Study on the surface packing cementation aluminizing processes of Q345 steel in an air environment

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Abstract
To address the requirement of a vacuum environment or a protective atmosphere in the process of aluminizing, pack cementation was used to aluminize the surface of Q345 steel in an air environment. The aluminized coating with a large hardness and corrosion resistance was prepared on the surface of Q345 steel. The influence of the aluminizing temperature and the holding time on the surface quality and thickness of the aluminized coating was studied to determine the optimum conditions for aluminizing. The surface quality of the coating was observed by an electron microscope and the thickness of the aluminized coating was measured. The main elemental distribution of the coating was also analyzed by an energy spectrometer. The phase composition of the aluminized coating was analyzed by an x-ray diffractometer and the change in coating hardness was measured by a microhardness tester. The results showed that when the holding time was 3 h and the heating temperature was 800 °C, the obtained thickness of the aluminized coating was 180 μm, with good quality, excellent hardness, and corrosion resistance.

1. Introduction
Due to the ideal mechanical properties, low cost, and resistance to some corrosive media, carbon steel is widely used in industry to manufacture metal components and equipment. However, there are many corrosive media in the processing of petroleum and the production of chemicals. In many working conditions, the lifetime of equipment and pipelines is greatly reduced due to the corrosion of carbon steel [1]. Recently in the field of surface engineering technology, chemical heat treatment technology of metals has been used to modify the surface of carbon steel to improve its corrosion resistance, high-temperature oxidation resistance, wear resistance, and other aspects of performance [2–6]. Currently, the research on powder aluminizing steel surfaces has been done all over the country. Researchers have worked to optimize the aluminizing process, performance, testing, and practical application, and have achieved some results [7–10]. In 2016, Meng Lei et al reviewed the research progress of a low-temperature aluminizing process for carbon steel powder embedding, which showed that the current research of this process had achieved gratifying research results. They found that the method of changing the formula of the aluminizing medium or the surface mechanical energy-assisted infiltration method can be used to realize the low-temperature, packed, cementation aluminizing of carbon steel, and the process has a great potential to be developed [11].

Unfortunately, although a good quality aluminizing layer can be obtained, the equipment requirements are high, and the operation is not simple and the cost is high, has never been explored. That is the reason why the present research work aims at studying the low-cost and simple process, i.e., in an air environment. In a first part, aluminized coatings were prepared by coating an aluminizing medium with refractory clay and heating at 700 °C–900 °C in an air environment for 2–5 h. Then, the effects of aluminizing time and temperature on the microstructure, phase, hardness and composition of aluminized coating were studied. At last, The corrosion resistance test was carried out in 30% sulfuric acid solution. This process is expected to replace the traditional operation process in either a vacuum or an aluminizing box.
2. Experimental

2.1. Test material and aluminizing medium formula

In this study, an aluminized coating was prepared on the surface of carbon steel by a packing cementation method. The aluminizing test material was Q345 steel and the chemical composition is shown in Table 1.

The aluminizing medium material was aluminum powder, ammonium chloride powder, and alumina powder. The composition (mass fraction, %) of the aluminizing medium was 20% pure aluminum powder, 79% alumina powder, and 1% ammonium chloride powder.

2.2. Preparation of aluminized coating

The surface of the sample was smoothed with 400–2000 grit abrasive paper, cleaned by 90 Hz ultrasonic vibration in absolute ethanol for 30 min, and then dried by cold air for standby. The sample and the prepared aluminizing medium were put into a crucible. Then, the refractory clay, water glass, and water were weighed and mixed according to the mass ratio of 40:8:1 and fully stirred in glove box to prevent oxygen from invading aluminizing medium during mixing. Then, the refractory clay, water glass, and water were weighed and mixed according to the mass ratio of 40:8:1 and fully stirred in glove box. And the Q345 sample was wrapped in the aluminizing medium with a thickness of about 10 mm. Then the mixture was wrapped in the outer layer of the formed aluminizing medium to create a uniform and dense protective coating with a thickness of about 20 mm. The temperature was kept at 100 °C for 2 h to remove moisture. After removing the water, the samples were heated to 600 °C, 700 °C, 800 °C, or 900 °C, respectively, and the aluminizing times were 2 h, 3 h, 4 h, or 5 h, respectively. During the experiment, there was no vacuum and no protective atmosphere. The specific aluminizing process is shown in Figure 1.

