Minor Addition with Substantial Effect - New Aluminum-Silicon Coating for a Reliable Hot-Forming Process

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Abstract. The well-known aluminum-silicon coating has managed to be on everyone's mind as the standard coating for the hot forming process for many years. This is not only due to its good scaling protection properties, but also due to the fact that both the production of the sheet material and the hot forming processes are stable and well established. One of the main challenges in hot forming is to avoid component failure due to macroscopic cracking by hydrogen embrittlement. This is particularly critical because the cracking may occur with delay, i.e. during processing in the manufacturing chain subsequently to hot stamping. To avoid this, it is necessary to reduce the diffusible hydrogen content below a critical value in the hot formed part. This contribution describes the causes for hydrogen formation in the hot forming process and possible countermeasures. The addition of magnesium between 0.1 up to 0.5 mass % into the coating has proven to effectively reduce the diffusible hydrogen content in the hardened part. We present a model describing the underlying microscopic processes of this beneficial behavior. Furthermore, we examined the impact of Mg addition on the material properties and discuss resulting advantages, which can be observed in the hot stamping process. One main feature is the reduced effort to meet the requirement for low dew points in the furnace. This leads to a more economical manufacturing process. Moreover and important for the applicator to know is, that all performance benefits of the standard aluminum-silicon coating are retained.

Keywords: Hot-dip aluminizing · AlSi coating · Magnesium · Press hardening · Hydrogen embrittlement · Delayed fracture

1 Introduction

Hot forming is widely established as manufacturing technology for high-strength automotive car body parts. The mass share of hot formed parts has reached a level at around 20% for selected car manufacturers – in some cases even up to almost 40% [1, 2]. Nevertheless, it is common ly known that high strength steels tend to have an increased

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susceptibility for hydrogen-induced cracks [3–5]. In order to prevent delayed fracture phenomena after hot forming, the amount of hydrogen in press-hardened parts has to be minimized during the processing in the manufacturing chain.

In recent years, studies were conducted for gaining insight into the influence of the dew point on coated material during the heat treatment step of the hot forming process. The majority of hot formed parts are produced with hot dip aluminized (AS) coating, which offers adequate scale protection and corrosion barrier effect on the hot formed part. It turned out that with a rising dew point also the amount of diffusive hydrogen increases in the hot formed part [5–7]. After hot forming and cooling down to ambient temperature the alloyed Al-Fe-Si coating layers have only a low permeability for hydrogen effusion. Thus, sufficiently long desorption times need to be considered or, alternatively, a tempering process is required, in order to reduce the hydrogen content in the press-hardened component by degassing through the alloyed coating [5–8].

To avoid these costly processual countermeasures, furnace manufacturers have developed different technologies to adjust low dew points in the furnace atmosphere as, for instance, the leading-in of dried air or nitrogen [9]. Nevertheless, furnace atmosphere regulation increases manufacturing costs and becomes technologically demanding when alternative furnace concepts like multi-chamber-furnaces are applied.

To overcome this drawback of increased complexity in controlling the furnace atmosphere one should raise the question if – instead of changing the hot stamping process – an improvement of the processed material itself can provide a suitable alternative in order to meet the high requirements regarding hydrogen-induced failure. Our approach in this context is a modified coating leading to a significantly reduced hydrogen uptake as described in reference [10].

Latter contains a summary of possible effects regarding hydrogen embrittlement in hot forming. It was revealed that the hydrogen uptake during hot forming of aluminum-silicon coated manganese boron steels can be reduced by an adapted coating chemistry. The effect of hydrogen formation during heat treatment is not an issue of hot stamping alone, but also affects the aluminum industry and largely occurs in high temperature metal corrosion processes [11]. By adding small amounts of alkaline earth elements the oxide layer located at the outer surface is modified in a way that significantly less hydrogen is detected inside the material after hot stamping. Already minor additions of magnesium to the coatings composition lead to a drop in diffusive hydrogen by more than 40% when typical hot forming parameters are applied. Even at furnace dew points of + 15 °C a diffusive hydrogen content of below 0.2 ppm was detected (Fig. 3). This reduced hydrogen intake paves the way to enlarge process windows regarding atmosphere regulation and significantly reduces energy consumption during hot forming – particularly at production sites in highly humid surroundings. The concept has proven to be reasonable and by now has matured to a novel product, which confirms the beneficial properties regarding hydrogen uptake without negatively affecting any other processing properties of the material system (Fig. 1).

