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Study on Microstructure and Property of Hot-dip 55% Al-Zn Alloy Coating on 35CrMo Sucker Rod Surface

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Abstract: The formation process and corrosion resistance of 55%Al-Zn alloy coating for 35CrMo sucker rod are studied in this paper. The study shows that reduction of Si content in coating bath can reduce Fe dissolving and also keep size of sucker rod stable at the same time. The coating is divided into intermediate layer and Al-Zn coating from inside to the outside. The main components of the intermediate compound layer are made up of Fe_2Al_5 , FeAl_3 and $\text{Al}_{0.5}\text{Fe}_3\text{Si}_{0.5}$ by XRD analysis. Corrosion results indicate that the ratio of the weight loss between coated and uncoated sucker rod is 5.9:1 and the corrosion current density is 3:1.

1. Introduction

With the eastern oil fields in China entering the late phase of oil production, the depth of oil well increases gradually, and the well condition becomes complex. Since the water content of produced crude becomes higher, the accident rates of corrosion and eccentric wear among sucker rods grow quickly. It directly causes oil field maintenance expenses increase significantly. At present, the main anti-corrosion measures for sucker rods in China are injecting corrosion inhibitor, installing centralizer and using high alloy steel, but each has its own shortcomings^[1].

55% Al-Zn alloy is an excellent coating. Its corrosion resistance is 2-6 times higher than that of galvanized coatings which has same thickness with 55%Al-Zn alloy, which is equivalent to that of the aluminized coatings^[2]. The coating of 55%Al-Zn alloy not only has excellent corrosion resistance and oxidation resistance, but also has sacrificial anode protection of zinc coating^[3]. Based on previous experiments, the dipping temperature of 55%Al-Zn alloy is about 100 °C lower than that of hot-dipping aluminum. Therefore, the purpose of this paper is to investigate the formation of 55%Al-Zn alloy and the effects of this alloy on the corrosion resistance of 35CrMo sucker rod.

2. Experiment

2.1. Experiment Materials

The test material is 35CrMo in quenched and tempered state. The sizes of the matrix is $\Phi 22 \times 50 \text{mm}$. Aluminum ingot with 99% purity, zinc ingot with 99.9%, Al-10.5%Si Alloy. Metallographic corrosive agent is 3% nitric acid, 10% hydrofluoric acid and absolute ethanol.



2.2. Experiment Procedures

The first polish the matrix on the pre-grinding machine. Then the oil contamination on the surface of the matrix is removed by alkali solution((NaOH,Na₂CO₃ and Na₃PO₄ are mixed in ration of 1:1:1 to form a mixture of 20% concentration),80°C,6min). And cleaning the residual alkali solution on the surface of matrixs with deionized water(room temperature,4min); rust removal(20%H₂SO₄,60°C,8min); cleaning the residual acid solution on the surface of matrix with deionized water(room temperature,4min); assistant plate(plate assistant agent is 25%NH₄Cl, 0.5%NaF, 1%SnCl₂ and 30% ZnCl₂,75°C,60s); drying(95°C,60s); hot dipping(630°C,4min).

2.3. Lab Equipment

SG2-5-12 intelligent Well Resistance Furnace; XMT-7000 digital display temp-box; HH-S6 digital display thermostat water bath; DL-820D Ultrasonic cleaner; XJP-3A Metallurgical Microscope; Japanese company: JEOL, XM-86010: EDS analysis; XPERT-PRO D/Max-Rc model X-ray Diffractometer: test hot-dipping 55% Al-Zn alloy coating.

3. Discussion on experimental result

3.1. Effect of Silicon Content in Coating Solution on Coating Quality

This test selects an internationally used alloy. Three sets of tests were designed. The effect of Silicon content in aluminum zinc coating solution on coating quality was analyzed by controlling Si content, i.e. 55%Al-Zn-X%Si(1.4, 1.2, 1.0) alloy as liquid coating metal.

