Galvanealed coating evolution for hot forming steel

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Abstract. The aim of the galvanealing experiments with three parameters of dew point, protective atmosphere and galvanealing time was to monitor the changes in coating quality and the evolution of coating after hot forming. The results show that, the three parameters have little effect on coating weight (thickness), and the average iron amount was within 9.51 to 14.9 %. The ζ, δ and Γ phase for the as-received galvanealed samples transformed to Γ-Fe_4Zn_9 and α-Fe (Zn) after reheating. The existence of a thin film of Γ-Fe_4Zn_9 increases the electrochemical potential to the base steel by a good amount and will not generate LME.

1. Introduction

Corrosion resistance and the avoidance of scale formation during the heating of the material are the main drivers for the development of new coatings for hot stamping [1].Currently there are three industrial relevant coating systems available in producing hot forming steel: Zinc, Aluminum/Silicon and x-tec. The friction coefficient of Al-Si coated steel was generally higher and unstable due to galling of the Al-Si coating on the tool [2]. Moreover, it is not sufficient in corrosive protection for Al-Si coated steel sheets to be applied to wet under body areas, compared with galvanized or galvannealed steel sheets [3, 4].X-tec is a paint system based on nanotechnology which avoids scale formation during heating but offers only a limited corrosion resistance for the formed component. The coating can be used for both process variants of hot stamping [5].

Zinc coated hot forming steels offer the chance to have cathodic corrosion protection as an advantage compared to today's standard applications with uncoated and AlSi coated materials. To utilize all the potential of the coating it is favourable to have at least a little amount of Γ-Fe4Zn9 in the coating. This increases the electrochemical potential to the base steel by a good amount [6]. In which, galvanealing (Zn-Fe coating) is a well knownalloying process whereby zinc from the galvanizecoating and iron from the steel substrate combine in various zinc-iron intermetallic phases.Previous research work [7-9] have mentioned the primary factors appear to be alloyingtime, alloying temperature, steel chemistry and pot aluminum. But the effect of dew point and protective atmosphere on the coating thickness and structure change also needs more attention. It is essential to permitthe alloying process to achieve desired coating thickness with proper alloying phases in avoiding "powdering" or flaking when the finished product is subjected to forming operations.

Despite of the industrial application of hot stamping for almost 20 years, there isstill only one base material that is used for this application, the boron alloyed steel 22MnB5. Therefore, by changing dew point, protective atmosphere and alloying time, the steel of 22MnB5 was used in the paper to study their effect on the thickness and structure of Zn-Fe coating.

2. Experimental procedure

The hot forming steel used in the paper was industrially produced with a regular cold-rolled mill finish to thickness of 1.5mm. The material chemistry was 22MnB5 (0.22C-0.25Si-1.35Mn-0.003B, wt%) with a small amount of Cr and Ti to achieve the desirable mechanical properties.

The galvannealed samples were conducted on Iwatani-Surtec HDPS simulator. The coupons comprised 110mm × 220mm with the long axis parallel to both the rolling and dipping directions, cleaned and dried per standard practice [10]. The samples were assembled to perform the following processes: heating by rate of 5 ℃/s to 800 ℃, with slow cooling rate of 4 ℃/s and fast cooling rate of 30 ℃/s to 475 ℃, dipping in the zinc bath with temperature stabilized at 460 ℃, after cooling by wiping knife, the hot dipped samples were reheated to 500 ℃ and cooling by rate of 10 ℃/s to room temperature. Changing the dew points from -50 to 30 ℃, protective atmosphere contents from 5 to 30 %H_2-N_2 and galvanealing time from 5 to 15 s to study their effects on coating quality. The galvanealed samples will be reheated on 910 ℃ for 5 min, and hot formed after that to analyze the coating evolution.

Surface state (zinc coating weight and thickness), average iron content of samples galvanealed by the simulator were analyzed by Glow Discharge Optical Emissivity Spectroscopy (GDOES) using a Horiba Jobin- Yvon Profiler. Coating quality and reactive wetting were assessed by the counting of bare spots and bare spot area in the uniform 90mm ×90mm coating area of the coated panel [11]. Samples were also taken from this area for SEM (HITACHI-S-4300) examination of the coating/substrate interfacial layer.

