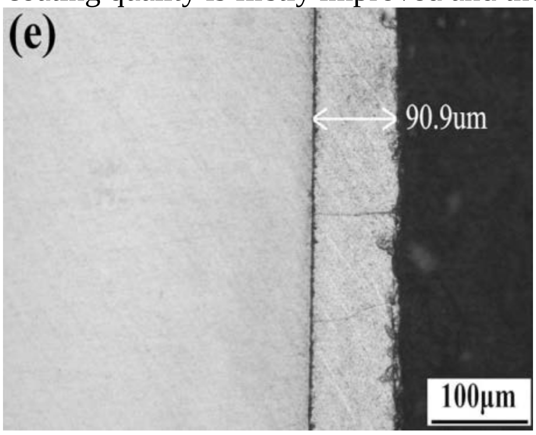


Fig. 1 The cross-sectional micrographs of the specimens heated at 400 °C for different holding time (a) 2 h, (b) 4 h, (c) 6 h, (d) 8 h, and (e) 10 h

According to previous literatures [6], when the heating temperature is constant, the relationship between thickness of coating (*d*) and heating time (*t*) is consistent with quadratic parabola. The equation is as follow:

$$d^2=kt \quad (1)$$

$$\frac{dd}{dt}=\frac{1}{2}\sqrt{\frac{k}{t}} \quad (2)$$

where k is diffusion coefficient. The growth rate of coating thickness decreases with the increase of heating time.

Fig. 2 shows the kinetics curve of coating growth. As can be seen, the thickness of the coating is increased gradually with increasing holding time, which is a parabola equation. This conforms to the result of the equation 1. The coating prepared by pack cementation is formed in three stages. Firstly, the active zinc atoms are formed during heating, and the active atoms move towards the steel substrate. Secondly, the active atoms are absorbed on the steel surface, which results in the formation of a surface layer. Thirdly, the surface layer is grown with the increase of holding time. The formation of the coating was attributed to the diffusion of active atoms. The thickness of the coating for the heating time of 2 h is 32.7 μm . It increases to 51.3 μm with increasing heating time to 4 h. The corresponding growth rate is 18.6μm·h^{-1}. The growth rate is 16.2 μm·h^{-1} with increasing heating time from 4 h to 6 h. The growth are 13.6 and 9.8 μm·h^{-1} for the rest two parts. The growth rate decreases with increasing heating time. The result is in great agreement with the equation 2. The thickness of the coating is 90.9 μm when the heating time is 10h. This is about 2.8 times as thick as that for 2 h of pack cementation. The thickness obviously increases with the increase of heating time.

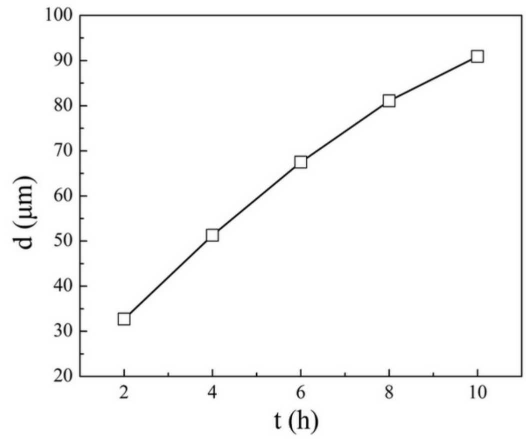
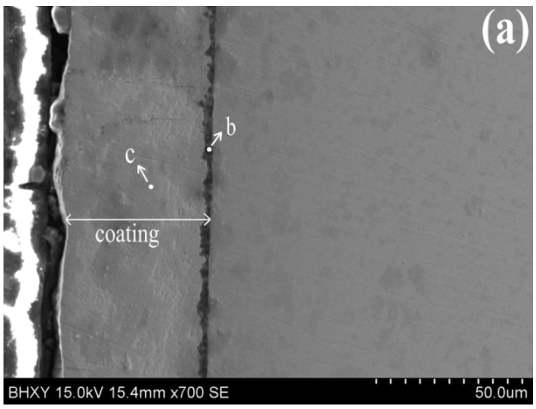


Fig. 2 The kinetics curve of the coating growth

The SEM image and chemical compositions of different areas of the coating prepared at 400°C for 4 h is presented in Fig. 3. It is obvious that the coating is composed of a thin inner layer and a thick outer layer. The inner layer is black and uneven. The chemical compositions of the inner layer are shown in Fig. 3b (noted b in Fig. 1a). The compositions of the outer layer are shown in Fig. 3c (noted c in Fig. 1a). The Fe concentration in the inner layer is much higher than that in the outer layer. On the contrary, the contents of Zn is lower in the inner layer. It demonstrates that the metallurgical bond between the coating and the steel substrate is realized. The thickness of the inner layer is less than 5 μm. The thickness of the outer layer is more than 10 times higher than that of the inner layer.