2.3. Analysis, characterization, and performance evaluation of the aluminized coating

After the furnace temperature was cooled to room temperature, the samples were cleaned with absolute ethanol by ultrasonic vibration, and then the samples were inlaid, ground, polished, and corroded. The morphology, phase composition, microstructure, section hardness, and corrosion resistance of the surface and cross-section of the aluminized coating were analyzed by a Quanta200 scanning electron microscope, D8Focus x-ray diffractometer, metallographic microscope, and microhardness tester. The chemical elements of the aluminized coating were analyzed by an energy spectrum analyzer attached to the scanning electron microscope, and the best aluminizing process was discussed. The Vickers hardness tester HVS-50 was used to test the hardness of aluminized samples. The measurement conditions included a load of 0.98 N (100 g) and a holding time of 10 s.

The corrosion resistance was evaluated by a weight-loss method. The formula for the calculation is given by equation (1):

\[ V' = \frac{W_0 - W_t}{S \times t} \cdot \text{g m}^{-2} \cdot \text{h}^{-1} \]  

(1)
where $V'$ is the corrosion rate underweight loss (g m$^{-2}$ h$^{-1}$); $W_0$ is the initial weight of the metal (g); $W_1$ is the weight of the metal after removing the corrosion products (g); $S$ is the metal area (m$^2$); and $t$ is the corrosion time (h).

The specific protocol was as follows: the sample of each process after sintering was weighed with an electronic analytical balance. The four sides of the sample were covered with 502 glue and then each sample was weighed again and the data was recorded. 30 ml of 30% sulfuric acid was measured and divided into 10 test tubes and the samples were put into the respective test tubes. The opening of the test tube was then sealed with a fresh cling film. The temperature was kept at room temperature for 5 h and then the samples were taken out and weighed after drying.

3. Results and analysis

3.1. Influence of heating temperature

3.1.1. Influence of heating temperature on surface morphology

Figure 2 shows the macroscopic morphologies of the samples heated at 600 °C, 700 °C, 800 °C, and 900 °C, respectively, with holding times of 3 h. It can be seen from figure 2(a) that when the surface aluminizing temperature was 600 °C, a black substance without a metallic luster was formed on the surface of the sample. This was because the melting temperature of the aluminum was not reached and there was no aluminizing reaction or coating on the surface. With the increase of the aluminizing temperature, some materials with metallic luster gradually appeared on the surface of the sample, as shown in figure 2(b). With a further increase in temperature, the surface of the sample was covered with a uniform gray-white material, as shown in figure 2(c).

Due to the increase in temperature, the activity of the Al atoms in the aluminizing medium increased, and the surface of the aluminizing layer appeared gray-black and smooth. However, when the temperature rose to 900 °C, a flowing molten substance appeared on the surface of the sample, and the surface was very uneven, (figure 2(d)), most likely due to the high aluminizing temperature. The aluminizing medium easily cement, which caused caking on the surface and reduced the properties of the aluminized steel. Also, the formation rate of active aluminum atoms increased, a large number of reactive aluminum atoms gathered on the steel surface, adhesion phenomenon appeared on the surface of the aluminized coating, the edge thickened, and the surface...
uniformity of aluminized coating was destroyed. Therefore, when the heating temperature is 800 °C, the surface quality of the sample in figure 2(c) is better than others.

3.1.2. Influence of heating temperature on the thickness of the aluminized coating

Figures 3(a)–(d) show the cross-sectional morphologies of aluminized samples prepared at different temperatures. Figure 3(a) shows the cross-sectional morphology at 600 °C, and no aluminized coating was found. When the temperature increased from 700 °C to 900 °C, the thickness of the aluminized coating increased gradually. Figure 3(b) shows the cross-sectional morphology at 700 °C, and the average thickness of the aluminized coating was about 110 μm. When the temperature was further increased to 800 °C, the average

![Figure 3. Cross-sectional monographs of aluminized steel packed at different temperatures. (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 900 °C.](image)

![Figure 4. Influence of the heating temperature on the aluminized coating thickness.](image)
thickness of the coating increased to 180 μm, and the coating was continuous and dense, showing metallurgical bonding and no holes, as shown in figure 3(c). When the temperature was further increased to 900 °C, the average thickness of the coating increased to 240 μm, and some holes appeared outside the coating. This was mainly because the atomic radius of Fe is larger than Al, and the diffusion rate of Fe is greater than Al during the aluminizing process. Therefore, due to the diffusion process, holes will appear in the structure, as shown in figure 3(d).

