Press hardening of zinc-coated boron steels: Role of steel composition in the development of phase structures within coating and interface regions

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ABSTRACT

Zn and ZnFe coated 22MnB5 and 34MnB5 steels were subjected to the direct press hardening process in order to investigate the influence of steel composition on the resulting phase structures. Microstructures were characterized using advanced methods of microscopy. In addition, X-ray diffraction, glow discharge optical emission spectroscopy and thermodynamic calculations with Thermo-Calc® were carried out to support the analysis. The results indicate that the steel composition has a clear effect on the phase development within coating and interface regions. Whereas the behavior of the 22MnB5 was comparable to earlier investigations, a clearly non-conventional behavior of the 34MnB5 was observed: the formation of martensitic micro constituents, designated here as α'-Fe(Zn), were identified after die-quenching. The regions of the α'-Fe(Zn) formed mainly in vicinity of steel/coating interface and were emerged into the steel by sharing martensitic morphology with the base steel. The thermodynamic calculations suggest that carbon is effective in stabilizing the γ-Fe(Zn) phase, which enables the formation of the α'-Fe(Zn) in fast cooling. Therefore, the higher initial C content of the 34MnB5 may result in the kinetic stabilization of the γ-Fe(Zn) as the inter-diffusion between Zn and Fe occurs during annealing. Simultaneously occurring carbon partitioning from α-Fe(Zn) to γ-Fe(Zn) could explain a clearly increased C content of the coating/steel interface as well as higher Zn contents in the α'-Fe(Zn) phase compared to 22MnB5. Actually, the present study shows that the same phenomenon occurs also in 22MnB5 steels, but in a much smaller scale. In Zn and ZnFe coated 34MnB5, the thickness of the α'-Fe(Zn) layer was increased with longer annealing times and at higher temperatures. The morphology of the α'-Fe(Zn) layer resembled plate-like martensite and can be assumed to be brittle. Regarding this, the formation of α'-Fe(Zn) interface layer needs to be taken into account in press hardening of 34MnB5 steels.

1. Introduction

Hot-dip galvanized press hardening steels (PHS) have turned out to be appealing materials for car body components by providing unique combination of ultra-high strength and galvanic corrosion resistance [1]. Consequently, automotive manufacturers aim to increase the use of zinc-coated steels in the press-hardened components [2]. In general, continuous galvanizing is used to produce two types of zinc-based coatings for PHS: conventional zinc coating (Zn) and zinc-iron alloy coating (ZnFe), i.e., galvannealed coating containing initially 8–12% of iron. The ZnFe coating is obtained by using a lower Al content of the zinc bath, and by applying a post dip annealing treatment [3]. Both

zinc-based coatings are applicable in press hardening technology, but ZnFe coating has higher thermal stability resulting in a broader processing window [4]. In addition, a suitability of electroplated ZnNi coatings have been investigated [5–7]. However, currently there are not any commercial solutions available utilizing the ZnNi coating [8].

The direct press hardening process combines three distinct steps: heating/austenitization of the blank, transferring from furnace to die, and a final step of hot forming and quenching performed in a water-cooled die. During these stages, zinc-based coatings undergo significant changes in their phase structure and composition. The coating reacts with the steel and becomes gradually more and more enriched with Fe through inter-diffusion, occurring between Zn from the coating and Fe

Table 1
Details and chemical compositions (wt%) of the as-received test materials.

Steel	Sheet thickness	Coating weight (side/side)	C %	Si %	Mn %	Cr %	Al %	B %	A_{c3} (°C)
22MnB5-Zn	1.5 mm	50/50 g/m²	0.24	0.26	1.18	0.20	0.033	0.0029	831
22MnB5-ZnFe	1.5 mm	70/70 g/m²	0.23	0.26	1.24	0.21	0.029	0.0031	830
34MnB5-Zn	1.1 mm	50/50 g/m²	0.35	0.26	1.30	0.15	0.033	0.0026	800
34MnB5-ZnFe	1.5 mm	70/70 g/m²	0.35	0.25	1.32	0.15	0.033	0.0014	803

from the steel [3,9]. The Fe-Zn phase diagram has been typically applied to understand the high temperature phase development of zinc-coated PHS. According to the diagram proposed by Burton and Perrot [10], the Fe-Zn system covers several phases as a function of Zn content when heated up to the typical annealing temperature of around 900 °C: pure zinc η, intermetallic Zn-Fe compounds ζ, δ, Γ_1, and Γ_2 as well as solid solution α-Fe(Zn). The intermetallic Zn rich phases melt during heating/annealing stage, but re-solidification of the coating occurs by the increasing Fe content and resulting formation of α-Fe(Zn). In the pure Fe-Zn system, the austenitic solid solution γ-Fe(Zn) phase may exist only above 900 °C.

