Rapid Heating Process of Ultra-high Strength Zinc-Coated Steel and Its Effect on Corrosion Resistance

Y. L. Wang[1(✉)], D. Y. Fang[1], K. Wang[2], and Y. S. Zhang[1]

[1] State Key Laboratory of Materials Processing and Die and Mould Technology, Huazhong University of Science and Technology, Wuhan 430074, China
wangyilin@hust.edu.cn

[2] School of Mechanical Engineering and Mechanics, Xiangtan University, Xiangtan 411105, China

Abstract. The hot stamping technology of ultra-high-strength boron steel is the most direct and effective way to realize the lightweight of automobiles. The high-strength zinc-coated (GA) steel with dual functions of barrier protection and cathodic protection have broad application prospects in the field of boron steel hot stamping. The essential issue for industrial application of hot stamping zinc-iron coating plate is how to achieve the optimal balance between microstructure, morphology as well as protective performance of the coating and properties of the steel by adjusting the heat treatment procedure. Based on rapid heating technology, this paper investigated and established a step-type rapid heating process path that can achieve short-term alloying of the coating and less Zn loss while ensuring sufficient austenitization of the matrix. On this basis, the corrosion resistance of zinc-iron coating sheet metal was systematically investigated. The corrosion behavior and corrosion resistance of zinc-iron coatings under different conditions were comprehensively evaluated by electrochemical characteristic test and neutral salt spray corrosion test. The results indicate that the corrosion resistance of the coating under the step-by-step rapid heating process is better than that of the initial zinc-iron coating and the coating under the radiation heating process, and the corrosion resistance of the fully alloyed coating is better than that of the incomplete alloyed coating, and the corrosion resistance of the over-alloyed coatings will be poor.

Keywords: Hot stamping · High-strength zinc-coated steel · Rapid heating · Corrosion resistance

1 Introduction

Corrosion of auto parts not only affects the quality, but also reduces the life and safety of the whole vehicle. In order to improve the corrosion resistance of car bodies, zinc-coated steel sheets have been used in automobile manufacturing since the 1970s. Fully galvanized steel sheet Body-In-White first introduced in Germany. The service life of

© The Author(s) 2023
Y. Zhang and M. Ma (Eds.): ICHSU 2022, AHMST 2, pp. 204–210, 2023.
https://doi.org/10.2991/978-94-6463-114-2_27

zinc-coated sheets in outdoor environment is several times longer than that of ordinary steel sheets, which significantly improves the corrosion resistance of the car body. The first application of zinc-based coated automotive steel sheets in hot stamping began in 2008. According to the initial coating phase composition, the zinc-based coating mainly includes pure zinc coating (GI) and alloyed zinc-iron coating (GA). Both types of coatings can be produced on the surface of hot stamped steel in continuous batches by hot dipping process at a temperature of around 460 °C. Although zinc-based coatings have good properties in many aspects, such as cathodic protection corrosion resistance, protection against oxidative decarburization of the matrix [1], good welding and coating properties, etc., their application in high-strength steel hot stamping process is still limited. First, the high temperature stability of the coating is weak, and the austenitization temperature of boron steel is close to the boiling point of liquid zinc, which is easy to cause evaporation of zinc, making the process window narrower. Second, during high temperature deformation, the liquid zinc existing in the coating will expand along the austenite and ferrite grain boundaries, resulting in the risk of liquid metal-induced embrittlement in the matrix [2]. Therefore, the research to solve the limitation of the application of zinc-based coating in hot stamping process has become one of the hotspots in recent years.

At present, there are many researches around the world on the phase structure [3, 4], high temperature oxidation [5] and coating cracking of hot stamped GA zinc-coated sheets, however, the effect of heating process on corrosion resistance is not fully studied. Most of the heating methods are based on traditional radiant heating in the furnace, and the average heating rate is less than 10 °C/s. The slower heating rate makes the phase transition relatively stable, and the alloying and oxidation process of the coating is relatively slow. But, during the austenitization process, a large amount of liquid zinc will be formed in the coating, and the continuous oxide layer on the surface has not been formed due to the slow oxidation progress, which cannot effectively inhibit the volatilization of the liquid zinc, thereby reducing the final effective zinc content of the coating. On the other hand, the heating time is usually longer than 5 min to ensure sufficient carbon diffusion and uniform austenitization of the matrix. Longer heating time will lead to excessive thickening of the oxide layer, which will also cause the loss of zinc in the coating.

