Improvement Study of Hydrogen Embrittlement Resistance of Al-Si Coated Hot Stamped Components

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Abstract. Because of its ultra-high strength, press hardening steel and hot stamped parts are widely used in the reinforcement and lightweight structure of car bodies. At present, there are hydrogen embrittlement barriers in PHS1500~PHS2000 materials with coating and PHS1800~PHS2000 materials without coating. In this paper, based on the conventional thickness coating PHS1500 without niobium and the thin thickness coating PHS1500 with niobium, the corresponding automobile hot stamped front crash beam parts are trial produced. The trial production process is completed under the dew point control condition of -20 °C. Samples were taken from hot stamped parts made of two materials. Firstly, based on the automotive industry standard T/CSAE 155-2020, a U-shaped constant bending load test was carried out to compare the hydrogen embrittlement resistance of parts made of two materials. The results show that under the same external load conditions, the fracture time of the sample of thin coating containing niobium with austenitizing time of 220 s is higher than that of the sample of conventional coating without niobium with austenitizing time of 300 s. Further, TDS and slow strain rate tensile tests were carried out on the samples of the two materials. The results show that the thin coating containing niobium has low diffusive hydrogen content and strong resistance to hydrogen damage. The fundamental reason why the samples with thin coatings containing niobium have stronger hydrogen embrittlement resistance is the regulation effect of niobium on grain boundaries, precipitation and retained austenite, and the stronger inhibition effect of thin coatings on hydrogen induced cracks.

Keywords: Press hardening steel · Hydrogen embrittlement · Microalloying · Al-Si coating

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1 Introduction

In recent years, with the complex changes of the global economic situation, the automobile manufacturing industry has paid more and more attention to the materials and products with high performance and high cost performance. Compared with light alloy and carbon fiber composite materials with high price and relatively complex process, high-strength steel materials are gradually favored by the majority of automobile enterprises [1–3]. As the largest automobile manufacturing country in the world, hot stamping technology has been developed in China for nearly 20 years. Based on the comprehensive advantages of performance and cost, hot stamping has become one of the most important advanced materials and manufacturing technologies for the future new energy vehicles and commercial vehicles to achieve lightweight [4]. At present, based on the comprehensive use requirements of oxidation resistance and corrosion resistance, Al-Si coated press hardening steel is more and more widely used in the industry, and hydrogen embrittlement has always been the most significant application risk of this kind of steel. Compared with bare sheet materials, coated press hardening steel has a higher risk of hydrogen embrittlement because it is easy to be penetrated by hydrogen atoms during high-temperature heating (especially when the dew point is not well controlled). In the process of material quenching, these hydrogen atoms will be fixed in the matrix, and in the subsequent part baking process, because of the existence of the coating, these hydrogen atoms are difficult to overflow the matrix, which will lead to hydrogen embrittlement during the use of the part. Therefore, the industry is paying high attention to the hydrogen embrittlement of coated hot stamped parts [5, 6]. In fact, it is difficult to really suppress the hydrogen embrittlement of the coated plate through the optimization of the hot stamping process. The industry still hopes to effectively suppress or even eliminate the hydrogen embrittlement of the coated plate through the modification of materials [7, 8]. In this paper, hydrogen embrittlement tests were carried out on two kinds of Al-Si coated press hardening steels with different composition and coating thickness. The mechanism of improving the hydrogen embrittlement resistance of Al-Si coated hot-stamped parts by microalloying and optimizing the coating structure was discussed through relevant micro characterization tests.

2 Test Material and Study Methods

In this paper, two kinds of Al-Si coated press hardening steel sheet materials are selected as the research object. There is little difference in the content of main alloy elements between the two steels, and only one of the materials added 0.03%–0.04% niobium. The thickness of both steels is 1.4 mm. In addition, the thickness of the coating on the surface of press hardening steel containing niobium is thin, while the surface of materials without niobium is a conventional Al-Si coating (Table 1).

Two kinds of Al-Si coated plates were hot stamped to obtain corresponding parts. The hot stamped part selected in this paper is the anti-collision beam. Figure 1 shows the appearance of the hot stamped anti-collision beam. There are two kinds of hot stamping process conditions. Among them, the maximum heating temperature involved in the two processes is 930 °C (using progressive heating). The heating and holding time of

Table 1. Chemical composition of two press hardening steels (wt.%).

