ZINC COATED PRESS-HARDENING STEEL
CHALLENGES AND SOLUTIONS
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ABSTRACT

Press-hardening steels get more and more popular for body in white applications as an approach to meet the demands of passenger safety and CO2 reduction. Unlike the larger part of the structure that is typically zinc coated, the majority of the PHS parts is either uncoated or aluminum silicon coated. This paper shall give an overview of press-hardening steels with zinc coatings with detailed results for corrosion resistance, weldability and mechanical properties for strength levels of 490 to 1800 MPa.
01 Introduction

Press-hardening steels are widely used in the body in white. The basic steel type used is a manganese boron type steel referred to as 22MnB5. In the first applications reaching back as long as the 1986 [1], uncoated sheet material has been used. The process of choice was direct hot forming. Due to the lack of corrosion protection and scaling issues AlSi coated material came into application after 2004 and is still dominating the PHS parts in the body in white.

The demand for a cathodic corrosion protection similar to the one known from galvanized or galvannealed sheet steel was present all the time, but it took several more years until 2008 to have the first zinc coated parts in serial applications [1]. These parts are produced in the indirect process with 100% cold forming, cutting and piercing followed by a form hardening step. The demand of a product and process for direct hot-forming of zinc-coated press-hardening steel without sacrificing corrosion protection is still high.

02 Zinc-coated Press-hardening Steels

As press-hardening steels are typically used in parts that are relevant for crash behavior and for passenger safety, steel ductility is of importance. The standard grade 22MnB5 typically has a total elongation in tensile test of 5 to 6 %. The three-point bending test [2] has turned out to be more relevant for predicting crash properties as it is closer to the material folding behavior under crash conditions.

As expected the bending angle in three-point bending test is lower with increasing strength level (figure 1). For the 490/500 MPa grades the bending angle is on a level, that is already beyond being meaningful, as it is dominated by geometrical factors of the testing device. Nevertheless the folding behavior is perfect in the investigated axial and bending crash test setups.

For the workhorse of coated press-hardening steels (1500 MPa grade 22MnB5 with AlSi coating) a significantly decreased bending angle of approximately 55° in transversal direction can be observed. It turned out that unlike other coated press-hardening steels the GI coated type can be pushed to way higher levels of a typical 65-67° at 1.5 mm sheet thickness.

Figure 1: typical transversal bending angles in three-point bending test according to ISO 7438 [2] of different strength levels of press-hardening steels of 1.5 mm sheet thickness. PHS 1500 AS and PHS 1500 GI are 22MnB5 type, PHS1500 as well, but GI coated, PHS1800/1900/200 is a 32MnB5 or 34MnB5 type.
02.01. Properties of annealed zinc coatings

An essential step for gaining knowledge of the corrosion behavior is the characterization of the initial state. Figure 2 shows a SEM image of the Fe-Zn reaction layer of hot-dip galvanized steel strip after the press hardening process. By using a back-scattering detector the intermetallic phases of different composition are represented by different shades of gray. Zinc rich phases then appear brighter than iron-rich phases, with the property that heavy elements the electrons more strongly re-infl ect than do lighter ones.

Clearly visible is the change of the zinc coating due to the press hardening process. The initial layer zinc of 10 micron thickness reacts to form a layer of approximately 20 micron consisting of two different zinc-iron phases [3], with significantly different composition. The brighter areas in the layer have a zinc content of 75.5 mass contents in % (71.5 molar mass fraction in %) and are located mainly at grain boundaries in the upper region of the layer. This composition is typical for $\Gamma$-ZnFe phases. The darker areas have a zinc content of 42 mass contents in % (38 molar mass fraction in %) and are Ferrite with zinc in solid solution.

Results for intermetallic phase formation proved that the existence of the $\Gamma$-Zn-Fe phase and thus the resulting layer system is a function of furnace dwell time as well as the initial zinc layer. Longer furnace dwell time leads to disappearance of the $\Gamma$-ZnFe phase, which is also true for initial lower Zinc coating weights. An illustration of which is shown in Figure 3 by means of a galvanostatic dissolution of press-hardened galvanized steel strip with several furnace dwell times. An estimation of the amount of each phase can be taken dissolution time, since it is directly proportional to the amount of each phase by Faraday law.

In the short annealed sample it takes 20 minutes to have $\Gamma$-ZnFe phase is completely dissolved. In the sample with the standardized dwell time $\Gamma$-ZnFe phase is dissolved in a few minutes and so on.