Figure 4 shows the influence of the heating temperature on the aluminized coating thickness. It can be seen from the figure that no aluminized coating was formed at 600 °C, but with the increase in temperature, the formed coating became thicker and thicker. This was because the surface aluminizing process of Q345 steel included vapor deposition and thermal diffusion. The growth of the aluminized coating was mainly controlled by the diffusion process and according to the diffusion law, the main factor affecting the diffusion is temperature. The diffusion of a continuous solid solution in an aluminizing process is called concentration diffusion. The relationship between the thickness of the coating formed in this way and the diffusion coefficient is parabolic, as shown in equation (2), where A is a constant and D is the diffusion coefficient. In an Arrhenius relationship, as shown in equation (3), R is the gas constant, Q is the activation energy per mole of atoms, and T is the thermodynamic temperature. In the same crystal, the increase in temperature made D increase significantly. In addition, at 900 °C, aluminum formed contacts with the matrix in the liquid phase, which effectively improved the contact area with the matrix and its wettability [13]. Therefore, with the increase of the aluminizing temperature, the thickness of the aluminized coating increased.

\[ \chi = A\sqrt{Dt} \]  
\[ D = D_0 e^{-Q/RT} \]

3.1.3. Influence of heating temperature on the corrosion resistance of aluminized coatings

Figure 5 shows the variation curve of the corrosion rate of aluminized Q345 steel samples with different heating temperatures. The corrosion rate of the aluminized sample first decreased and then increased with the increase of the heating temperature (holding time). The corrosion resistance of the samples with an aluminized coating was better than without the aluminized coating. When the aluminizing temperature was 600 °C, there was no percolation layer on the surface of the sample (figure 3(a)) and the corrosion rate was the highest. When the aluminizing temperature was 800 °C, the corrosion rate was the lowest. With the increase of the aluminizing temperature, the corrosion rate increased and the corrosion resistance decreased. It can be seen from figure 3(d) that when the aluminizing temperature was too high, holes appeared on the surface of the sample, the compactness decreased, the corrosion of the aluminized layer began to increase, and the corrosion transitioned from uniform to pitting, resulting in increased corrosion.

The aluminized coating on the steel surface had good corrosion resistance in some environments. Mo Liming et al carried out electrochemical experiments on aluminized samples in corrosive environments. Compared with the non-aluminized steel, the self-corrosion current of aluminized samples was reduced by 1–3 orders of magnitude, and the passivation zone of aluminized steel was wider [12]. Shen T H et al carried out electrochemical tests on an aluminized sample in a 3.5% sodium chloride solution. The results also showed that
Figure 6. Surface morphologies of samples at 800 °C for different holding times. (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h.

Figure 7. Cross-section morphologies of aluminized samples with different aluminizing times. (a) 2 h; (b) 3 h; (c) 4 h; (d) 5 h.
the self-corrosion potential of the aluminized sample was lower than that of the non-aluminized sample, and the self-corrosion current of the aluminized sample was significantly lower than that of the non-aluminized sample \[14\]. All these indicated that the corrosion resistance of the aluminized sample improved.

3.2. Influence of holding time

3.2.1. Influence of holding time on surface morphology

Figure 6 shows the macroscopic condition of the sample surface after aluminizing at 800 °C. When the aluminizing time was 2 h, the surface of the aluminized coating was smooth, but the surface had no obvious white luster, as shown in figure 6(a). When the aluminizing time was 3 h, the surface of the aluminized coating was smooth, as shown in figure 6(b). When the aluminizing times were 4 h and 5 h, surface bonding phenomena appeared, and the surface qualities of the aluminized coatings decreased, as shown in figures 6(c) and (d). This was because, with the prolongation of the aluminizing time, the reactants in the aluminizing medium were exhausted. After long-duration, high-temperature heating, Al₂O₃ as a filler was easy to produce cementation and adhere to the sample surface. When the aluminizing process was performed for a long time, some of the aluminizing reaction catalyst, NH₄Cl escaped and volatilized from the cracks and pores of the clay, preventing the formation of active aluminum atoms. The remaining Al powder in the aluminizing medium was fused and bonded to the surface of the sample. Therefore, when the holding time is 3 h, the surface quality of the sample in figure 6(b) is better than others.

