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Phosphating and Accelerating Corrosion Behavior on Al-Si Coating of Hot Stamping 22MnB5 Steel

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Abstract: In order to study the relevant of corrosion resistance with hot treatment process condition, verify whether Al-Si alloy coating surface can be treated with zinc salt phosphating. It is prepared several different kinds of hot stamping Al-Si coating of 22MnB5 steel plates. The heating treatment temperature, holding time, thickness of coating and diffusion layer are discussed in this paper. Then phosphating to above plates which are obtained under several different hot treatment conditions. It is found that there exists some phosphating films on surface of several plates, such as No. 4, No. 5 and No. 9 sample, others have none. By scanning electron microscopy analysis method, morphology and microstructure of Al-Si coating and phosphating film are analyzed. By energy spectrum analysis method, all element contents are characterized. The content of Al element in the coating is decreased fom 87% to 8% through phosphating treatment. The content of Si element in the coating is decreased from 10% to below 1%. Because of corrosion of phosphating liquid, Al-Si alloy coating is broken at acid environment. Al is oxidated and become aluminum ion, Si is dissociated and deposited. With the decreasing of Al, anode region is oxidated. Because reduction in hydrogen concentration at cathode zone, pH become higher, when condition reachs to the solubility of zinc phosphate, the phosphating films appeared on surface metal material. The films element increasing, Zn is up to 20%, P is near to 9%, O is up to 34%, phosphating film crystal is main Zn3(PO4)2•4H2O and small amount of Zn2Fe(PO4)2•4H2O. In order to research corrosion resistance between phosphating film and Al-Si alloy coating, it is adopted CCT method to evaluate two passivation films. The result shows that phosphating film can not improve corrosion resistance of materials. On the other side, Al-Si alloy coating has better corrosion resistance, it can reduce corrosion rate of substrate. Through 50CCTs and 70CCTs, the sample NO. 8 shows excellent corrosion resistance. The result shows that the corrosion resistance of relatively good sample of heating treatment process condition is as follows: When heating treatment temperature is 930-950°C and holding time is 3-5min, hot dip plating and stamping of 22MnB5 steel with aluminum, silicon and other elements. It is obtained a continuous and complete coating, which toatal thickness is 42-52um.

Keywords: Hot Stamping, 22MnB5, Al-Si Coating, Phosphating, Corrosion Resistance

1. Introduction

With the worsening of environment and energy shortage, environmental protection, safety, and consideration of energy conservation has become a main development direction of automobile manufacturing industry. The most effect is to reduce vehicle weight to reduce fuel consumption and exhaust emission. Data show that 10% reduction of vehicle weight can save fuel 3%~7% [1-3], so vehicle lightweight has become a key to improve competitiveness of major automobile manufacturers.

Ultra-high strength steel can meet requirements of improving vehicle safety and fuel economy at the same time, it has become a mainstream trend of automotive materials [4-12]. Through a new forming technology, the hot stamping steel is heated to 850-950°C, and holding time is maintained for 3-10min to make it uniformly austenitized, then it is quickly transferred to the die with cooling system for stamping and forming, and the austenitic is transformed into martensite by rapid cooling in the die, so the strength of material is improved. The traditional hot stamping steel without coating will cause the decarburization and oxidation of steel plate surface when it is heated, which will reduce steel surface strength, increase friction coefficient, decrease coating performance and decrease corrosion resistance.

Al-Si coating is the most commonly used in hot-formed steel coating, which is an eutectic Al-Si alloy containing 10wt%Si. The coating has excellent corrosion resistance and high temperature oxidation resistance, which can prevent oxidation and decarburization of the steel plate surface.

In this paper, Al-Si coating high-strength steel plates under different heat treatment conditions are prepared, heating temperature from 890 to 950°C, holding time from 3 to 7 min. The thickness of coatings from 38 to 52um and the thickness of diffusion layers from 2 to 7um are obtained. In order to verify the phosphating performance of Al-Si coating surface. Through zinc phosphating surface treatment, the result shows that if there exists cracks in coating, it will easy to deposite phosphating film grains. however, the cracking of coating indicates that heat treatment process is not good. Whether phosphating film can enhance the protection ability of coating to substrate, it will be tested by accelerating cyclic corrosion method. Through 50CCTs and 70CCTs test conditions, it found that the coating without phosphating film has better corrosion resistance. For example, No. 8 sample has the lowest thinning amount of per unit area. It has no phosphating film and no cracks in Al-Si coating.