Figure 2: SEM & EDX analysis of the microstructure of the Fe-Zn-layer of a hot dip galvanized press-hardening steel after annealing.

02.02. Corrosion Properties

When it comes to corrosion properties the expectations on coated steel, especially zinc coated steel, are to see no red corrosion products. Due to the intense thermal heat treatment during austenitization the iron content of the coating is significantly increased. Therefore already the first corrosion products are of reddish appearance as they do contain iron, which is form the coating and not form the base material. This behavior is observed in all pre annealed coatings, be it standard galvannealed or press-hardened coatings like AlSi or zinc coatings.
To determine the corrosion progress or the start of base material attack, cross sections were taken of the corroded samples and examined by SEM. Figure 4 shows cross sections according to different test times in VDA 233-102 test. After 6 cycles no base material corrosion is observed. In comparison to the uncured state base material corrosion occurs already after 4 weeks. The timing of the base material attack was not determined. The main reason for the greater protection is the higher layer thickness, which is created by the press hardening process, since the corrosion rates of Zinc and the annealed coating are comparable. In VDA 233-102 Γ-ZnFe phase corrodes first. Corrosive attack on α-Fe(Zn) takes place only after the exhaustion of Γ-ZnFe phase. Both Zn-Fe phases represent a cathodic protection to the base material.

In consideration of the corroded cross sections, compared to the initial state it is further noticeable that the Γ-ZnFe-phase, represented by the light gray areas is preferably corroded. That behavior is expected due to the significant difference in potential in comparison to α-Fe. Only after the Γ-ZnFe phase is used up, the attack is carried out on the zinc-containing Γ-Fe(Zn), which in turn is a cathodic protection for the base material.

Figure 3: Galvanostatic dissolution of a hot dip galvanized steel sheet with different furnace dwell times. Electrolyte: 100 g l-1 ZnSO4 • 7H2O + 200 g l-1 NaCl; T = 25°C; ventilated; I = 11,76 mA cm-2

Γ-ZnFe phase corroded due to the lower potential compared to the α-Fe(Zn) and provides cathodic protection for α-Fe(Zn), which in turn protects the base material cathodically. The timing of the base material attack is significantly delayed in all tests. The reasons for this are the higher layer thickness, which is caused by the press-hardening process and the much lower corrosion rate.
Press-hardened galvanized steel shows red corrosion products directly after start of the removal. These red corrosion products show no sign of base material corrosion and are made of Simonkolleit Zn₅(OH)₈Cl₂, Akaganeite β-FeOOH and Hydrozinkit Zn₅(CO₃)₂(OH)₆ [4-6] and are formed under basic conditions and high chloride concentrations. The anodic dissolution of zinc-iron layer is compensated by the cathodic oxygen reduction, which provides basic conditions. High chloride concentrations are caused by dry phase of the VDA tests.

So press-hardened material based on galvanized steel strip provides corrosion protection after the cathodic mechanism similar to classic galvanized material.

02.03. Resistance spot welding

Since the very first days of the development of zinc coated press-hardening steels it is a fact that resistance spot welding has to be performed by using DC double pulse technology to achieve the optimal results. Thereby a width of the welding range of more than 2.0 kA and larger nugget diameters with a high ratio of plug failure can be attained.

The aim of double pulse welding is to ensure stable welding conditions and to favor the expansion of the nugget. The FeZn-layer is rehashed within the 1st pulse and surface resistance is reduced respectively homogenized by “cleaning off” insulating oxides. To affect favorable expansion of the nugget, the 2nd pulse is performed.

The schematic figure 7 (a) shows the temporal dependency of welding resistance (dashed line) and welding current, as well as the definition of the welding range by this 2nd pulse. The set of voestalpine standard parameter for welding 1.5 mm material of 22MnB5 GI70/70 is given in figure 7 (b).

![Figure 7](image-url)

**Figure 7:** (a) Temporal dependency of welding resistance and welding pulses as well as definition of welding range, (b) voestalpine standard parameter for welding 1.5 mm material of 22MnB5 GI70/70
As shown in figure 8, this set of parameters allows a very stable welding process over a wide range of process variation respectively furnace dwell time. This standard parameter also enables welding of alternative Zn-layers, i.e., GI90/90 or GA70/70 and GA80/80 as well as welding Zn-coated PHS-materials with higher manganese content (i.e., 22MnB8) in a reliable way with wide welding range and just slightly varying nugget diameter.