Brand	C	Si	Mn	P	S	Cr	Nb	Ti
Conventional coating	0.24	0.23	1.24	0.008	0.003	0.15	0.002	0.032
Thin coating	0.23	0.22	1.25	0.008	0.002	0.16	0.035	0.033

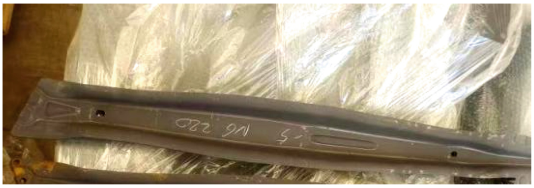


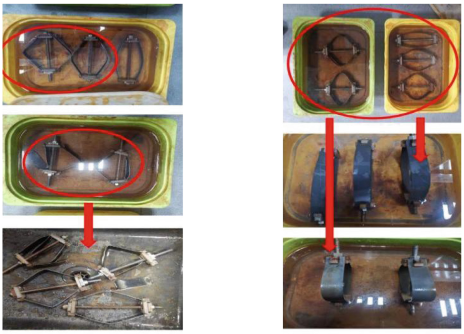
Fig. 1. Hot stamped anti-collision beam.

conventional Al-Si coated hot stamped sheet is 300 s, and the dew point is controlled (-20 °C) during the heating process. The heating and holding time of niobium microalloyed sheet with thin coating is 220 °C with -20 °C dew point control. The transfer time during the trial production of two groups of samples is uniformly controlled to be about 10 s. In addition, the hot stamping quenching pressure of the two groups of samples is 800 tons, and the quenching pressure holding time is 10 s.

Samples were taken from three groups of hot stamped samples of coatings obtained under two different process conditions to carry out relevant microstructure and property tests. Sampling, testing and analysis items include tensile and hydrogen embrittlement. Relevant micro characterization tests (OM/SEM/EBSD/TDS/APT) were carried out. Through the above research work, the mechanism of Nb microalloying and thin coating treatment to improve the hydrogen embrittlement resistance of coated press hardening steel sheet was discussed.

3 Hydrogen Embrittlement Test Results

Firstly, two groups of hot stamped samples were tested for hydrogen embrittlement in accordance with the requirements of T/CSAE 155-2020 standard. It should be pointed out that the work in this paper is not oriented to enterprise material certification, and the test goal is to make differences. Therefore, the loading load range in the test process is from the yield strength close to the material to the tensile strength close to the material, and the working conditions are relatively bad. It is intended to show the advantages of hydrogen embrittlement resistance of hot stamped parts containing niobium and with thin coating. Figure 2 shows the photos of two groups of samples after the test. The results are shown in Table 2. It can be seen that the hot stamped samples of Al-Si coating without niobium in conventional thickness did not break under the maximum set span of 145 mm (close to the yield strength of the material), and all the other samples broke within 300 h. The hot stamped samples of thin coatings containing niobium did not fracture within 300 h under dew point control. From the above results, the risk of hydrogen embrittlement in



Spans: 135-90mm fractured(300h)

(a) Conventional coating

Spans: 145-90mm not fractured(300h)

(b) Thin coating

Fig. 2. Hydrogen embrittlement test process and appearance after test of two groups of hot stamped samples.

Table 2. Hydrogen embrittlement test results.

Group & span		Observation time point (h)							
		0	20	44	68	92	116	140	300
Conventional coating	145	√	√	√	√	√	√	√	√
	135	√	×						
	120	√	×						
	105	√	×						
	90	√	×						
		0	24	48	72	96	120	144	300
Thin coating	145	√	√	√	√	√	√	√	√
	135	√	√	√	√	√	√	√	√
	120	√	√	√	√	√	√	√	√
	105	√	√	√	√	√	√	√	√
	90	√	√	√	√	√	√	√	√
Cracked × **Not cracked** √									

the actual hot stamping process of thin coated press hardening steel containing niobium is much lower than that of conventional coated press hardening steel.