By this method, the quality of product can be effectively improved and heat treatment condition can be improved and optimized.

2. Experiment

2.1. Raw Material

Test material is Usibor 1500P which produced by Ancelor&Mitto co., Itd. with 22MnB5 steel as substrate. The Usibor 1500P steel plate is cut into 101mm*90mm rectangular samples with a thickness of 1.6mm. The chemical contents of base are as follows.

Table 1. *Chemical composition of 22MnB5 steel.*

Element	Content (%)	Element	Content (%)
C	0.20~0.25	B	0.002~0.005
Mn	1.10~1.40	Cr	≤0.35
Si	0.15~0.40	Al	0.020~0.060
P	≤0.025	Ti	0.020~0.050
S	≤0.005	Mo	≤0.35

Coating element composition: coating with 87%Al, 10%Si, 3%Fe. The total mass of coating per unit area is 150.0g/m^2, the thickness is 19-30um. The heating treatment temperature is 890-950°C and the holding time is 3-9min.

2.2. Instrument and Reagent

Test instrument: Q-Fog cyclic corrosion tester; JAC-3010 ultrasonic generator; Electronic analytical balance; Su-70 SEM and EDS; Metal in situ spectrometer; other laboratory conventional instruments.

Phosphating treatment liquid: PB-L3035 low temperature zinc phosphating agent and degreasing agent, surface adjustor.

Other chemical reagents: acetone (analytically pure), sodium chloride (analytically pure), 37% hydrochloric acid (analytically pure), Hexamethylenetetramine (analytically pure), all chemical reagents are provided by domestic chemical reagents.

Deionized water for the test: self-made, with conductivity less than 2us/cm.

2.3. Pretreament

Firstly, the surface of substrate is degreased. It is used FC-E2011 low temperature environmental degreasing agent, which is composed of 20g/L FC-E2011AC, 10g/L FC-E2011B, residual deionized water. Immersion swing degreasing method is adopted, the temperature of bath solution is 40°C, and degreasing time is 3min. After degreasing step, rinse with tap water and deionized water for 2-3 times respectively. Observe water droplets on the surface of plate horizontally, it is showed cleaned if water film dose not break in 10s.

The second step is surface adjustment. It is used PL-X liquid surface adjustor [13], which is composed of 2g/L PL-X, 0.6g/L AD-4977, residual deionized water. Immersion surface adjustment method is adopted, the temperature of liquid is 25°C and soaking time is less than 60s.

The third step is phosphating treament. PB-L3035 low temperature zinc phosphating agent is used to treat the samples under different hot stamping treatment processes. 48g/L main salt PB-L3035, 5g/L AD-4813 and17g/L AD-4856 ion concentration regulator, and 9-11g/L neutralizing agent NT-4055 are added to adjust total acidity and free acidity of the phosphating bath to 25-27 points and 0.8-1.2 points [14], and 0.6-0.7g/L accelerator AC-131 is added to adjust the active chemical component concentration to 3.0-4.0 points. The immersion oscillating phosphating method is adopted to keep the temperature of tank solution at 37-40°C for 3min. After phosphating, rinsing phosphated plates with tap water and deionized water for 2-3 times, then soaking them in boiling water at 100°C for 1min, finally drying with hot air at 120°C until there is no water droplets on the surface, and puting to dryer for sealing and storage.