The corrosion resistance of zinc-iron coated sheets is related to the phase structure, crack distribution and surface roughness of the coating, and the final zinc content after hot stamping is the main influencing factor. Therefore, a rapid heating process is proposed in this paper and its relationship with the corrosion resistance of parts is studied.

2 Experimental Procedure

The experimental material is a high-strength steel sheets with zinc-iron coating produced by a china steel company, and the thickness of the sheet is 1.6 mm. The composition and content of the main alloying elements in the matrix are shown in Table 1. Figure 1(a) shows the microstructure of the original coating section, and the initial thickness of the coating is 11.5 μm; the EDS elemental analysis shows that the coating is basically composed of δ phase, and the Zn element content is about 90 wt.%. Figure 1(b) is the

Table 1. The chemical composition of high-strength steel sheet (wt.%)

C	Mn	Si	Cr	Ti	Ni	Nb	B
0.20–0.25	1.02	0.24	0.16	0.023	0.029	0.012	0.001

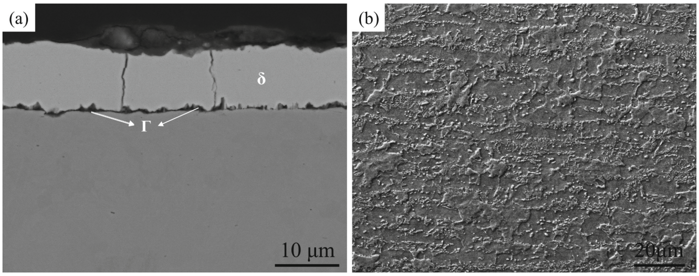

Fig. 1. Microstructure and morphology: (a) cross section of coating; (b) substrate.

SEM morphology of the matrix structure, it can be seen that the matrix structure is composed of ferrite and pearlite.

The corrosion test materials are selected from the step-type rapid heating zinc-iron coated sheets with different degrees of coating alloying. At the same time, the original zinc-iron coated sheet, the bare sheet and the zinc-iron coated sheet under the radiation heating in the traditional furnace were used as the reference target. The specific heating process parameters are shown in Table 2. All heat treatment processes were carried out on a Gleeble thermal simulation testing machine.

The heating rate and pre-oxidation process parameters of the zinc-iron coated sheet in the step-type rapid heating process are 100 °C/s and 820 °C for 40 s, respectively. The alloying state of the coating under the rapid heating process corresponds to three grades according to the austenitizing time. The initial zinc-iron coated sheet is in the supply state, and the bare sheet sample is obtained by removing the coating on the surface of the initial zinc-iron coated sheet with 1500 # emery paper. The degree of alloying of the coating under the radiant heating process in the furnace is fully alloyed for 190 s and over-alloyed for 300 s.

The neutral salt spray corrosion test refers to the NSS test in the national standard GE/T 10125-2012 "Artificial Atmosphere Corrosion Test - Salt Spray Test". The salt solution used in the experiment is 5.0 wt.% NaCl solution. In order to obtain good samples, at first, use a cutting machine to cut the uniform temperature zone of the heat-treated sheet, then use an ultrasonic cleaner to remove surface oxides and impurities, then use anhydrous ethanol to clean the surface and dry it, and finally use a waterproof tape to seal the side of the sample. Seal with the back side to ensure that only one side of the sheet is exposed for corrosion, and the exposed area is approximately 22 mm × 10 mm.

According to the national standard requirements and laboratory safety regulations, this experiment is set to be carried out in 6 cycles, and each cycle is 24 h long. The samples were first corroded in a salt spray atmosphere for 2 h, and then demisted for

Table 2. Heating process and analysis experiments of different experimental materials.