3. Results and Discussions

3.1. Effect of galvanealing parameters on coating weight (thickness)

It is widely accepted that dew point affect greatly the selective oxidation formed on the steel surface during annealing, the increase of dew point will transfer the external oxidation to inner oxidation which will contribute to galvanizing [12]. However, the results obtained in the experiment displayed that the change of dew point has no significant effect on coating weight, as shown in figure 1a. When dew point changed from dry to moist (-60 to 30 ℃), the coating weight was among 46.2 and 59.2 g/m^2, and coating thickness was among 6.66 and 8.25 μm. Although there is a minute difference of coating weight and thickness, the trend is not regular.

However, when controlling the H_2 content from 5 to 30%, as shown in figure 1b, the coating weight and thickness decreased from 84.15 to 53 g/m^2 and from 12 to 7.63 μm, respectively. Especially, the trend become obvious when H_2 content was above 20%, which enlarge the Hydrogen reduction ability on steel surface to suppress the diffusion of Fe and alloying elements from steel to coat.
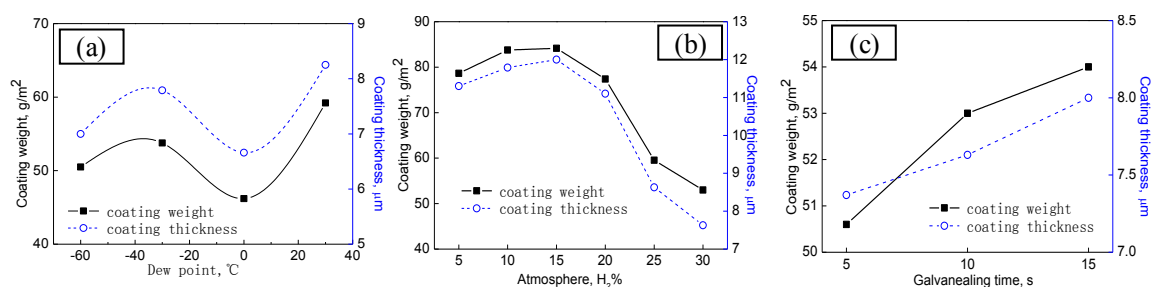

Figure 1. Coating weight and thickness controlled by:
(a) dew point, (b) H_2 content, (c) galvanealing time detected by GDOES.

Generally, the coating weight increase with longer dipping and reheating (galvanealing) time, as shown in figure 1c, the trend is obvious. The specific data showed that, the coating weight and thickness decreased from 50.6 to 54 g/m^2 and from 7.37 to 8 μm, respectively. Although the trend is

obvious, the differences were not large enough to specify if there is a relationship of galvanealing time with coating weight, but the phase structure may differentiate with the time, which will be discussed next.

3.2. Effect of galvanealing parameters on iron content

The iron amount has a close relationship with phase structure for galvanealed coating. The average content of iron amount was measured under different galvanealing parameters, as shown in figure 2. When dew point changed from -60 to 30 ℃, the iron amount was within 9.67 and 10.9%; when H_2 content changed from 5 to 30 %, the iron amount was within 9.51 and 10.3%; when galvanealing time changed from 5 to 15 s, the iron amount was within 10.2 and 14.9%. All of the iron contents correspond to the existence of ζ and δ phases in the coat, and the existence of Γ phase need further analysis which will be shown later. The iron contents were stable by changing of dew point and H_2 content, but increase with galvanealing time. So that, if the time increase further, the iron content will reach another range and Γ phase will appear.
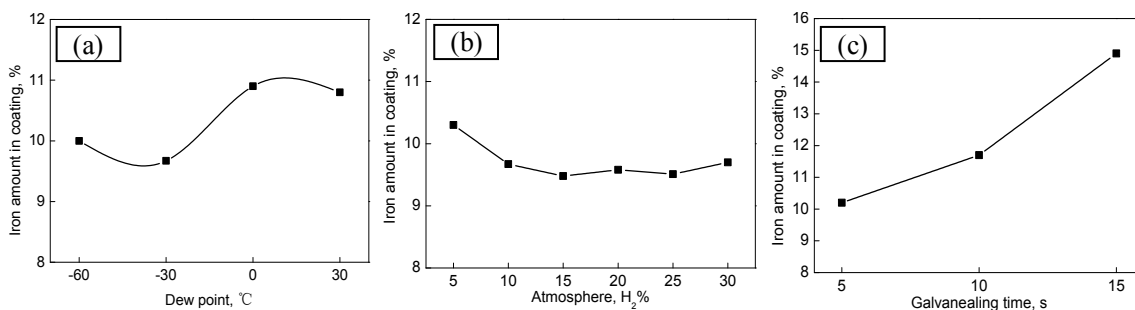

Figure 2. Iron amount controlled by:
(a) dew point, (b) H_2 content, (c) galvanealing time detected by GDOES.

