Research on the corrosion resistance of micro alloyed press hardened steel with thin aluminum silicon coating

Yi Feng[1,2,†], Hui Wang[3], Deliang Zhang[2], Hongzhou Lu[4], Jie He[1], Shilong Zhou[5], Xiang Gao[2] and Guangjie Huang[1]

[1]*Chongqing University, Chongqing 400044, China*
[2]*China Automotive Engineering Research Institute Co., Ltd. Chongqing 401122, China*
[3]*Southwest technology and engineering research institute, Chongqing 400039, China*
[4]*CITIC-CBMM Microalloying Technical Center, CITIC Metal Co., Ltd, Beijing 100004, China*
[5]*Maanshan Iron & Steel Co., Ltd, Ma'anshan 243003, China*
[†]*E-mail: fengyi@caeri.com.cn/ringer2003@163.com*

In recent years, the press hardening steel with thin aluminum silicon coating independently developed by relevant domestic institutions has gradually been applied in the automotive industry. The issue of whether thin aluminum silicon coated press hardening steel can replace traditional aluminum silicon coated press hardening steel in terms of corrosion resistance has always been a concern for the domestic industry. This article compares the salt spray corrosion performance of three sets of samples, including traditional aluminum silicon coated press hardening steel and microalloyed thin aluminum silicon coated press hardening steel. The results showed that the weight loss rate and corrosion rate of the two groups of microalloyed samples in different states were lower than those of traditional aluminum silicon coated press hardening steel after salt spray corrosion treatment for 3-15 days, demonstrating better corrosion resistance. The refinement of the matrix structure of steel through microalloying treatment and the suppression of high stress corrosion tendency of steel quenching microcracks through thinning treatment of coatings may be the two main reasons for the stronger corrosion resistance of the second and third group samples.

Keywords: Hot stamping; Salt spray corrosion; Microalloying; Thin aluminum silicon coating.

1. Introduction

In recent years, with the increasing demand for vehicle quality in the consumer market, various coated press hardened steels have been widely used in the manufacturing of passenger car safety parts. Aluminum silicon coated hot stamped steel is a type of steel that has strong high-temperature oxidation resistance and corrosion resistance by coating a layer of aluminum silicon alloy film (mainly composed of aluminum, silicon, and a small amount of other alloy elements) on the surface of the steel plate. Aluminum silicon coated hot stamped steel is also the most widely used and successful type of steel in the global coated hot stamped steel field[1]. At present, the global annual usage is over 4 million tons, while the usage in China is about 1 million tons per year. Although traditional aluminum silicon coated hot stamped steel has significant performance advantages, it also faces some shortcomings[2]. Firstly, the presence of aluminum silicon coating is not conducive to ensuring the toughness of the hot stamped parts matrix. This is because the aluminum silicon coating is an intermetallic compound, which belongs to brittle materials. Moreover,

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after quenching, a carbon rich layer will form between the aluminum silicon coating on the surface of the steel plate and the matrix, which is harmful to the toughness of the parts[3]. Therefore, in recent years, China's automotive hot stamping industry has also been committed to the research and promotion of various advanced coated hot stamped steel products, among which one of the most representative achievements is thin aluminum silicon coated hot stamped steel. Currently, the domestic industry has been highly concerned about whether thin coated aluminum silicon hot stamped steel can achieve the same level of corrosion resistance as traditional aluminum silicon coated hot stamped steel. Based on this, this article takes traditional and thin aluminum silicon coated press hardened steel as the research objective, conducts salt spray corrosion performance comparison experiments, and combines relevant material microstructure characterization methods to analyze the corrosion resistance advantages and disadvantages of the two materials.

2. Test materials and methods

There are three sets of materials tested in this article. The first group is traditional press hardened steel with aluminum silicon coating; The second and third groups are both press hardened steel with thin aluminum silicon coating. All three sets of samples are in the quenched state, and their composition is shown in Table 1. In addition to conventional elements, a certain amount of niobium and vanadium were added to the matrix of the second and third groups of steel to enhance the strength and toughness of the steel. In addition, the hot stamping process conditions of the three groups of samples were also different. The first and second groups of samples were obtained based on conventional process conditions, while the third group of samples did not apply dew point control during the heating process. Table 2 shows the relevant mechanical properties of the three groups of samples in the quenched state. The hot stamping process parameter conditions are 930°C+5 minutes. It can be seen that the mechanical properties of the three groups of samples in the quenched state meet the general requirements of the current industry.