Material	820 °C Pre-oxidation holding time (s)	850 °C Austenitizing holding time (s)	Neutral salt spray corrosion test	Category number
Step-by-step rapid heating	40	20	✓	RH40 s + 20 s
		50	—	RH40 s + 50 s
		100	✓	RH40 s + 100 s
In-furnace radiant heating	—	190	✓	RH190 s
	—	300	—	RH300 s
Initial zinc-iron coated sheet	—	—	✓	—
bare sheet	—	—	✓	—

10 min and left for 3 h; then continued to corrode in a salt spray atmosphere for 2 h, and then left to stand until the next cycle began. The surface and cross-section corrosion morphology are observed by an optical microscope.

3 Results and Discussion

Figure 2 shows the surface corrosion state of the six test samples under 2, 4, and 6 cycles of neutral salt spray, respectively. The comparison shows that under the same corrosion cycle, the surface color gradually becomes darker from left to right. The surface of the initial galvanized sheet is the lightest gray-white; the bare sheet is reddish-brown, and partially black; the surface color of the zinc-iron coating under the rapid heating process is gray-white and reddish-brown; the surface of the zinc-iron coating under the radiation heating process is compared with the rapid heating process, the area of the gray-white area is significantly reduced. When the heat preservation is 300 s, the surface of the zinc-iron coating is basically reddish-brown. According to the literature, the gray-white area is white rust, and the main component is zinc compounds; the reddish-brown area is red rust, and the main component is iron oxide, and the structure of the two is relatively loose under the microscope.

For the bare sheet sample, as the corrosion time increases from the second cycle to the sixth cycle, the color of the surface gradually increases, and an obvious rust layer appears on the surface, which is easy to fall off.

For the initial zinc-iron coated sheet, when the corrosion reaches the second cycle, the white rust on the surface is discontinuous, and the local area does not change significantly compared with the initial state; when the corrosion time increases to the fourth cycle, the white rust area increases significantly. And the thickness is thickened; when the time

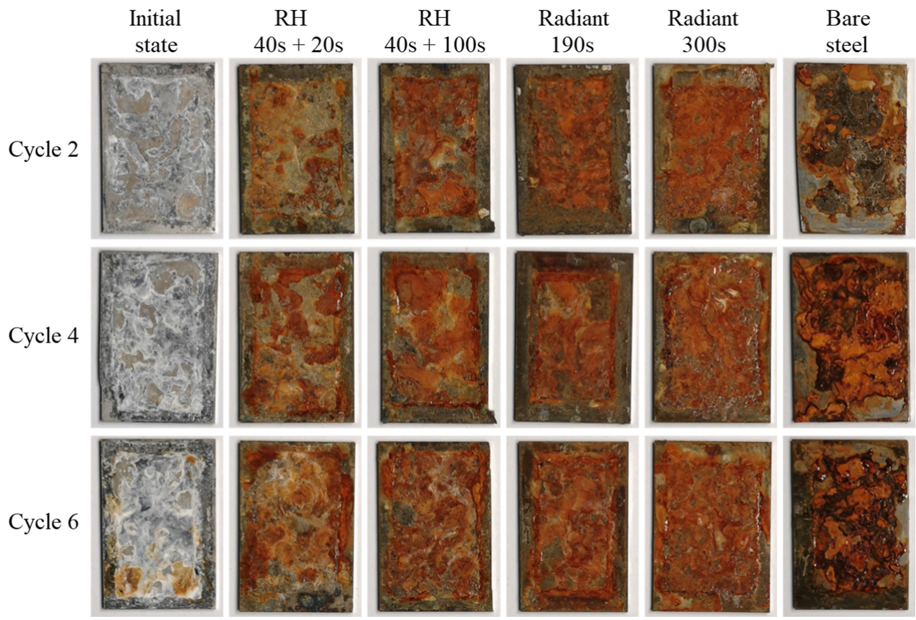

Fig. 2. Surface morphology changes of different experimental samples under different corrosion cycles.

is extended to the 6th cycle, the white rust basically covers the entire surface, and the lighter red rust appears in the local area.