Before real welding tests, surface transition resistance is measured as a standard procedure at voestalpine. This method allows the prediction of weldability during material-/-surface-developing phase.

As shown in figure 9, differing welding current at longer furnace dwell time is related to higher values of the surface resistance, but there is no major effect by the variation neither of Zn-coating nor of chemical composition [7,8].

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### 03 Processes for press-hardening

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#### 03.01. Classical processes for press-hardening

The direct hot-forming is the dominating process in today’s industrial production of press-hardening parts. It is used for uncoated material as well as for AlSi coated material.

For zinc-coated material, the direct process is limited to low coating weights resulting in coatings with no \( \Gamma \)-Zn-Fe phase or with even higher Fe-content in the coating. This is due to the threat of liquid metal embrittlement (LME) [9-12], that one has to be aware of in any condition of the Zn-Fe-layer that has liquid zinc phases in the moment the deformation takes place, which is a pre-condition to receive a decent amount of favorable \( \Gamma \)-Zn-Fe-phase in hardened condition. Therefore, the indirect process is in industrial application, as it separates deformation (cold forming) from the liquid zinc-phases that are only die cooled, but not any more deformed.
03.02. Direct press-hardening with pre-cooling

To tackle the problem of micro-cracks appearing due to liquid Zn-phases during hot-forming [9-12], we introduce the so-called direct process with pre-cooling (figure 11).

Figure 11: Adapted direct process with pre-cooling

Figure 12 shows the temperature-time development of a laboratory sample that is processed with pre-cooling: after exiting the furnace, the sample is transferred to a pre-cooling unit. Along the way (“transfer 1”), it cools down mainly due to radiation. During pre-cooling, minimal cooling rates of 50 K∙s⁻¹ should be aimed for. It is of importance that the sample must not be deformed up until this step, to avoid cracking as a result of liquid metal embrittlement. After pre-cooling, no more liquid Zn-phases are present in the coating and it is safe to transfer the sample into the die (figure 12: “transfer 2”) where the sample is then hot-formed and hardened.

Figure 12: Phases of the direct hot forming process with pre-cooling shown by a typical time-temperature graph

The temperature for transfer 2 as specified in figure 12 is above martensite start temperature. Therefore the hot-forming is still carried out with austenitic microstructure, but at lower temperature as the standard hot-forming process. In the die the same martensitic microstructure is formed as in standard hot-forming processes. Therefore the mechanical properties are similar and basically determined by the chemical composition. As the heat to be dissipated is lower for the pre-cooling process slightly higher cooling rates and reduced hold times in the die can be expected.
Figure 13 shows the results of this procedure at a larger scale. For testing purposes a hat-shaped profile geometry has been chosen. Along a certain length, the geometry features an indentation of varying depth at the top of the profile. The resulting cross-section looks similar to the letter “M” (compare figure 13 (a)).

In figure 13 (b) several cross-section polishes (out of the left half of such an M-shaped part) of a sample that was produced in the conventional direct process are shown. Especially in the more heavily deformed top section, which features small radii, deep cracks (>100 micron) into the substrate material can be observed, but cracks reaching into the steel substrate can also be registered at the lower end of the shroud, where also frictional effects influence the surface stresses. These side wall cracks are over 10 micron in depth and therefore also not acceptable by today’s OEM specifications.

In figure 13 (c) the very same section of an M-shaped geometry is shown, with the difference that the part had been pre-cooled before the actual hot-forming started. This part is free of micro-cracks in the steel substrate.

04 Summary/Conclusions

Zinc-coated press-hardening 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 favorable to have at least a minor amount of γ-Zn-Fe-phase in the coating. This increases the electrochemical potential to the base steel by a good amount.
The spot-weldability of zinc-coated press hardening steels is good in terms of welding range and nugget diameters. A two pulse welding process ensures this robust welding process. For adhesive bonding 100% cohesive failure can be expected and no delamination of the coating is observed.

Today the indirect form-hardening is the dominating production process for zinc-coated press hardening steels, but two new processes are on the edge to industrialization: roll-form hardening, with the option of partially hardened parts and direct hot-forming with pre-cooling, which is the process of choice to deal with liquid metal embrittlement and therefore deal with micro-cracks, while sustaining the cathodic corrosion protection with zinc-rich coatings.

References


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