3.3. Structure changes before and after hot forming process

The morphology of zinc coating before and after hot forming was analyzed by SEM shown in figure 3. As the average iron content of coating was shown in figure 2, the detailed energy spectrum were measured to make sure if there exists Γ phase. As shown in figure 3a, Spectrum 1 to 3 displayed iron content as 5.87, 8.48 and 25.89 wt %, which correspond to ζ, δ and Γ phase. Combined figure 2 and figure 3a, the amount of Γ phase was very little, which will not damage the whole coating affiliation with steel matrix.
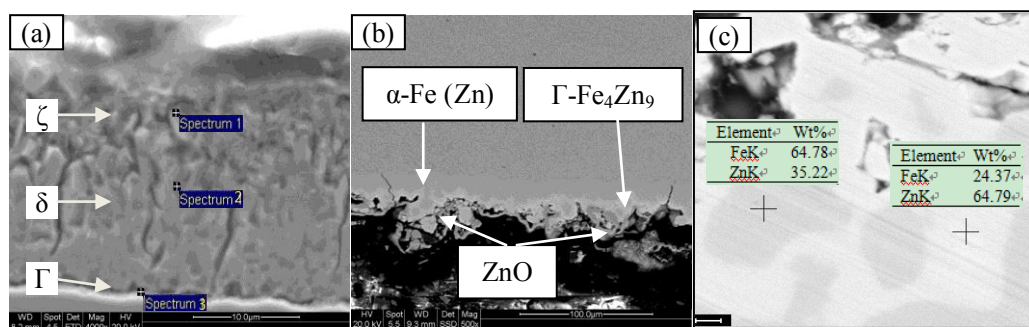
Figure3. SEM Morphology of zinc coating before and after hot forming:
(a) beforeand (b) after hot forming, (c) elements distribution after hot forming.

The coating morphology and elements distribution after hot forming were shown in figure 3b and 3c. The coating generally contained two distinctive phases, i.e. the Zn-rich gamma phase (Γ-Fe_4Zn_9) and Fe-rich alpha phase (α-Fe (Zn)). Surface oxidation occurred during annealing, leading to a surface covered with ZnO (figure 3b). Coatings contained greater than 30 % Zn in α-Fe (Zn) which verified

cathodic protection potential through corrosion testing and electrochemical work. The coating become thicker significantlyafter hot forming, caused by the elements in the matrix diffuse into the coating. There is a thin film of Γ-Fe$_4$Zn$_9$distributed above α-Fe (Zn) phase, the little amount of Zn in the Γ phase can not generate liquid metal brittlement (LME) in the later welding process. Also, as it was mantioned in the beginning of the paper, the Γ phase increases the electrochemical potential to the base steel by a good amount. However, the Zn coating can easily be oxidized in the reheating procedure, the oxides need to be removed by shot blasting.

4. Conclusions

(1) The coating weight (thickness) measured by GDOES displayed that: the change of dew point has no significant effect; the more H$_2$ content, the thinner of coating thickness, especially when H$_2$ was above 20%; when galvanealing time was limited within 5 to 15 s, the differences were not large enough to specify if there is a relationship of galvanealing time with coating weight;

(2) The average contents of iron amount were almost the same when changing dew point from -60 to 30 ℃ and H$_2$ content from 5 to 30%, but increase obviously with the rising galvanealing time. The iron amount was within 9.51 to 14.9 % for all the parameters, correspond to the existence of ζ and δ phases;

(3) The result of energy spectrum for the different area of coat make sure that Γ phase exited on the interface of coat and matrix. The three phases transformed to Γ-Fe$_4$Zn$_9$and α-Fe (Zn).

References

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