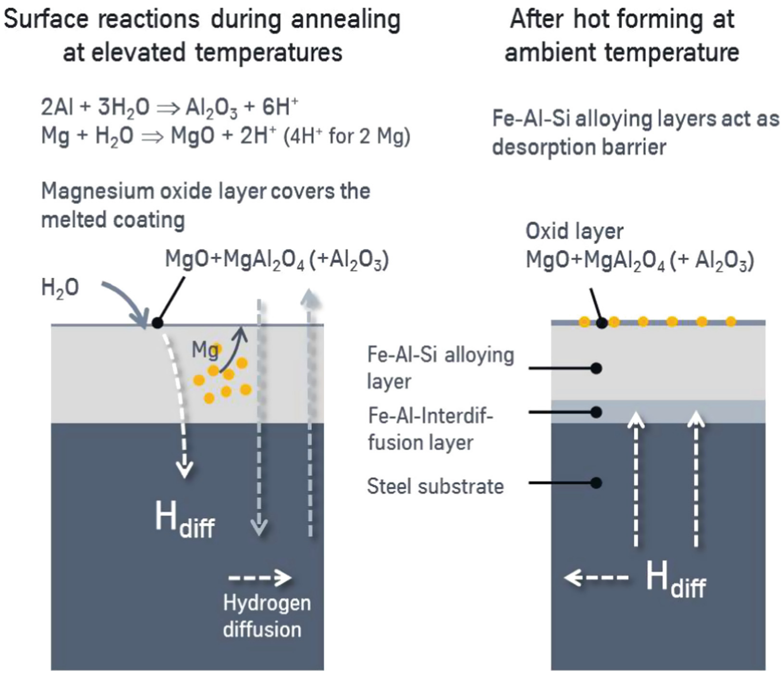

Fig. 1. Surface reactions during austenitizing process of AS Pro coated MBW® 1500.

1.1 Technical Aspects for Industrial Production of Hot-Dip Aluminized Material with a Modified Composition

Adding small amounts of magnesium during an aluminizing process is a challenging task. Due to higher oxygen affinity, increasing magnesium content can cause enhanced slag formation, which leads to a poor surface quality. Furthermore, higher magnesium contents can cause an increased hydrogen formation at elevated temperatures. Thus, the Mg level should be limited to 0.5% mass contents to ensure a proper hot dip aluminizing process.

Inhomogeneity in bath composition favors the formation of dross, which in turn provokes typical surface defects known from standard production. These defects include pimples or striations causing uncoated areas on the surface spread all over the material. More in-depth micrographic and SEM analyses showed that these defective regions are zones where the formation of the alloy layer is disturbed during coating. Additionally, the coating exhibits larger build-ups near these spots. Within these build-ups, agglomerated particles were detected – directly neighboring the sites of disturbed alloy layer formation. As measured by EDX these particles contain high amounts of magnesium and oxygen. Considering also their shape, a formation of thin MgO films can be assumed [12]. During the hot dip process, thin oxide films tend to float on the melt's surface and prevent the steel from reacting with the liquid metal when the strip immerges into the melting bath inside the snout area. This effect is known from the hot dip galvanizing process and is described in detail in Ref. [13]. Less favorable conditions during the aluminizing process make the occurring of these defects more likely. But since dross defects are well known from the standard production of the non-modified AlSi coating, there exists a variety of counter measures to effectively gain back control over the resulting coating quality. This includes measures like keeping the bath at a constant level or minimizing bath movement. Another aspect is an improved technique to add small amounts of elements (like the magnesium) to the liquid aluminum melt in order to keep the chemical composition of the melt at its nominal values. Generally, modifying the flowing conditions in the melting bath, especially in the snout area, makes it possible to achieve an even and technically defect-free surface appearance. Therefore, AlSi-coatings with added magnesium can be deposited possessing the same surface quality as standard AlSi. The optimized AlSi coating can thus be applied on the hot forming steel grade 22MnB5 as well as on other grades of a variety of strength levels.