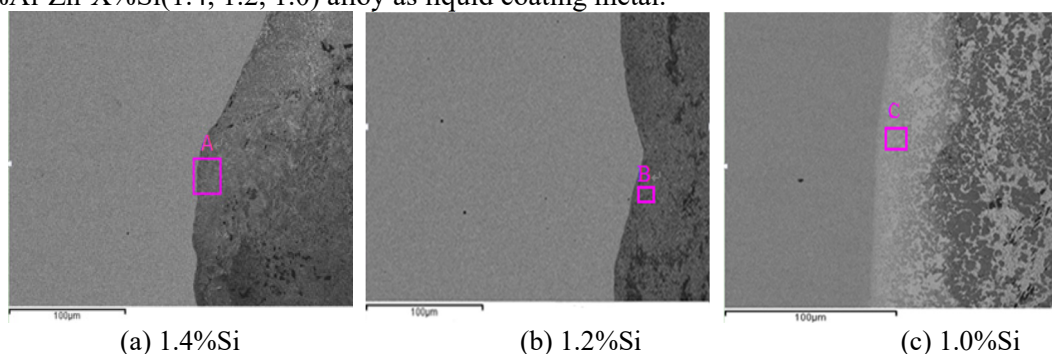


Figure1. Cross-sectional Microstructure of Al-Zn-Si Coatings with Different Si Contents.

From Figure 1, it can be seen that when the silicon content is high, the coating part has undergone serious erosion, resulting in a pit. As the silicon content decreases, the coating part-coating liquid transition joint surface is basically flat and smooth. From the energy spectrum analysis table 1, where the erosion occurred, the content of iron and silicon was generally relatively high. This shows that the silicon content in the coating solution has a great influence on the growth of the intermediate compound layer in the 35CrMo matrix during hot dip coating. The melting may be due to the large content of silicon in the coating solution, which reduces its viscosity, thereby accelerating the dissolution of iron on the surface of the coating part. Although this will expose a large number of fresh surfaces on the matrix, it will also cause the surface to dissolve continuously, which will increase the difficulty of adsorption of atoms such as aluminum and zinc, and thus increase the corrosion. On the other hand, the type and amount of elements dissolved into the iron base mainly depend on the characteristics of the diffused atoms themselves, rather than the simple number ratio in the coating solution^[4]. Check the chemical element radius table. The silicon atomic radius is slightly smaller than the iron atomic radius. According to Hume-Rothery's law, the size between atoms is less than 15 %, which can form an infinite solid solution and produce a unique negative volume size effect. The dissolution of silicon atoms reduces the spacing between iron atoms, releases a large amount of energy, makes the surrounding silicon atoms a low-energy region, promotes the reaction between the two, and the larger atoms such as aluminum and zinc form a solid solution with iron, which cause higher additional lattice transformation energy. Therefore, diffusion is relatively difficult. This shows that the

content of silicon in the melting zone exceeds the content in the coating solution. Under the conditions of this test, it is more appropriate to choose the silicon content of the coating solution to be 1.0 %.

Table 1. Table of EDS Element Content at A, B and C.

Element	A		B		C	
	WT (%)	atom (%)	WT (%)	atom (%)	WT (%)	atom (%)
Si K	1.89	6.47	1.67	6.23	1.39	5.11
Al K	48.34	60.80	49.85	42.58	43.83	56.04
Fe K	31.13	20.93	21.88	16.70	35.62	25.57
Zn K	20.53	11.80	26.60	34.49	19.16	13.28

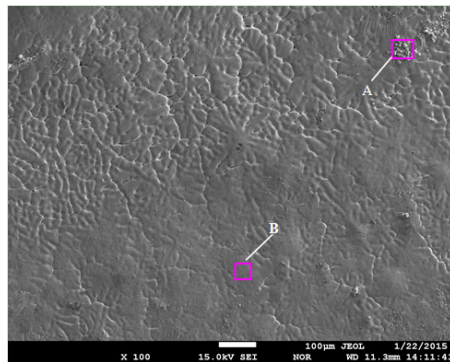


Figure 2. Surface morphology and EDS analysis of hot dipping 55% Al-Zn-1.2%Si sample.

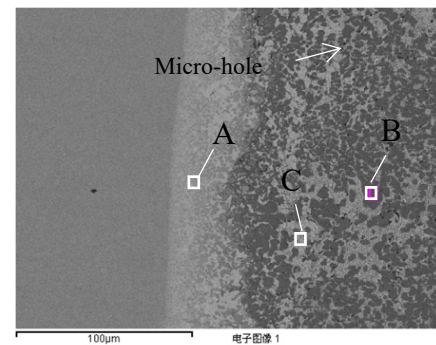


Figure 3. Cross-sectional morphology and EDS analysis of hot dipping 55% Al-Zn-1.0%Si sample.