3.2.2. Influence of holding time on the thickness of the aluminized coating

Figure 7 shows the cross-sectional morphologies of aluminized samples at different holding times. Figure 7(a) shows the scanning section morphology of the coating after aluminizing for 2 h. The aluminized coating was thin, dense, and had no holes, but there was a transition layer. Figure 7(b) shows the scanning section morphology of the aluminized coating after 3 h. In the figure, the thickness of the aluminized coating increased, the thickness of the transition layer did not change noticeably, and the aluminized coating was continuous and dense, showing metallurgical bonding. Figure 7(c) shows the scanning section morphology of the coating after aluminizing for 4 h. In the figure, the thickness of the aluminized coating increased noticeably, and the thickness of the transition layer increased, but some holes appeared in the aluminized coating. Figure 7(d) shows the scanning section morphology of the aluminized coating after 5 h. In the figure, the sample continued to thicken and more large holes appear in the outer layer.

Figure 8 shows the influence of different aluminizing times on the change in thickness of the aluminized coating. The thickness increased with the increase of the aluminizing time. The thickness grew fast at the beginning and gradually leveled off after 3 h. The effect of the duration of the aluminizing reaction was relatively small. In a certain time range, the thickness of the aluminized coating was gradually thickened. The packing cementation aluminizing on the surface of carbon steel was carried out by the reactions shown in equations (4)–(8).

\[
2NH₄Cl \rightarrow 2HCl + N₂ + 3H₂ \tag{4}
\]

\[
2HCl + 2Al \rightarrow 2AlCl + H₂ \tag{5}
\]
The aluminizing process was divided into three steps: gas-phase diffusion, surface reaction, and solid diffusion. The surface reaction occurred very fast, so the kinetics of the aluminizing process was mainly controlled by the gas phase diffusion in the medium and the solid diffusion in the coating. When the aluminizing time was extended to a certain time and the decomposition of NH₄Cl as a catalyst occurred in the aluminizing process, the generated gas slowly escaped from gaps in the clay, decreasing the Cl⁻ concentration of the catalytically active aluminum atoms in the infiltration tank, and hence stopped the reaction [15]. Secondly, at high temperatures, the viscosity of softened aluminum powder was enhanced, and the content of effective aluminum powder participating in the reaction was reduced. Therefore, even if the aluminizing reaction time was prolonged, the increased rate of the aluminized coating was reduced to a certain extent. When the concentration of Cl⁻ decreased to a certain range, even if the aluminizing reaction time continued to increase, the aluminizing reaction cannot be carried out without enough Cl⁻. In addition, with the increased aluminized coating thickness, the formed high aluminum phase Fe-Al alloy layer hindered the diffusion of new active aluminum atoms. Therefore, although the holding time increased, the thickening rate of the aluminized coating decreased. Long term high-temperature conditions caused serious damage to the structure of the steel parts, and the serious cementing of the aluminizing medium made it difficult to remove the parts, which caused a certain waste of production energy.

3.2.3. Influence of holding time on corrosion resistance of the aluminized coating

Figure 9 shows the variation curve for the corrosion rate of the sample with aluminizing time. The corrosion rate first decreased and then increased with the increase in the heating temperature (holding time). When the aluminizing time was 5 h, the corrosion rate was the highest. When the aluminizing time was 3 h, the corrosion rate was the lowest. With further increases in the aluminizing time, the corrosion rate increased and the corrosion resistance decreased. The corrosion rate reached the highest when the aluminizing time was 5 h. According to figure 7(d), when the aluminizing time was too long, a large number of holes appeared on the surface of the sample, the compactness decreased, the corrosion of the aluminized coating began to aggravate, and the corrosion transitioned from uniform to pitting, resulting in the aggravation of corrosion.