2.4. Analysis and Detection

Physical and chemical properties of phosphating plates are tested. Through indoor accelerated cyclic corrosion test, the corrosion condition of phosphating film and Al-Si alloy coating under condition of 50CCTs and 70CCTs cyclic corrosion are investigated (1 cycle period contains 8h, which is including continuous spraying of 5% NaCl solution at 35°C for 4h, drying at 50°C for 2h, wetting at 95% humidity for 2h). After completion of test time node, the test plates are placed in the room temperature for drying 1-2h, then removing surface corrosive products with hydrochloric acid and corrosion inhibitor [15] solution. The derusting condition is as follows: soaking for 1min at 25°C, and setting at ultrasonic generator for 15min until there is no obvious red rust on plates surface. After derusting step, the surface of test plates are quickly washed with tap water and deionized water, then washing with acetone solvent ultrasonic for 5min, and dried by blowing. Finally, placing the samples in the oven and baking at 150°C for 10min, cool to room temperature, and weighing quality of samples accurately (precision: 0.0001g).

3. Result and Discussion

3.1. Heating Treatment Process and Microstructure of Coating and Phosphating Film

The surface phosphating film of Al-Si coating under different heating treatment condition has certain difference. The microscopic morphologies of six samples are shown in Figure 1. These pictures are magnified by 100 times. There are some alphbets "YES" on pictures, which instead of exist of phosphating film.

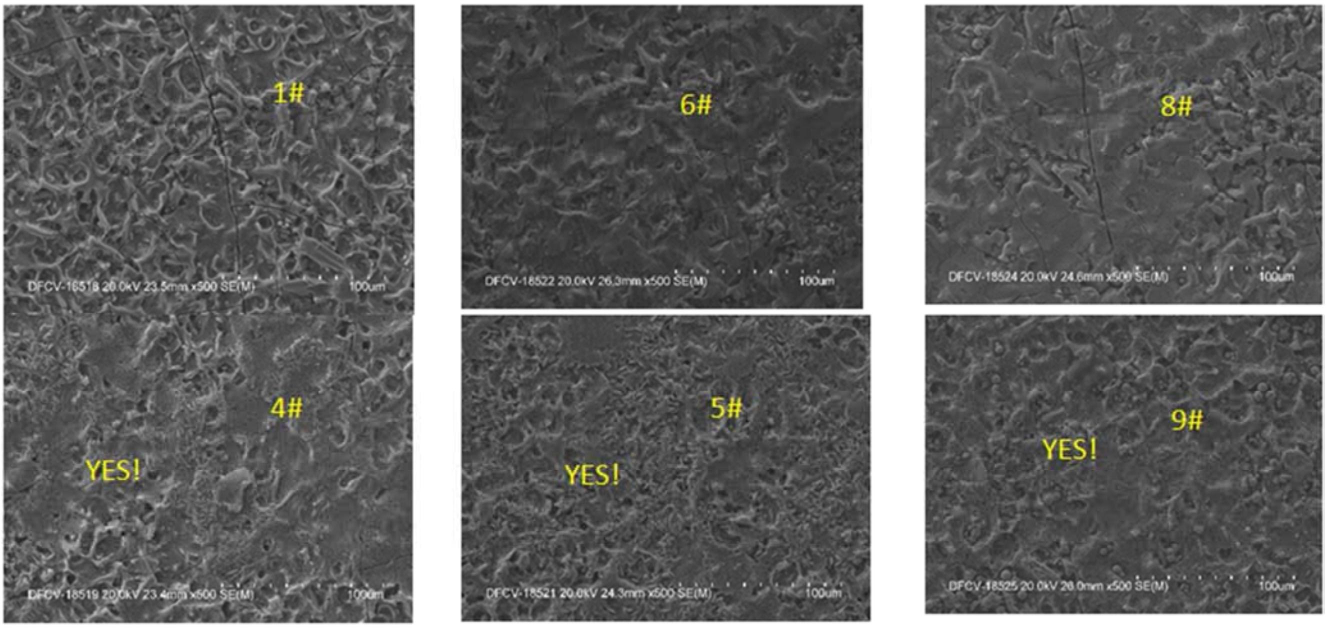
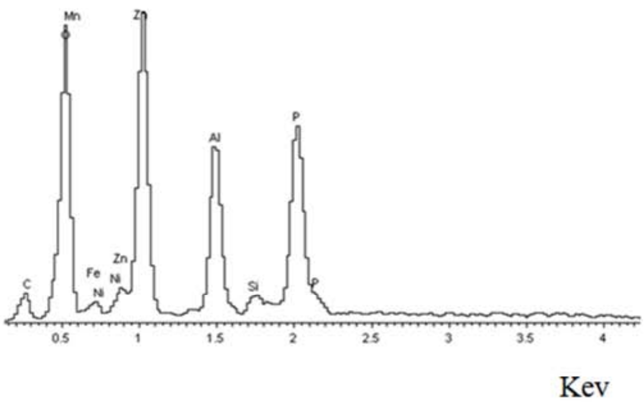