3.2. Surface Morphology of hot-dipping sample

From figure 2, the sample surface mainly is composed of gray matter. The whole surface is relatively flat. However, there are a few micro-pore and micro-fold. The reason of this phenomenon is the coating solution adhering to the surface of the coating parts rapidly cooled in air after being taken out from the high temperature coating bath. Due to the rapid cooling of the coating solution attached to the surface of the coating parts, the contact interface between the liquid phase and air is bent, which made the coating solution change from a plane to a micro-surface. In addition, dendrites with high melting point (such as primary dendrite and secondary dendrite) begin to solidify at first, and its arm grows up. During the growth process, the surrounding liquid is needed to fill the dendrite. Then the solidification position will be depressed because there is no superfluous liquid to replenish, and micro-folds and micro-holes will be formed on the surface^[5]. From Table 2, we can see that the content of oxygen in area A is very high. It is inferred that the area is mainly composed of oxide impurity particles. In addition to aluminum, zinc and silicon, there are a large number of impurity elements calcium, chlorine and potassium. These elements are the main components of the covering agent. They should be formed by cooling crystallization adhering to the surface of the coating parts during the lifting process. The iron element is dissolved and diffused into the bath during hot dipping, and appears on the coating surface during cooling. The main components of area B are aluminum, zinc and silicon, which are the main components of the bath as well.

Table 2. Element content of position A and B in the surface of the sample.

Elements	Norm percentage (WT %)							
	Al	Zn	Fe	O	Si	Ca	Cl	K

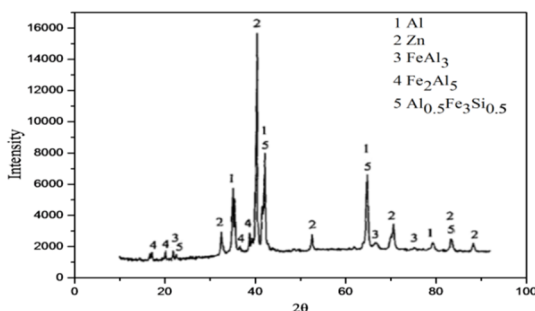
A	17.97	31.11	1.67	38.61	0.65	0.87	5.62	2.42
B	46.01	49.03	1.13	3.12	0.71	0	0	0

3.3. The Structure and Formation Mechanism of Hot Dip Coating

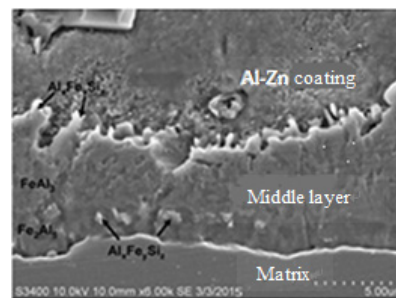
From figure 3, it can be seen that the coating can be divided into two layers from inside to outside, namely the middle gray layer and the outside hemp suit layer. Among them, the hemp color layer can be divided into dark gray and dark gray and white. At the same time, there are a small number of holes in the coating. It may be that the auxiliary coating film is not uniform, and the gas generated under high temperature immersion can't be spilled, and it forms after cooling of the coating liquid.

Table 3. Element content of position A B and C in the surface of the sample.

Elements	Norm percent (wt%)				
	Al	Zn	Fe	Si	Cr
A	43.03	19.16	35.62	1.49	0.6
B	68.34	30.04	1.13	0.49	0
C	10.73	87.53	1.31	0.43	0



(a)XRD map



(b)Component calibration

Figure 4. Calibration and XRD map of 55%Al-Zn-1.2%Si coating on the sample surface.

The EDS analysis results at Gray-White Area A, Dark Gray Area B and Dark Gray Area C in Figure 3 are shown in Table 3. As can be seen from Table 3, the main constituent elements at A are aluminum, iron, and a certain amount of zinc, silicon, and trace elements of chromium, which originate from the matrix metal 35CrMo. Aluminum at B accounts for 68.34 % and zinc accounts for 30.04 %. It can be seen that it is an aluminum-rich phase, which forms a fine grid, accounting for about 65 % of the volume of the outer layer. The opposite is true at C. The zinc mass ratio is 87.53 % and aluminum is 10.73 %. Therefore, it is a zinc-rich phase, which accounts for about 35 % of the volume of the outer layer. The reason why the aluminum-rich phase and zinc-rich phase are produced is that aluminum and zinc can't form compounds. According to the aluminum and zinc binary alloy phase diagram, there is a eutectic transition of the Al-Zn alloy at about 380 °C. Dendritic aluminum-rich phase precipitates preferentially during crystallization. Then the zinc and silicon atoms will gather around the aluminum-rich phase. As these two atoms continue to increase, the density of the aluminum atom will decrease accordingly, and the aluminum-rich phase of the dendrite boundary will precipitate the zinc-rich phase. Thus, the outermost layer becomes an aluminum-rich phase and a zinc-rich phase.