For the zinc-iron coated sheet under the RH40 s + 20 s process, when the corrosion reaches the second cycle, there is a thin and continuous layer of white rust on the surface, and the area of red rust is very small; with the prolongation of corrosion time, the area of white rust decreases, the color deepens slightly, and the area of red rust gradually increases. For the zinc-iron coated sheet under the RH40 s + 100 s process, compared with the RH40 s + 20 s process, the coating surface has less white rust area and more red rust area under the same corrosion cycle.

For the radiation heating process, compared with the RH40 s + 100 s process, the white rust area is smaller and the red area is larger when the heat preservation is 190 s under the same corrosion cycle; when the heat preservation is 300 s, the surface is basically all red rust, with very little white rust.

Compared with the bare sheet, both the initial zinc-iron coated sheet and the heat-treated zinc-iron coated sheet have certain corrosion resistance; in terms of the red rust area, the zinc-iron coated sheet under the radiation heating process is larger than the rapid heating process. It shows that the corrosion resistance of the fully alloyed coating under the stepped rapid heating process is better than that of the fully alloyed coating under the radiation heating process.

4 Conclusion

In this paper, the corrosion behavior of high-strength steel zinc-iron coated sheets under different stepped rapid heating processes was studied through neutral salt spray tests by comparing with the initial galvanized sheets, bare sheets and radiation heating zinc-iron coatings The overall corrosion resistance in different states was comprehensively evaluated from the aspects of surface corrosion morphology, cross-sectional corrosion morphology and average thickness of the uncorroded area of the coating.

The neutral salt spray test shows that there are obvious corrosion pits on the bare sheet, with a maximum of 35.55 μm, and the zinc-iron coating can effectively prevent the corrosion of the substrate. In the zinc-iron coating after heat treatment, the Γ phase with higher Zn content is preferentially corroded. After 6 cycles of corrosion, there is still a certain thickness of uncorroded area in the coating, the substrate is not corroded, and the surface of the coating shows the morphology of the interval distribution of white rust and red rust. After 6 corrosion cycles, all the coatings were corroded, and corrosion pits appeared on the substrate with a depth of up to 19.72 μm, and the corrosion resistance was poor. The corrosion resistance of the coating under the stepped rapid heating process is better than that under the radiation heating, and the corrosion resistance of the initially fully alloyed coating is better than that of the incompletely alloyed coating; the corrosion resistance of the overly alloyed coating becomes worse. When the corrosion progresses to a certain extent, the corrosion layer will inhibit the further corrosion of the coating.

Acknowledgments. This research work was financially supported by the National Major Science Technology Project of China (grant no. 2018zx04023001).

References

1. G. Vourlias, N. Pistofidis, E. Pavlidou and K. Chrissafis, Zinc coatings for oxidation protection of ferrous substrates, *Journal of Thermal Analysis and Calorimetry* **90**, 777 (2007).
2. C. W. Lee, D. W. Fan, I. R. Sohn, S. Lee and B. C. D. Cooman, Liquid-metal-induced embrittlement of Zn-coated hot stamping steel, *Metallurgical and Materials Transactions A* **43**, 5122 (2012).
3. K. Wang, B. Zhu, Z. J. Wang, Y. Liu, L. Wang and Y. S. Zhang, Successive phase and morphology evolution of galvannealed coating in hot stamping and diffusion modeling of α-Fe(Zn)/steel system considering the effect of Zn concentration, *Surface and Coatings Technology* **380**, 125036 (2019).
4. H. Järvinen, M. Honkanen, M. Patnamsetty, S. Järn, E. Heinonen and H. Jiang, Press hardening of zinc-coated boron steels: Role of steel composition in the development of phase structures within coating and interface regions, *Surface and Coatings Technology* **352**, 378 (2018).
5. J. K. Chang, C. S. Lin, W. J. Cheng, I. H. Lo and W. R. Wang, Oxidation resistant silane coating for hot-dip galvanized hot stamping steel, *Corrosion Science* **164**, 108307 (2020).

Open Access This chapter is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License (http://creativecommons.org/licenses/by-nc/4.0/), which permits any noncommercial use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.