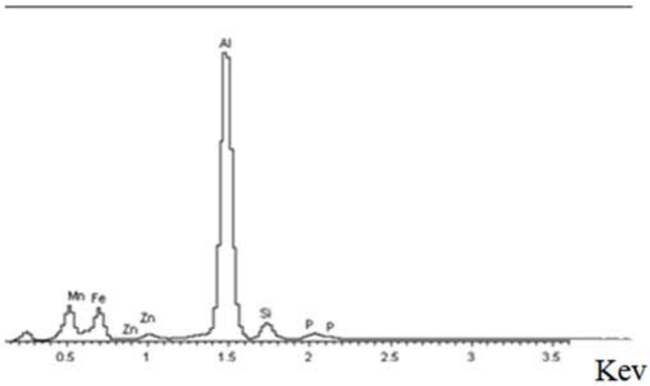
Figure 1. *Microstructure of phosphating film and coating on the surface of six samples (100X).*

It can be seen from Figure 1: No. 4, No. 5, and No. 9 samples have a lot of obvious acicular and granular phosphating film grains, which size are between 3 to 5um and discontinuously distributed in the sag area gaps among coatings. While the other three groups of samples No. 1, No. 6, No. 8 have not been observed obviously phosphating film or only a small amount of phosphating film exists in pictures.



Element	Weight Percentage Content （%）	Atomic percentage content （%）
C K	13.07	24.58
O K	34.66	48.96
Al K	7.74	6.48
Si K	0.66	0.53
P K	8.85	6.45
Mn K	2.00	0.82
Fe K	12.20	4.94
Ni K	0.73	0.28
Zn K	20.09	6.95
Total	100.00	

(a) Complete phosphating film on the coating surface



Element	Weight percentage content (%)	Atomic percentage content (%)
Al K	50.00	65.22
Si K	4.61	5.78
P K	1.02	1.16
Mn K	0.64	0.41
Fe K	42.34	26.68
Zn K	1.40	0.75
Total	100.00	

(b) Incomplete phosphating film on the coating surface

Figure 2. *Composition of coating and phosphating film elements.*

The composition of phosphating film elements on coating surface are quantitatively analyzed, and results are shown in Figure 2. When the coating surface is phosphated, such as No. 4, the element composition is as follows: P accounted for 8.85%, Zn accounted for 20.09%, and O accounted for 34.66%. However, for samples without phosphating on coating surface, such as No. 1, the content of P, Zn, O and other film-forming element is very small, just less than 2%. The reason for difference of phosphating film element on coating surface may be related to the heating treatment process. If coating is good, it will be continuous and complete, the gap between coatings will be small, and iron matrix is well protected, but it prevents chemical reaction with active components in phosphating solution, and deposition of phosphating film cannot be formed. On the contrary, poor heating treatment process will lead to discontinuous and incomplete Al-Si coating, and there will be a large number of gaps among the coatings, so that the substrate can react with external media, which is conducive to the formation of phosphating film.

3.2. Effect of Corrosion Resistance Test Period on Coating and Phosphating Film

3.2.1. Effect of 50CCTs Cyclic Corrosion Test on Coating

By CCT accelerating cyclic corrosion test [16], the coatings of six groups of thermoforming steel plates under different heating treatment processes are analyzed. The test cycle number of accelerating corrosion is 50, and time of every cycle is 8h. The test results are shown in table 2.