From figure 4, the main components of the coating are Al, Zn, Fe_2Al_5 , FeAl_3 , and $\text{Al}_{0.5}\text{Fe}_3\text{Si}_{0.5}$. Combined with micrometallographic 4(b), at the beginning of the hot dip, silicon and iron combine to form a Fe-Si compound layer to prevent the further diffusion of aluminum and zinc elements, but the aluminum-zinc-iron-silicon atoms will infiltrate each other. There are still many aluminum atoms that dissolve into the iron matrix to form the FeAl_3 compound with the lowest reaction heat, and the thickness continues to increase. At the same time, the iron atom on the side of the 35CrMo matrix continuously spreads to the FeAl_3 compound layer under thermal action, causing its concentration to

fluctuate, resulting in a thin layer of Fe_2Al_5 . The Fe_2Al_5 phase is a special orthorhombic crystal structure. The atomic saturation is low, often only about 70 %. It provides a channel for the diffusion of aluminum. This phase often produces rapid growth^[6]. The intermediate alloy layer is far from the matrix side, and due to the hindrance of silicon elements, a complex Al-Fi-Si compound barrier layer is formed.

3.4. Static full immersion test

The static corrosion test results in 5% NaCl aqueous solution are shown in Fig.5. During the test, red rust spots were observed on the second day edge of the non-coated matrix until the 20th day, when the surface was covered with thick rust. The aluminum zinc Silicon coating sample did not appear to have a small amount of gray spots until 12 days. At 20 days, it began to corrode partially, showing gray flocculating substances. As can be seen from Figure 5, the corrosion and weightlessness of the 35CrMo matrix and the hot-dip aluminum-zinc alloy coatings have increased with the extension of time, but the weightlessness rate is much greater than that of the coating. It is shown that the corrosion resistance of the matrix can be improved by coating the surface of the matrix with a layer of aluminum and zinc alloy.

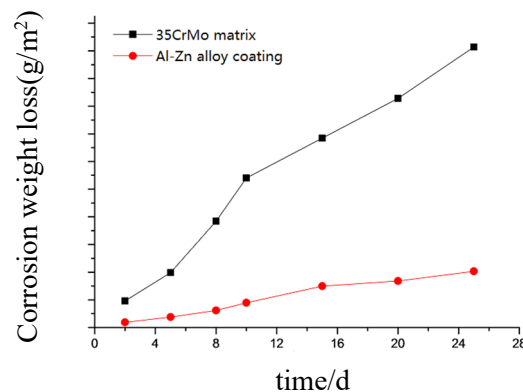
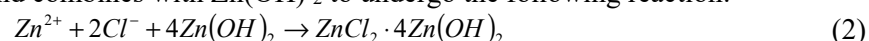


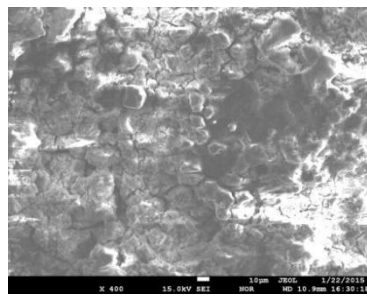
Figure 5. The relationship between weightlessness and time of coating and substrate corrosion.

In order to further study the corrosion resistance of 55 %Al-Zn alloy coatings, the coating after 25 days of corrosion in 5 % NaCl aqueous solution was selected and the surface corrosion area was scanned by SEM. Figure 6(a) is the morphology of the corrosion area of the coating. From the energy spectrum analysis of Figure 6(b), it can be seen that the local corrosion zone of the aluminum-zinc alloy coating contains zinc, aluminum, oxygen, iron, chlorine, silicon elements, and the content of iron and silicon elements has little change before and after corrosion, indicating that local corrosion occurs only on the surface of the coating. The addition of oxygen and chlorine elements means that the coating not only oxidizes but also corrodes with NaCl solution. Compared with the aluminum-rich phase in the coating, the zinc element dropped by about 35%, and the aluminum element changed slightly. Therefore, it can be considered that the corrosion of the zinc element in the initial 55 % corrosion layer is mainly the corrosion of the zinc element. According to the metal chemical point position principle, Zinc rich compared to aluminum rich phase point, the coating is in the process of corrosion, the zinc rich phase of the outer coating tissue dendritic gap has a strong cathode protection effect, Zn rich phase began to corrode:

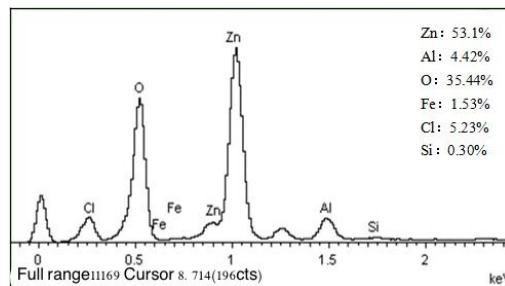


At the same time, because of the presence of Cl^- in the NaCl corrosion medium, it accumulates and erodes locally, and combines with $\text{Zn}(\text{OH})_2$ to undergo the following reaction:





(a) The morphology of the corrosion area of the coating.



(b) EDS scanning results

Figure 6. The static corrosion results of 55%Al-Zn-1.0%Si coating.

Combined with EDS element analysis, the ratio of zinc, chlorine, and oxygen atoms is approximately 3.5:1, and the generator is $\text{ZnCl}_2 \cdot 4\text{Zn}(\text{OH})_2$, which is the same as the result of the above chemical reaction. The above-mentioned corrosion products will cover the zinc rich layer surface. When these two corrosion products accumulate to a certain extent, the flocculant corrosion will be filled in the mesh-rich aluminum phase. Dendritic clearance, It acts as an isolation barrier to slow the corrosion media further into the coating, and the conductivity of these two corrosion products is very low, which has a cathode diffusion effect that inhibits the corrosion media phase^[7]. This process also produces a certain amount of ZnO and $\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$ due to oxidation. With the further deepening of corrosion, the aluminum-rich phase also began to corrode, resulting in $\text{Al}(\text{OH})_3$, covering the surface of the coating to form a dense colloid, which can effectively prevent the corrosion medium factor from penetrating the coating. Finally, the whole coating is gradually transformed into aluminum and zinc phase corrosion^[8].

3.5 Tafel Curve Test

Figure 7 shows Tafel polarization curves of plated and matrix matrixs in 3.5% NaCl aqueous solution. It can be seen from Fig. 7 that after hot dipping the alloy coating, the self-corrosion potential of the matrix sample decreases from -0.6127V to -1.0211V. There is no passivation zone in the both Tafel curves of the coating and the matrix. Therefore, the corrosion of both samples is characterized by active dissolution. The priority of corrosion depends on the self-corrosion potential and self-corrosion current of both samples. However, $i_{\text{corr,matrix}} = 3.921 \times 10^{-5} \text{ A/cm}^2$, $i_{\text{corr,coating}} = 1.325 \times 10^{-5} \text{ A/cm}^2$. As a result, the ratio of self-corrosion current density between hot-dip coating and 35CrMo is about 3:1. According to the principle of electrochemical corrosion, the smaller the self-corrosion current density, the better the corrosion resistance. Therefore, the hot-dipping coating has excellent corrosion resistance. This result is consistent with the static corrosion test results of the coating parts.

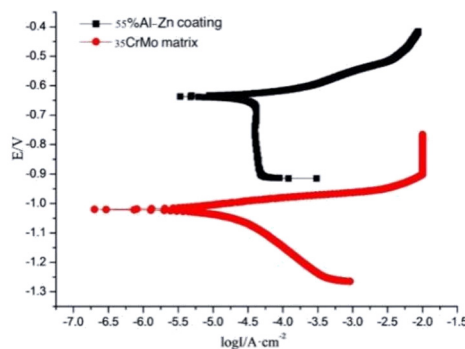


Figure 7. Tafel Polarization curves of the sample before-and-after hot dipping 55%Al-Zn

4. Conclusion:

1. In this experiment, the content of Si in the coating solution is 1.0%, and the quality of coating interface is good.

2. Due to the rapid cooling of the coating solution attached to the surface of the coating parts, the contact interface between the liquid phase and air is bent, resulting in a little micro-folds on the coating surface.

3. XRD analysis indicates after hot dipping 55%Al-Zn-1.0%Si, the major compounds of 35CrMo sucker rod compound layer are Fe_2Al_5 , FeAl_3 and $\text{Al}_{0.5}\text{Fe}_3\text{Si}_{0.5}$.

4. The ratio of weight loss before and after hot dipping is 5.9:1. The ratio of self-corrosion current density is 3:1. It indicates hot-dipping 55%Al-Zn-1.0%Si alloy on the surface of 35CrMo sucker rod can improve the corrosion resistance of 35CrMo sucker rod significantly.

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