4 Discussion

4.1 Further Test Verification

From the above test results, it can be seen that the fundamental reason for the stronger hydrogen embrittlement resistance of hot stamped parts with thin coatings containing

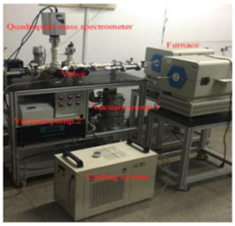
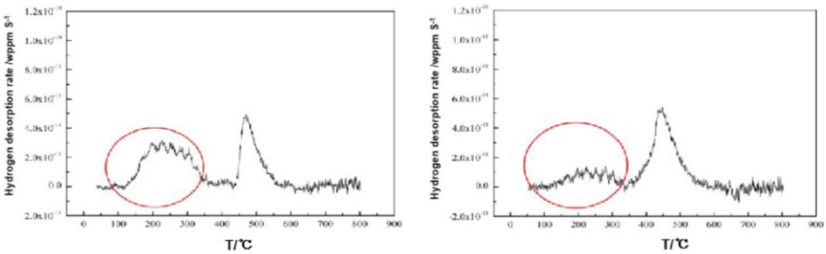


Fig. 3. TDS test equipment.

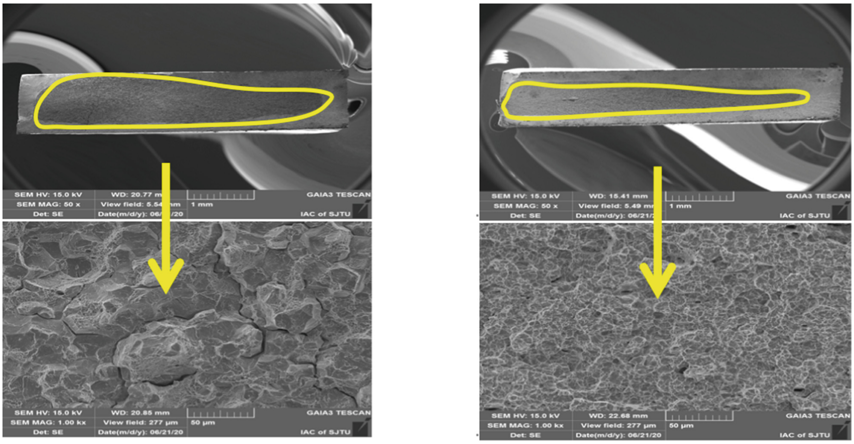
Fig. 4. Slow strain rate tensile test equipment.

niobium comes from the influence of niobium and thin specification coatings. TDS and slow strain rate tensile tests were carried out on the two materials. First, Fig. 3 shows the appearance of TDS test equipment. Figure 4 shows the appearance of slow strain rate stretching test equipment. As is shown in Fig. 5, it can be seen that the diffusible hydrogen content in the matrix of thin coated press hardening steel containing niobium is lower than the conventional coating materials without niobium. The former has more obvious hydrogen precipitation peak in the range of 200–400 °C. Obviously, the former is less likely to form enough diffusible hydrogen in the matrix, that is, hydrogen is less likely to accumulate, and thus has a lower risk of hydrogen embrittlement. Secondly, as can be seen from Table 3, as the same as the TDS test results, under the same test conditions, the strength plastic loss of thin coated press hardening steel containing niobium is weaker than that of conventional steel, indicating that the former has stronger resistance to the negative impact of hydrogen than the latter, that is, the former is less prone to failure after hydrogen permeation. Figure 6 shows the fracture morphology of the two materials after slow strain rate tension. It can be seen that the area of brittle fracture zone (reflecting the effect of hydrogen embrittlement on fracture) on the fracture surface of Nb containing steel is significantly smaller than that of Nb free steel. In addition, the fracture morphology in the hydrogen embrittlement dominated region of Nb containing steel still retains significant ductile fracture characteristics, while the same fracture region of Nb free steel shows significant brittle fracture characteristics. The above test results further verify the advantages of hydrogen embrittlement resistance of press hardening steel with thin coating containing niobium.



(a)Conventional coating (b)Thin coating

Fig. 5. TDS test results.