Table 2. *Thinning amount of high strength steel plate after phosphating by 50CCTs cyclic corrosion test.*

Sample number	Thickness of coating and diffusion layer (um)	Pre-corrosion mass (g)	After 50CCTs corrosion mass (g)	Thinning per unit area (g/m^2)
No. 1	42/5	108.1325	106.8781	137.9978
No. 4	48/8	108.9188	107.5858	146.6447
No. 5	47/15	108.3368	106.1083	245.1595
No. 6	52/2	108.9753	107.7920	130.1760
No. 8	42/3	107.1165	106.3025	89.5490
No. 9	38/8	108.1973	106.8669	146.3586

(Note: the single side of board is sealed with adhesive tape. The thickness of board is not considered when calculating the area. The effective area S=0.101m X0.09m=0.00909m^2).

The thinning amount per unit area of sample No. 8 is the least one in all samples, which is only 89.5490 g/m^2. The thinning amount per unit area of sample No. 5 is 245.1595 g/m^2, which is 2.74 times than that of sample No. 8.

From the microscopic morphology of 22MnB5 steel plates with two types of surface treatment in Figure 1 and the energy spectrum data in Figure 2, it can be seen that No. 4, No. 5 and No. 9 plates are phosphated plates, and No. 1, No. 6 and No. 8 plates are Al-Si coated plates, but the cyclic corrosion resistance of phosphated plates is not as good as that of Al-Si coated plates. The following conclusions can be drawn: 1) The substrate surface coating with good heat treatment process is continuous and complete, with better quality, better corrosion resistance, lower thinning amount per unit area, but poor phosphating effect; 2) The corrosion resistance of zinc phosphating film to 22MnB5 steel is worse than that of Al-Si coating to 22MnB5 steel.

3.2.2. Effect of 70CCTs Cyclic Corrosion on Coating

The above six groups of samples are subjected to 70CCTs cyclic corrosion test with a test period of 70 cycles. The results are shown in table 3.

Table 3. *Thinning amount of high strength steel plate after phosphating by 70CCTs cyclic corrosion test.*

Sample number	Pre-corrosion mass (g)	After 70CCTs corrosion mass (g)	Quality change (g)	Thinning per unit area (g/m^2)
1#	109.733	107.5658	2.1672	238.4158
4#	109.3063	106.9443	2.362	259.846
5#	110.3317	108.0652	2.2665	249.3399
6#	108.2879	106.2323	2.0556	226.1386
8#	109.9881	108.4898	1.4983	164.8295
9#	110.4078	107.9995	2.4083	264.9395

No. 8 plate has the best corrosion resistance, with the thinning amount per unit area of 164.8295 g/m^2; No. 9 plate has the worst corrosion resistance, with the thinning amount per unit area of 264.9395 g/m^2. By comparing the thinning amount per unit area of the six groups of samples under the cyclic corrosion of 50CCTs and 70CCTs, sample No. 8 showed the best corrosion resistance under both cyclic corrosion test conditions of 50CCTs and 70CCTs. Even if the cyclic corrosion time is increased to 70CCTs, the thinning amount of the plate did not reach 165 g/m^2. Sample No. 9 had the worst performance, and the thinning amount per unit area is close to 300 g/m^2. The thinning amount per unit area is close to 265 g/m^2. No. 4 is close to No. 5, and the thinning amount per unit area is 250-260 g/m^2. The results showed that the corrosion resistance of phosphated film plate is not as good as that of Al-Si coating after 70CCTs cyclic corrosion test, and the more complete Al-Si coating is, the lower thinning amount is after cyclic corrosion test.

3.3. Effect of Metallographic Structure and Element

Hot stamping of Al-Si coating, high strength steel matrix organization for dense alpha Fe horses, austenite in the middle of a very thin layer of narrow strip is given priority to alpha Fe phase diffusion layer. The outermost layer of Al, Fe and Si element based coating alloy phase, due to the layer contact with the outside world, under the influence of external conditions, lead to closer to the surface area in the process of heat treatment, coating will be more discrete, easy to produce porosity, and even rupture.