Table 1 Chemical composition of three sets of samples（wt%）

Element	C	Si	Mn	P	S	Cr	Nb	V	Ti
Group 1#	0.23	0.20	1.23	0.009	0.002	0.17	0.003	0.004	0.032
Group 2、3#	0.23	0.22	1.26	0.008	0.002	0.16	0.034	0.033	0.030

Table 2 Mechanical properties of three sets of samples (quenched state)

-	$R_{p0.2}$/MPa	R_m/MPa	$A_{50\ mm}$/%	HV10
Group 1#	1142	1516	6.3	473
Group 2#	1138	1511	6.3	469
Group 3#	1148	1503	6.4	470

Salt spray corrosion comparative tests were conducted on three groups of samples. The experimental equipment was YWX-020F-GB salt spray box. The test process have been carried out in accordance with standards such as GB/T10125-2021 and GB/T16545-2015. The entire experimental process was divided into two steps: neutral salt spray test and weighing of corrosion products removed through acid washing. The size of the neutral salt spray corrosion test sample is 20mm × 50mm × 1.4mm. 24 hours is a test cycle, in which the spray time is 11 hours. Each group has 5 samples, and at each interval of 3 days, 6 days, 9 days, 12 days, and 15 days, one samples were taken from the salt spray box to observe the surface morphology of the samples and evaluate their degree of corrosion. The parameters of the salt spray test are shown in Table 3.

Table 3 Neutral salt spray test parameters

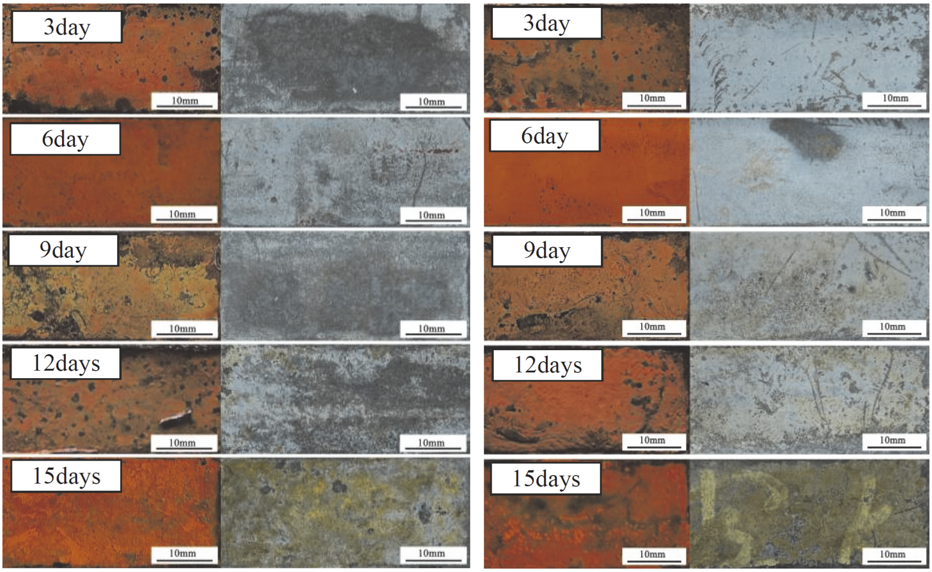
Parameter	Value
Solution concentration(NaCl)	50±5g/L
PH value	6.5~7.2
Salt spray box temperature/°C	35±2
Settlement rate/(mL/80cm^2·h)	1.0~2.0
Spray time/h	11
Interval time/h	13

The surface corrosion of each sample have been removed using acid washing method after completing the neutral salt spray test. Then we used a vessel to weigh the weight of corrosive substances on the surface of each sample. The corrosion resistance of each sample have been evaluated based on parameters such as the weight of corrosive substances produced and their corrosion rate (the weight of corrosive substances produced per hour per unit area of the sample) under the same salt spray corrosion time conditions. In addition, using microscopic characterization methods such as OM and SEM, the surface corrosion morphology of the samples was observed, and the salt spray corrosion resistance performance of the different groups of samples was analyzed.