Aluminized steel has good corrosion resistance in many corrosive media, and has achieved obvious effect in metal corrosion protection. Of course, the aluminized layer of steel can improve its ability to resist sulfide corrosion. Sulfur containing gases such as hydrogen sulfide, sulfur dioxide and sulfur trioxide will corrode the steel in the presence of water vapor. Relevant experimental data show that the corrosion resistance of 9Cr-1Mo steel in the environment containing hydrogen sulfide steam at 371 °C is 35 times of that of the base material, and the corrosion resistance of 9Cr-1Mo steel at 482 °C is 161 times that of the base material [16]. J R Regina et al studied the corrosion of iron aluminum alloy in three kinds of sulfur-containing gases, and the results showed that the increase of sample mass can be effectively prevented when the aluminum content in the sample reaches a certain value [17].
4. Composition and phase analysis of the aluminized coating

Energy Dispersion Spectrum (EDS) was used to scan the cross-section of the aluminized sample, and the line scan photos are shown in figure 10. The distributions of elemental Fe and Al were uniform in the aluminized coating but had sudden changes at the boundary between the transition layer and the aluminized coating. The strength of the aluminum decreased slowly after the sudden change to a certain value, and the final strength became zero. The area where the strength of Al decreased gradually was the transition layer. This slow change enhanced the bonding of the coating to the matrix. It can also be seen from the figure that the concentration of aluminum atoms in the aluminide layer was unchanged. At the transition layer, the proportion of aluminum atoms began to decrease, and the proportion of iron atoms began to increase. At the interface between the transition layer and the matrix, the aluminum atom number fraction decreased to zero. According to the Fe-Al equilibrium phase diagram, with the decrease of aluminum content, there existed stable phases between iron and aluminum, including FeAl3, Fe2Al5, FeAl2, FeAl, and Fe3Al. To further determine the phase composition of the aluminized coating, it was necessary to carry out XRD on the aluminized samples.

It can be seen from figure 11 that the results were mainly FeAl3 and Fe2Al5 intermetallic compounds. FeAl3 and Fe2Al5 intermetallic compounds can form an Al2O3 oxide film in the presence of an oxidizing gas, so the oxidation rate was lower than that of other ferrous alloys with no oxide film on the surface. The experiment showed that the oxidation resistance of the same steel after aluminizing was significantly increased compared with that before aluminizing [3, 14, 18]. In the oxidation resistance test, the mass of the unaluminized sample...
increased rapidly, but the mass of the aluminized steel changed slowly. This was mainly due to the formation of loose iron oxides in the oxidation of unaluminized steel, which had no protective effect on the matrix. Also, oxygen continuously reacted with the matrix through loose oxides. However, after aluminizing, a Fe–Al intermetallic compound layer was formed on the steel surface, and an alumina film was formed on the outermost layer of the sample at high temperature. The dense alumina film covered the steel surface to block the contact between the oxygen and matrix, thus preventing the continuous oxidation of the matrix. Ideal high-temperature oxidation resistance was an important advantage of aluminized steel [18].

5. Microhardness analysis of aluminized coating

Figure 12 shows the hardness variation curve of the aluminized coating section that was obtained after holding at 800 °C for 3 h. The hardness of the aluminizing layer was about 880HV0.1. In the transition layer, the hardness decreased to about 300HV0.1, and while in the matrix the hardness was 110HV0.1. From the XRD analysis, it can be seen that during the aluminizing process, Al was soluble with Fe at 800 °C, and the Fe2Al5 and FeAl3 intermetallic compounds with strengthening effects were formed. After aluminizing, the hardness of the aluminizing layer was much higher than that of the matrix, which improved the wear resistance of the sample. The transition layer connected the high-hardness aluminizing layer with the matrix. This was conducive to the combination of the aluminizing layer and the matrix and prevented the aluminizing layer from falling off under the action of positive pressure.

6. Conclusions

(1) An aluminized coating on steel was obtained by coating an aluminizing medium with refractory clay and heating at 700 °C–900 °C in an air environment for 2–5 h. This process was expected to replace the traditional operational processing in a vacuum environment or an aluminizing box.

(2) When the aluminizing temperature was too low (600 °C), the aluminized coating could not be formed on the surface of Q345 steel; when the aluminizing temperature was 700 °C–900 °C and the aluminizing time was 2–5 h, the thickness of the aluminized coating increased gradually with the increase of aluminizing time or temperature. The higher the aluminizing temperature or the longer the holding time, the greater the tendency to form holes in the aluminized coating, as well as the greater the chances of melting or fusion bonding on the surface.

(3) When the aluminizing temperature was 800 °C and the aluminizing time was 3 h, dense intermetallic layers of Fe2Al5 and FeAl3 were formed. The hardness of the compound layer was much higher than that of the matrix, reaching 895HV0.1. The corrosion resistance of the compound layer was noticeably improved as compared with that of the unaluminized sample.
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