(a) Conventional coating (b) Thin coating

Fig. 6. Slow strain tensile fracture morphology of two materials.

Table 3. Slow strain rate tensile test results.

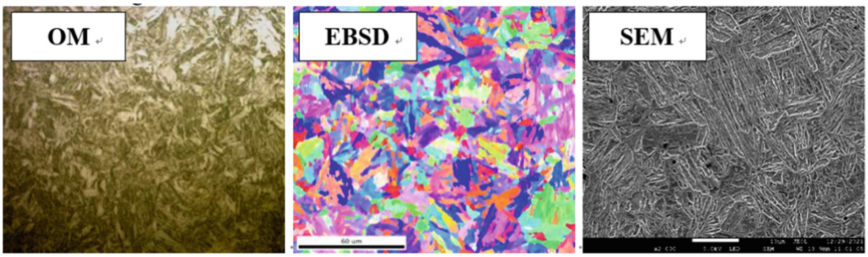
Component	State	No.	Elongation *A/%*		HIC index */%*
Conventional coating	H^-	1#	A_0	6.5	46.2
	H^+	2#	A_H	3.5	
Thin coating	H^-	1#	A_0	6.7	41.8
	H^+	2#	A_H	3.9	
Remarks	H^-: not charged, H^+: charged. The hydrogen charging solution is 0.2 mol/L NaOH, the hydrogen charging current is 3.6 mA/cm^2, and the tensile rate is 0.015 mm/min. HIC = $[(A_0\text{-}A_H)/A_0]\bullet100(\%)$				

4.2 Effect of Microalloying

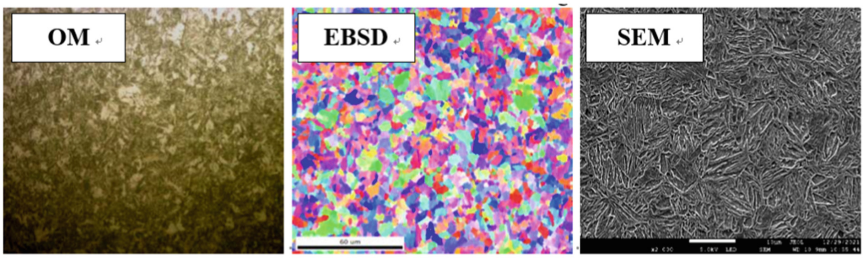
As described above, the hydrogen embrittlement resistance of the thin coated press hardening steel sheet added with niobium element is stronger than that of the conventional coated press hardening steel without niobium. There is no doubt that the role of niobium is dominant. There have been many studies on the effect of niobium on improving the service properties of press hardening steel [7–10]. Refining the structure, second phase precipitation as a hydrogen trap, reducing the matrix carbon content and then introducing a small amount of retained austenite are the three key factors to improve the hydrogen resistance of press hardening steel. First, as shown in Fig. 7(a)–(b), the matrix lath martensite of Nb containing press hardening steel is small, and the number of grain boundaries increases, which will play a stronger role in inhibiting the diffusion of hydrogen in the matrix, that is, it can more effectively inhibit the accumulation of hydrogen in the matrix. In addition, it can be seen from Fig. 7(c) that the number and proportion of large angle grain boundaries in the matrix of niobium microalloyed steel are higher than those of traditional steel. Since the large angle grain boundaries have stronger hydrogen trapping effect, the finer matrix will enhance the barrier effect of grain boundary system on hydrogen diffusion. As shown in Fig. 8(a), the results of three-dimensional atom probe test on the matrix of niobium containing steel show that there is a certain enrichment of hydrogen at the interface between niobium carbide and matrix, which verifies its trapping effect on hydrogen. The relevant literature on the hydrogen trapping effect of the second phase of niobium has been finalized [11], which will not be detailed here. The test results in this paper are consistent with the test conclusions in literature [11]. Third, the addition of niobium reduces the hardenability of the matrix properly, so that a small amount of retained austenite will appear in the matrix after quenching, which will play a role of hydrogen trap (the diffusion coefficient of hydrogen in austenite is significantly lower than that in martensite). As can be seen from Fig. 8(b), through the three-dimensional atom probe test, the hydrogen element enriched in the residual austenite in the matrix is observed, which verifies the above conclusion. In a word, the modification of the matrix by niobium is one of the main reasons to improve the hydrogen embrittlement resistance of the coated press hardening steel.