3. Test result

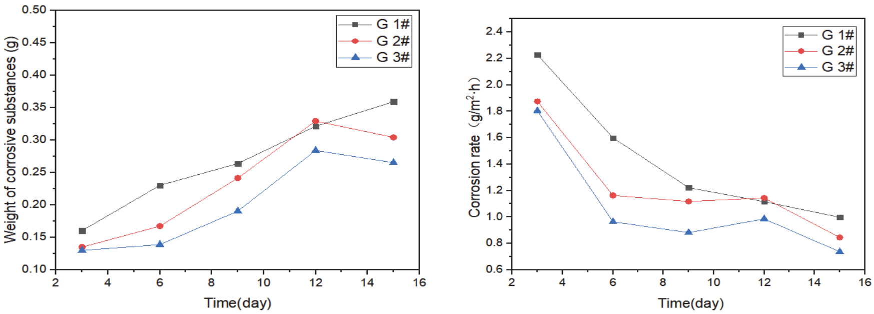
Figure 1 shows the morphology of neutral salt spray corrosion and acid washing states of press hardened steel with conventional and thin aluminum silicon coatings under different time conditions. It can be seen that as the corrosion time increases, the degree of corrosion on the surface of the two types of steel is not significantly different from a macro level.

Figure 2 shows the changes in the weight and rate of corrosives of the three groups of samples after spray treatment at different times. It can be seen that as the corrosion time prolongs, the weight of corrosive substances produced on the surface of the three groups of samples gradually increases, which is also in line with general cognition. Secondly, with the prolongation of corrosion time, the corrosion rate of all three groups of samples showed a gradually decreasing trend, that is, the intensity of corrosion reaction gradually weakened with the prolongation of time. In addition, under the same corrosion time conditions, the weight and corrosion rate of surface corrosion substances in the second and third groups of samples are smaller than those in the first group, indicating that the salt spray corrosion resistance of the second and third groups of samples is stronger than that of the first group.



(a) Group 1#—conventional coating (b) Group 2#—thin coating

Figure 1 Surface corrosion morphology of press hardened steel with two types of aluminum silicon coatings

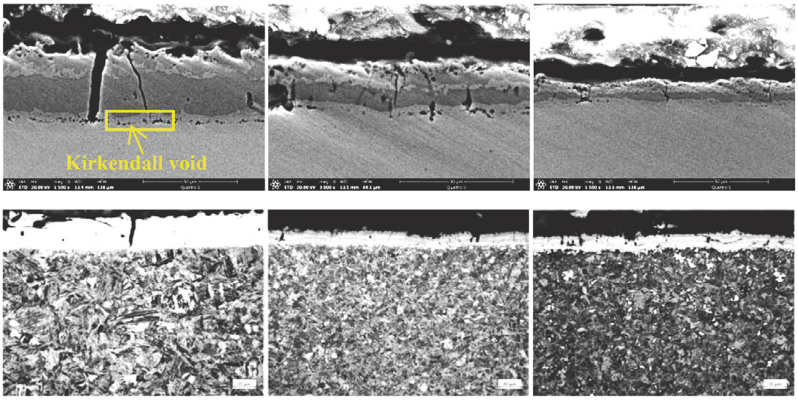


(a) Weight&Time (b) Speed&Time

Figure 2 Comparison results of salt spray corrosion resistance of three groups of samples

4. Discussion

Firstly, Figure 3 shows the cross-sectional microstructure of three groups of steel after 15 days of salt spray corrosion. It can be seen that the surface corrosion layers of the three groups of steel have not diffused into the steel substrate, indicating that under the experimental conditions in this article, the thin aluminum silicon coating can also meet the corrosion resistance requirements of press hardened steel (not inferior to conventional coatings).



(3) Group 1# (b) Group 2# (c) Group 3#

Figure 3 The microstructure of three groups of samples after 15 days of corrosion

Secondly, as the corrosion time prolongs, the weight of corrosive substances on the surface of the three groups of samples gradually increases, but the corrosion rate gradually decreases. Previous studies have shown that the rust layer on steel in salt spray environments is generally composed of stable α-FeOOH, unstable β-FeOOH, and Fe_3O_4 phases[4]. Due to the presence of chloride ions, as the corrosion time increases, the active β-FeOOH will transform into loose Fe_3O_4, allowing chloride ions to penetrate the oxide layer on the surface of the steel plate and microcracks in the coating into the steel substrate, thereby accelerating the corrosion of the steel. However, on the other hand, the formation of α-FeOOH phase can hinder the penetration of chloride ions into the steel matrix, thereby reducing the corrosion rate of the steel[4]. As the corrosion time prolongs, there is no doubt that the thickness of the stable α-FeOOH phase structure layer will gradually increase, resulting in a gradual decrease in the macroscopic corrosion rate of the sample.