PHS components are austenitized prior to hot forming, and thus high temperature phase development of hot-dip galvanized 22MnB5 has been extensively addressed in previous studies [4,11–15]. When conventionally heated up to the minimum austenitization temperatures of around 850 °C, the coating attains a structure consisting of a mixture of liquid and solid phases, i.e., Zn rich liquid phase and ferritic solid solution of Fe and Zn, i.e., α-Fe(Zn) [16,17]. The fraction of solid α-Fe (Zn) phase increases as a function of annealing time and temperature as the coating is enriched more and more with Fe, and some Zn is also oxidized in the surface to form ZnO [16]. The formation of ferritic α-Fe (Zn) is generally faster in ZnFe coating than in conventional Zn coating [4,13]. During the subsequent die-quenching step, liquid (if still present) and some of the α-Fe(Zn) phase transforms to the Zn rich Γ-Fe_3Zn_{10} phase (hereafter referred to as Γ-ZnFe), and the remaining α-Fe (Zn) is stabilized when the material is quickly cooled into room temperature [18]. Thus, a short annealing tends to result in the layered phase structure: ZnO (oxide) on the top, some intermetallic Γ-ZnFe phase in the middle, and solid solution of α-Fe(Zn) on the bottom. Regardless of the oxide layer, a coating consisting only of a solid α-Fe (Zn) phase can be attained with prolonged soaking times [12,19,20]. At typical annealing temperatures of 900 °C, the maximum Zn content of α-Fe(Zn) is around 35%, which is retained when the steel is quenched [18]. It has been observed that the Zn content of the α-Fe(Zn) phase decreases only slightly towards the coating/steel interface [9]. More interestingly, there is a sharp drop of the Zn content after reaching the α-Fe(Zn)/steel interface [9].

According to earlier studies [9,12,19–21] the final Zn content and galvanic capacity of the press-hardened coating is determined by the coating type, initial coating thickness and annealing parameters. When it comes to the influence of annealing parameters, a constant decrease in the Zn content of the coating occurs as a function of annealing time [9,19]. It has been also widely noted [9,12,19–22] that the coating thickness increases significantly during the thermal cycle of the direct press hardening process. Janik et al. [9] pointed out that the coating growth occurs by means of inter-diffusion as the grain boundaries of the α-Fe(Zn) phase move towards steel. Regarding this, the coating layer gets thicker at the expense of steel. The contribution of steel alloying elements has not been paid much attention, but is obviously worth considering due to nature of the inter-diffusion layer. Accordingly, Janik et al. [22] used a FactSage software to calculate a phase diagram for 22MnB5-Zn system instead of the conventionally used Fe-Zn. It was noticed that the phase region of austenitic γ-Fe(Zn) phase is significantly larger compared to the pure Fe-Zn system. Therefore, the γ-Fe (Zn) phase may be theoretically present at typical austenitization temperatures around 900 °C [22]. If this is the case, the austenitic phase

constituents of the coating might transform into martensite during subsequent quenching. However, none of the previous studies has addressed the formation of martensitic micro constituents α'-Fe(Zn) in Zn or ZnFe coated 22MnB5.

Currently, there is a demand for novel PHS providing tensile strength reaching 2000 MPa [8]. In order to attain the desired strength, steels of 34MnB5 type with the C content around 0.35%, have been recently investigated [23–25]. None of the previous studies has addressed the high temperature phase development of zinc-coated 34MnB5 steels at least known to the authors. Based on the previous study of Janik et al. [22], the steel composition may have a significant effect on the high temperature phase equilibrium of the Fe-Zn system. In the present study, Zn and ZnFe coated boron steels are subjected to the direct press hardening process and phase structures of the die-quenched samples are comprehensively analyzed and compared. The results will show significant differences between 22MnB5 and 34MnB5 grades. Finally, the behavior of both grades and the role of steel composition will be discussed in detail.

2. Materials and methods

2.1. Test materials

The as-received materials consisted of two commercial 22MnB5 steels along with two commercial 34MnB5 steels, both coated with Zn and ZnFe coatings. The details and chemical compositions of the as-received steels are described in Table 1. The expressed A_{c3} temperatures were calculated using the equation presented by Kasatkin et al. [26].

As indicated in Table 1, the differences in the chemical compositions are small except to the difference in C contents between the 22MnB5 and 34MnB5 grades. The received samples of the 34MnB5-Zn had a smaller sheet thickness compared to the samples of other investigated steels.

2.2. Press hardening experiments

Press hardening experiments were carried out using an experimental press hardening equipment described more in detail in an earlier study [27]. The experiments were conducted for steel sheet samples of the size of $110 \times 100 \times$ (sheet thickness). The annealing parameters, described specifically in Table 2, were chosen to examine a wide range of annealing cycles. The cycles were determined based on two methods.

Table 2
Parameters of the examined annealing cycles. The attained peak temperature of each cycle is expressed in the parenthesis.

Steel	880 °C: A_{c3} + 30 s, A_{c3} + 330 s	900 °C: total dwell times	930 °C: A_{c3} + 330 s
22MnB5-Zn		180 s (820 °C), 450 s (900 °C)	
22MnB5-ZnFe		180 s (890 °C), 450 s (900 °C)	
34MnB5-Zn	170 s (850 °C), 470 s (880 °C)	180 s (890 °C), 450 s (900 °C)	430 s (930 °C)
34MnB5-ZnFe		180 s (890 °C), 450 s (900 °C)	