4.3 Effect of Coating

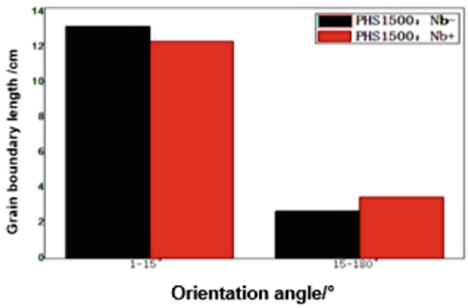
In order to avoid oxidation and decarburization on the surface of hot stamped automobile parts, Al-Si coated press hardening steel plates have been widely used in automobile manufacturing industry at home and abroad in recent years. Compared with the press hardening bare sheet materials with the same strength, the Al-Si coated press hardening steel with the traditional thickness often has the problem of relatively low toughness. Therefore, in recent years, the industry at home and abroad are also trying to improve the toughness of the coating by modifying the design to meet the comprehensive service performance requirements of automotive parts. At present, the main modification method for Al-Si coating in domestic industry is to appropriately reduce the thickness of the coating, so as to avoid many problems of conventional coating. Literature [12] makes a comparative analysis on the conventional evaluation of the microstructure, mechanical



(a) Conventional coating.

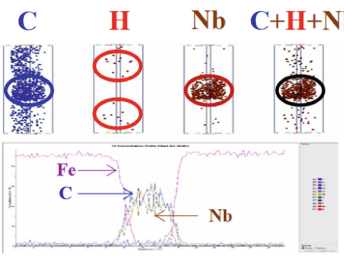


(b) Thin coating.

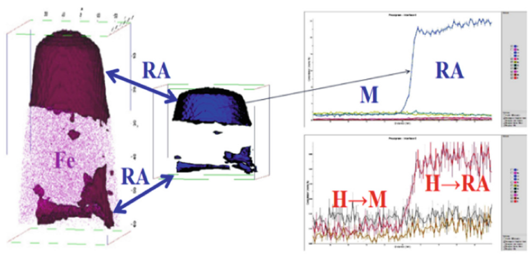


(c)The total length of grain boundaries at different angles in the matrix of two materials.

Fig. 7. Comparison of lath martensite size in matrix of two materials.

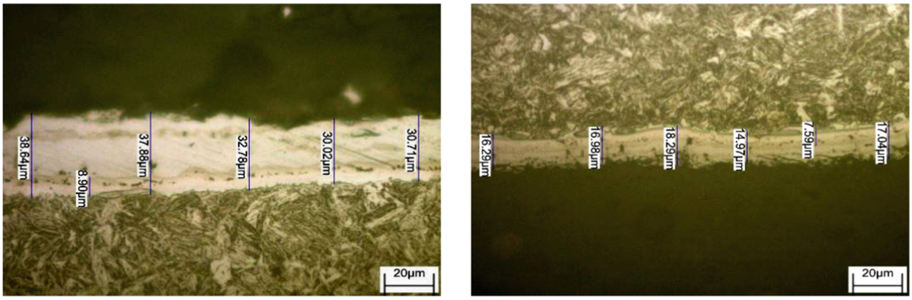


(a) Second phase & hydrogen



(b) Retained austenite & hydrogen

Fig. 8. Examples of hydrogen trapping effect of the second phase and retained austenite.



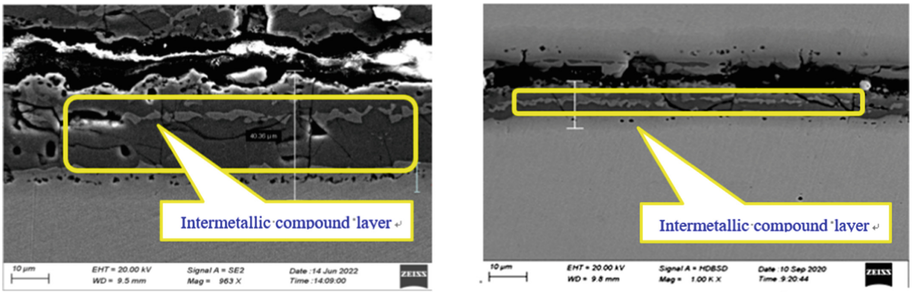
(a)Conventional coating. (b)Thin coating.