It can be seen from Figure 3 that diffusion layer consists of three elements, such as Al, Si, Fe. According to the coating line scanning as Figure 4, different element own different depth of displacement. It shows that the depth of diffusion layer is 30-40um, which is distributed in a long narrow strip, most of them are Fe elements, which is given priority to alpha Fe phase. The area adjacent to the diffusion layer is coating area, which depth of displacement is less than 30um and distributed in a wide strip. Among them, Al element is the main element. At the junction of coating area and diffusion layer, the depth of displacement is in the area with high content which is called high Si sandwich area in coating.

In the process of heat treatment, iron atoms are diffused to the coating at high temperature and permeate into the phase of Al-Si alloy. The diffusion layer with a certain thickness at interface between substrate and coating, which is dominated by the alpha Fe phase and contains a small amount of Al and Si element. In the diffusion layer near the matrix region, the content of iron element is high and the distribution is dense and uniorm, that is due tp the high temperature and the fast diffusion rate of iron atoms. As show in Figure 3, forming an uniform narrow and long strip. On the contrary, the temperature close to the coating area is low, the diffusion rate of iron atoms is slow, and the distribution is sparse and the content is low.

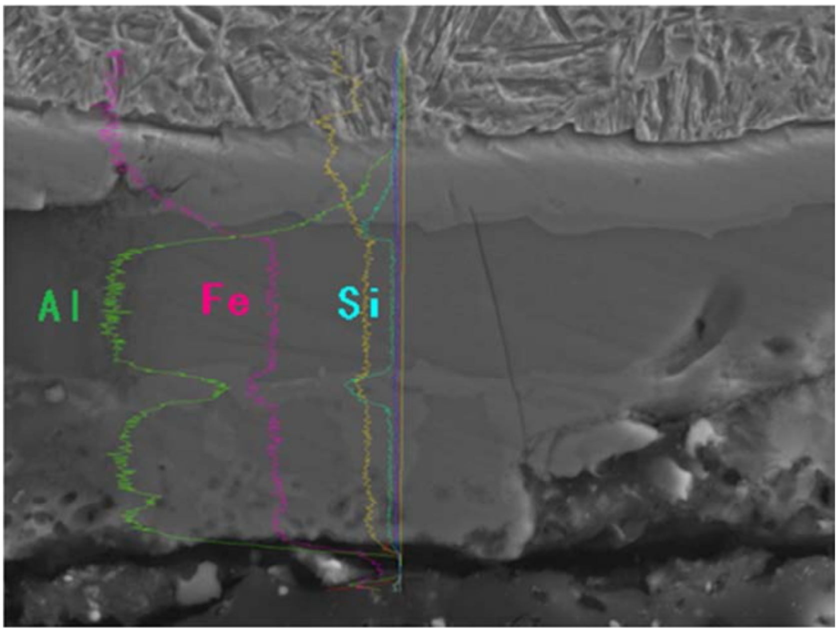


Figure 3. *Plating line scan position.*

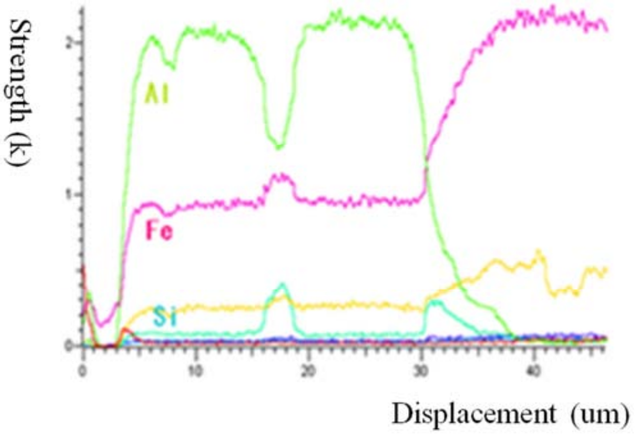


Figure 4. *Coating line scanning element distribution.*

Iron atoms permeate to Al and Si coating areas through thermal diffusion, so that the content of alpha Fe phase in the coating increases. In addition, due to the uneven distribution of materials and energy in the heat and mass trasfer process, the coating surface area will crack, which will inevitably lead to the corrosion resistance level of the entire coating system is reduced.