The inner layer is composed of 60.67 at.% Fe and 39.33 at.% Zn, and the outet layer is composed of 10.30 at.% Fe and 89.70 at.% Zn. It is obtained that the concentration of Fe gradually decreases with increasing the distance from steel substrate. The Zn concentration shows a reverse trend to that of Fe concration. For the pack cementation, the fomation mechanism of the coating is principally the gas phase in a minimum three reaction steps [7]. The first reaction including NH_4Cl decomposition to NH_3 and HCl occurs during the heating. Subsequently, the composition reactions that Zn compounds with Cl and NH_3 are formed. The third one refers to replacement reaction between Fe and Zn, which lead to the deposition of Zn on the steel substrate. During the replacement process, the compounds of Fe and Zn are formed.



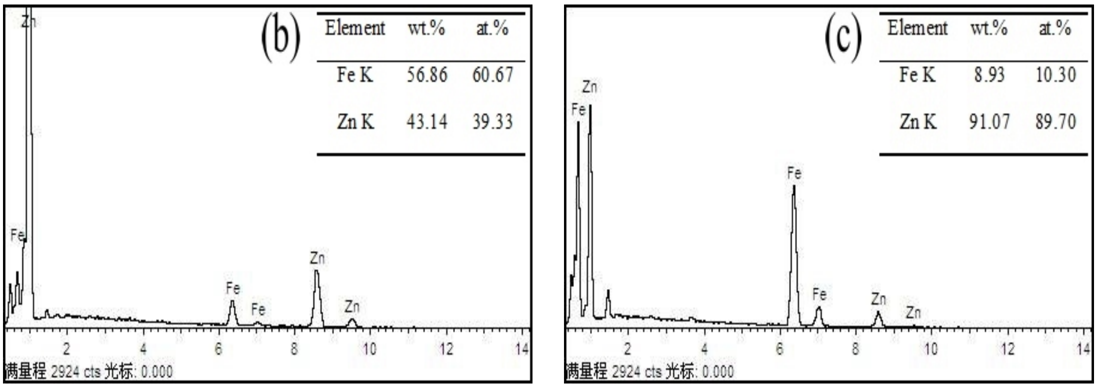


Fig. 3 SEM image of the coating prepared at 400 °C for 4h and EDX of the different sections on the coating (a) SEM image of the coating, (b) the inner layer, (c) the outer layer

The phase compositions of the outer coating after 4 h of pack cementation are listed in Fig. 4. The outer layer is consist of Zn, $Fe_{11}Zn_{40}$, $FeZn_7$ and $FeZn_9$ phases. The existence of Zn is probably due to the remaining Zn powder without being washed off. The $Fe_{11}Zn_{40}$ phase has higher hardness and better plasticity [8]. The dense Fe-Zn coating can effectively protect the steel substrate, and increase the corrosion resistance of the coating itself.

The vickers hardness values of the coatings prepared for different heating durations are presented in Fig. 5. The hardness of the coating is much higher than that of the Q235 steel substrate. The hardenss apparently increases with increasing the heating time. The $Fe_{11}Zn_{40}$ phase with high hardness accounts for more than 80% of the coating. Hence, the thicker the coating is, the larger the hardness is.

Conclusions

The Zn coating was prepared by pack cementation at 400 °C for different time (2 h, 4 h, 6 h, 8 h and 10 h). All the coatings were of compact and uniform structures. The thickness and hardness of the coating increased with the increase of immersion time. The hardness of the coating was much higher than that of the steel substrate. The coating was composed of two layers. The outer layer was much thicker than the inner layer. The inner layer was composed of 60.67 at.% Fe and 39.33 at.% Zn, and the outet layer was composed of 10.30 at.% Fe and 89.70 at.% Zn. The outer layer consisted of Zn, $Fe_{11}Zn_{40}$, $FeZn_7$ and $FeZn_9$ phases.

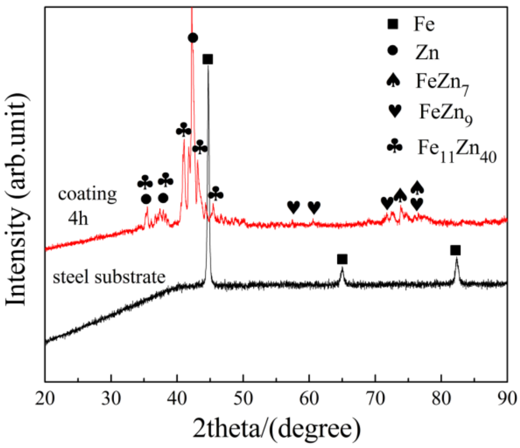


Fig. 4 The phase compositions of the out layer of the coating after 4 h of cementation

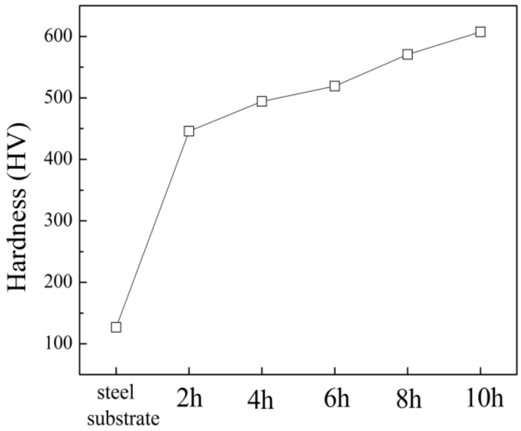


Fig. 5 The vickers hardness values of the coatings prepared for different heating durations

Acknowledgements

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