Fig. 9. Test results of surface coating thickness.

properties, bending toughness and corrosion resistance of two coating materials with different thickness specifications. It is verified that properly reducing the coating thickness can bring certain performance improvement advantages and reduce the production cost of steel enterprises. However, there are relatively few studies on the influence of coating characteristics on the hydrogen embrittlement resistance of press hardening steel. According to the test results in this paper, the press hardening steel with thin coating has stronger hydrogen embrittlement resistance. However, thin coated press hardening steel also contains niobium, so it can't be simply said that thinning the coating will improve the hydrogen embrittlement resistance. However, we can make a preliminary qualitative analysis of the impact of the thinned coating on the hydrogen embrittlement resistance of the material by comparing the microstructure. Figure 9 shows the microstructure of two coated press hardening steels with different thickness specifications. Firstly, the thickness of the coating was tested. The thickness of the conventional coating was about 30–40 μm. The thickness of thin coating is about 10–20 μm. The tensile properties of two kinds of Al-Si coating thickness samples were further evaluated. The results are shown in Table 4. It can be seen that there is no significant difference in the yield strength and tensile strength of the samples in the two states, but the elongation of the thin coating samples is higher than that of the conventional coating samples. The author of this paper had tested the tensile properties of press hardening steels containing and without niobium in the past. The results show that Nb plays an important role in improving the toughness of press hardening steels, but has no significant effect on the elongation. Based on this, it is considered that the proper improvement of the strength plasticity should come from the thinning of the coating. The failure of the material in the tensile process generally starts from the appearance of micro cracks on the surface of the sample. Due to the relatively poor strength and plasticity of the coating compared with the matrix, the coating will first fail, initiate cracks and then extend to the matrix during the tensile process. Therefore, this drawback is weakened by thinning the thickness of the coating, thus improving the overall strength and plasticity of the material. The improvement of strength plasticity and toughness [13, 14] is obviously conducive to improving the hydrogen embrittlement resistance of the material. After all, the hydrogen embrittlement performance is essentially a reflection of the toughness of the material.

Table 4. Tensile results of samples in two states.

Brand	No.	R_{el} (Pa)	R_m (MPa)	A (%)
Conventional coating	1#	1113	1466	5.2
	2#	1086	1469	5.3
Thin coating	1#	1077	1482	7.0
	2#	1090	1486	6.6

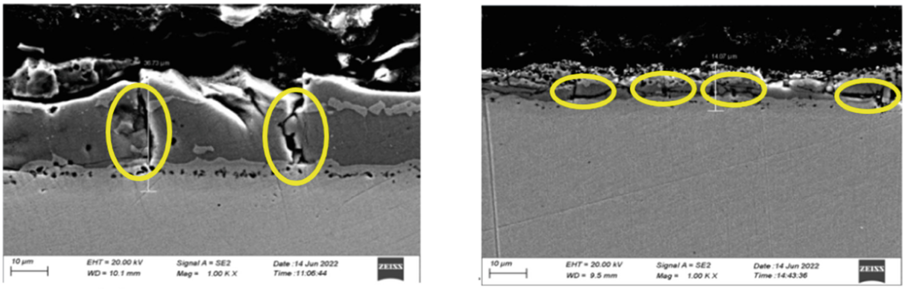


(a) Conventional coating. (b) Thin coating.

Fig. 10. Surface structure of two coating specifications.