In addition, the salt spray corrosion resistance of press hardened steel with thin aluminum silicon coating for microalloying is better than that of conventional press hardened steel with aluminum silicon coating. The author believes that there may be two possible reasons. Firstly, the thickness of the aluminum silicon coating will have an impact on the salt spray corrosion resistance of the material. The thickness of the aluminum silicon coating on conventional hot stamped steel in this article is 35~40 μm, and the thickness of the aluminum silicon coating on two groups of microalloyed hot stamped steel is 13~18 μm. As shown in Figure 3, after conventional coating hot stamping quenching, a large number of longer and wider microcracks will form, and the tip of these cracks has a very high stress concentration effect. The longer the length of a crack, the higher the stress intensity factor at its tip, which means that the stress concentration effect at that location is stronger, making it easier to induce stress corrosion at the crack tip due to the dual effects of stress concentration and corrosive media. In addition, although the wider the crack width, the weaker the stress concentration effect at its tip, the larger the spatial volume of the wide crack, and the easier it is for external harmful substances to enter the material matrix through the crack and cause corrosion.

The second reason may come from the differences in the structural characteristics of the matrix structure between the two press hardened steels with different compositions in this article. The second and third groups of samples have finer microstructures due to the addition of microalloying elements such as niobium and vanadium (Figure 3). Previous research has shown that the grain size of metal materials has a significant impact on their corrosion resistance. The smaller the grain size, the weaker the segregation of various harmful elements at the grain boundaries, and the lower the local corrosion current density (higher self corrosion potential)[5]. These factors are all beneficial for improving the corrosion resistance of steel. In addition, after the reduction of grain size, the number of small angle grain boundaries in the steel matrix increases. Due to the relatively low migration rate of small angle grain boundaries (low interface energy), they are relatively more stable, further improving the corrosion resistance of the steel[6]. Of course, there is also a view in the industry that an increase in grain boundaries leads to an increase in the total number of defects in the matrix, which will reduce the corrosion resistance of the steel[7]. From these research results, the author believes that the influence of grain size on the corrosion resistance of steel is related to the range of grain size. When the grain size is within a very small range, increasing the grain size is dominated by the above-mentioned unfavorable factors, which reduces the corrosion resistance of the steel; When the grain size increases to a certain value, the dominant factor is the decrease in the total number of defects in the matrix, which significantly improves the corrosion resistance of the steel. From the current range of grain size in general automotive steel, reducing grain size is still more conducive to improving the corrosion resistance of steel.

In addition, as shown in Figure 3, it can also be seen that the first group of samples has a large number of micro voids near the coating area, and their number is more than that of the second and third groups. These micropores are known as Kirkendall voids. Kirkendall voids are formed during the hot stamping process due to the inconsistent diffusion rates of iron and aluminum elements. Due to the thin coating thickness of the second and third groups of samples, the diffusion distance of elements is shorter, resulting in weaker diffusion differences between elements compared to the first group. Ultimately, the number of Kirkendall voids formed in the coating area of the second and third groups of samples is less than that of the first group. The impact of these Kirkendall voids on corrosion resistance is similar to cracks, and their presence will increase stress concentration at the junction of the coating and substrate, which is detrimental to the corrosion resistance of the material. By thinning the coating thickness, reducing the number of Kirkendall voids in the coating/substrate area is obviously beneficial for further improving the corrosion resistance of steel.

In summary, the refinement effect of microstructure brought by microalloying and the negative impact of reducing coating thickness to suppress quenching cracks may be the two main reasons for the better corrosion resistance of the second and third group samples. At present, the price of aluminum silicon coated hot stamped steel remains high. Adopting the route of thin coating and microalloying composite technology may be a new choice for automotive companies, hot stamped parts and steel production enterprises to better balance product performance and cost.

5. Conclusions

This article conducts a systematic comparative test on the neutral salt spray corrosion resistance of three sets of press hardened steel quenched samples with two alloy compositions and aluminum silicon coating thickness specifications. The results showed that with the extension of test time, the weight of corrosive substances indicated by the steel gradually increased in the three groups of samples, but the corrosion rate gradually decreased. In addition, press hardened steel samples based on niobium vanadium composite microalloying and thin coating treatment have stronger salt spray corrosion resistance. The refinement of the matrix structure of steel through microalloying treatment and the suppression of high stress corrosion tendency of steel quenching microcracks through thinning treatment of coatings may be the two main reasons for the stronger corrosion resistance of the second and third group samples.

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