The above data show that in the process of heat treatment, the lower the temperature is, the smaller the heat and mass transfer rate is proportional to the mass transfer rate (temperature), the shorter the time is, the formation of the diffusion layer thickness is smaller and dose not produce the diffusion layer, and Al-Si coating surface area are less likely to appear crack, smaller influence on corrosion resistance of the coating. The higher the heat treatment temperature (such as no less than 950°C), the higher the heat transfer rate and the shorter the time (such as with 3min), the thinner the formed diffusion layer thickness, will not significantly reduce the effective thickness of Al, Si coating, The coating corrosion resistance will not cause too much impact. Under the same temperature, the longer the time is, the thicker the diffusion layer is, the lower the effective thickness of Al-Si coating will be, and the probability of cracking on the surface area will be increased, which will have a negative impact on the corrosion resistance of coating.

3.4. Analysis of the Influence of Heat Treatment Conditions on Corrosion Resistance

The relationship between different heat treatment process conditions and the thinning amount per unit area under 50CCTs accelerated cyclic corrosion test conditions is studied. The corresponding data are shown in table 4.

Table 4. *Heating treatment process conditions and thinning amount per unit area of 50CCTs.*

Sample number	Heating temperature (°C)	Holding time (min)	Thickness of coating and diffusion layer (um)	Whether contain phosphating film	50CCTs thinning amount per unit area (g/m^2)
1#	890	5	42/5	NO	137.9978
6#	930	3	52/2	NO	130.1760
8#	950	3	42/3	NO	89.5490
4#	910	5	48/8	YES	146.6447
5#	910	7	47/15	YES	249.3399
9#	950	5	38/8	YES	146.3586

The No. 8 sample has owned the best corrosion resistance, the heating treatment condition is as follows: heating temperature is 950°C, holding time is 3min, and the thickness of diffusion layer is 3um. The No. 5 sample has the worst corrosion resistance, the heating treament condition is as follows: heating temperature is 910°C, holding time is 7min, and the thickness of diffusion layer is 15um. Low temperature and uneven heating are not conducive to the diffusion and mixing of Al and Si atoms, and it is difficult to form a complete Al-Si alloy phase on the surface of 22MnB5 steel substrate, resulting in defects in the coating, resulting in incomplete coating on the substrate, poor corrosion resistance, the appropriate temperature is 930-950°C. To control the insulation time, the time is too long, the brittle deformation of the crystal tendency to increase, the integrity of the coating becomes worse, 3-5min is more suitable. When the temperature is 930-950°C and the holding time is 3-5min, the thickness of the diffusion layer in the Al-Si coating is not more than 5um, and the thickness of the coating is 42-52um. Under this condition, the corrosion resistance of the coating is better.

4. Summary

1) The negative growth law of phosphating fim under different heating treatment condition is obtained through zinc salt phosphating treatment of Al-Si coating steel plate formed by hot stamping, and the microscopic morphology of coating surface is analyzed. The better the heating treatment conditions, the more complete the coating, but the worse the phosphating effect. Conversely, the heating treatment process is poor, the formation of discontinuous and incomplete coating, but the phosphating effect is very good, phosphating film density is higher.
2) By 50CCTs and 70CCTs accelerated corrosion test, six kinds of Al-Si coating plates under different hot treament stamping process are tested. No. 8 sample has the lowest thinning amount per unit area through 50CCTs and 70CCTs. The data of corrosion resistance shows that the better heating treatment process, the more complete and dense of coating, but the worse phosphating effect.

3) When the heating treatment temperature is 930-950°C and the holding time is 3-5min, after the hot dip plating and stamping of 22MnB5 steel with Al, Si and other elements, the thickness of Al-Si coating is 42-52 um, a continuous and complete strip. The diffusion layer is thin and uniform, and the thickness is no more than 5um. Under this condition, the corrosion resistance is better.

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