The characteristics of the coating itself were further analyzed. Generally, the structure distribution of Al-Si coating from matrix to surface is matrix (Fe, Fe_3Al), ferrite layer and intermetallic compound layer (Fe_2Al_5, $FeAl_2$, $FeAl_3$, Fe_3SiAl_5, etc.) [15]. The intermetallic compound layer has strong brittleness, and it is easy to crack in the hot stamping process, but when the crack extends to the ferrite layer, it is often prevented by ferrite layer and will not extend to the matrix. However, in the actual hot stamping process, this so-called inhibition will be discounted. Firstly, the plasticity and toughness of the ferrite layer on the surface of Al-Si coated press hardening steel are generally greatly weakened due to the solid solution effect of Al and Si. Secondly, the thickness of this layer of ferrite structure is generally very thin, which is difficult to effectively prevent the growth of quenching cracks in the coating. As shown in Fig. 10, the surface structure of the coating samples of two thickness specifications with dew point control was tested. The thickness of the intermetallic compound layer of the thick coating plate was about 20–25 μ, while that of the thin coating plate was about 5–10 μ. The intermetallic compound layer is the reason for the brittleness of the coating. The thickness of the intermetallic compound layer of the thin plated plate is lower than that of the thick plated plate, so the negative impact of the intermetallic compound layer on the toughness of the plate is reduced.

As can be further seen from Fig. 11, significant cracks appear on the surface of the two specifications of coated plates after quenching, but the surface quenching crack length of the thick specifications of coated plates is significantly longer. The existing fracture theory research shows that the length of general crack is directly proportional to



(a) Conventional coating. (b) Thin coating.

Fig. 11. Surface cracks of two kinds of coatings.

the degree of stress concentration [16], and the longer the crack, the stronger the stress concentration effect. Secondly, the external hydrogen element will inevitably penetrate into the substrate due to the existence of coating cracks in the hydrogen embrittlement test of two kinds of thickness coated plates after quenching. At this time, the hydrogen element infiltrated during the heating process will also diffuse here due to the induction of stress concentration, especially at the contact part between the crack and the matrix, so as to accelerate the local plastic deformation in this area which will promote the crack to further expand into the matrix and finally lead to the fracture of the sample. So, on the one hand, the coating crack length of Nb coated sheet is lower than that of traditional coated sheet. On the other hand, the influence of niobium leads to a large diffusion resistance of hydrogen in the substrate during the test. In conclusion, the hydrogen enrichment and stress concentration at the contact between quenching crack and matrix of thin coating containing niobium are weaker than those of traditional coating without niobium, so it has stronger hydrogen embrittlement resistance.

In conclusion, the combined effect of Nb addition and coating thinning is conducive to further improve the hydrogen embrittlement resistance of Al-Si coated press hardening steel, which can become one of the development directions of such materials in the future. Finally, it is explained again that the corresponding conditions of the U-shaped constant bending load hydrogen embrittlement performance test carried out in this paper are harsh conditions, which are quite different from the actual service environment conditions of automobile parts. Therefore, the relevant test results can't be used as a basis to determine whether the two press hardening materials selected in this paper will have hydrogen embrittlement failure in practical application, but only provide a slight reference for the development direction of Al-Si coated press hardening steel materials in the future.

5 Conclusions

In this paper, the hydrogen embrittlement comparison test under U-shaped constant bending load is carried out for two kinds of hot stamped door crash beam parts with different composition and coating thickness under the working condition with dew point control. The results show that the thin coated press hardening steel samples containing niobium have relatively stronger resistance to hydrogen embrittlement under severe working conditions. The part samples obtained with dew point control do not break after immersion in 0.1 mol/L hydrochloric acid aqueous solution for 300 h under the bending load close to the tensile strength of the material. TDS and slow strain rate tensile tests of two kinds of press hardening steels were carried out to verify the above conclusions. The addition of niobium and the appropriate thinning of Al-Si coating are two important factors to improve the hydrogen embrittlement resistance of press hardening steels. The main functions of niobium are to promote the uniform distribution of hydrogen in the matrix, increase the number of large angle grain boundaries, capture hydrogen in the second phase and retained austenite. In addition, on the premise of ensuring corrosion resistance and oxidation resistance, properly thinning the thickness of Al-Si coating can reduce its negative effect on the toughness of press hardening steels (reduce the stress concentration at the contact between the quenching crack of the coating and the matrix), and further improve the hydrogen embrittlement resistance of the materials. Micro alloyed thin coating press hardening steels may be one of the important development directions of such materials in the future.

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