2 Experimental Details

22MnB5 material was coated on an industrial scale plant at thyssenkrupp Steel Europe. Two different coatings were applied: the optimized version of the AlSi coating with added magnesium (referred to as “AS Pro”) and the standard AlSi coating (referred to as “AS”) which served as a reference. The nominal coating weight was 150 g/m^2 (added value for both sides). The aluminizing process was carried out under normal conditions used for standard production. Specimens were cut from coiled material and press hardened in a laboratory scale hot forming line equipped with a multi-zone roller hearth furnace with dew point regulation and a 1250 kN press in order to quench and harden the specimens in a water-cooled flat die. The annealing step was carried out at a temperature of 920 °C. Further specimens were formed to a hat-like shape and to B-pillar mid-segments. Sheet thickness and humidity during annealing in the hot stamping facility were varied during the series of experiments – the sheet thickness ranging from 1.0 to 2.0 mm and the dew point ranging from -5 to 25 °C. The annealing time was set according to sheet thickness and oven atmosphere. The dew point during annealing was measured by a chilled mirror hygrometer.

Polished cross sections were prepared after hot forming and analyzed by optical and electron microscopy to evaluate the microstructure and the alloyed coating. Specimens for hydrogen measurements were stored in liquid nitrogen directly after hot forming to avoid hydrogen effusion. The diffusive hydrogen was determined by thermal desorption mass spectrometry (TDMS) [12]. In addition to standard hot forming experiments described above, hot strip drawing tests were conducted to investigate the influence on the coefficient of friction by differences in the oxide layer formation during the heat treatment. These tests were conducted at drawing temperatures of 600 and 700 °C, after a fully austenization at 920 °C, in order to resemble typical temperatures during the actual forming process in the die. The test methodology and equipment is reported in more detail in Ref. [14].

Welding tests were performed according to the technical test specification SEP 1220. Resistance spot welding was carried out according to SEP 1220-2. Paint adhesion properties were determined by cathodic dip-paint coating (KTL) experiments using a paint thickness of 20 μm. These samples were provided with a cross-cut according to DIN

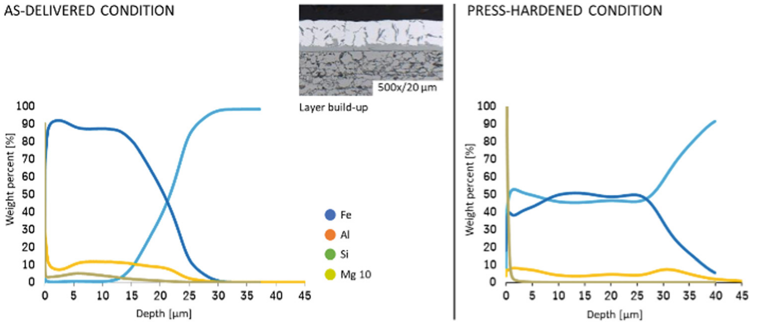

Fig. 2. Polished cross sections and GDOES of AS Pro before (left) and after hot forming (right) under typical processing conditions.

EN ISO 2409 and tested with and without exposing them to a corrosive atmosphere. Corrosion behavior generally was tested according to the testing standard VDA233-102 (2013.06).

To evaluate the potential of the AS Pro coating for the use in flexible rolled materials, a post aluminizing cold rolling procedure was conducted on samples with an initial thickness of 2.0 mm. The material was cold rolled in a laboratory scale cold roll mill with a thickness reduction of 30 and 50% respectively and subsequently press hardened.

In some cases, results were published already in Ref. [10]. In these cases, the present paper validates these results with improved statistical validation.

3 Results and Discussion

Figure 2 shows polished cross sections of an AS Pro sample before and after hot stamping. For all tested specimens, the overall coating thickness after hot stamping was in the range of 35–40 µm, which is a typical value for this type of coating. AS Pro also shows a comparable behavior to standard AlSi coating ("AS") regarding the development of interdiffusion layer thickness. SEM measurements on hot formed samples yielded a modified oxidation behavior of AS Pro compared to AS. AS Pro samples developed a covering magnesium oxide layer which was fully covering the surface whereas this was not the case with standard AS.

Figure 3 summarizes measurements on the diffusible hydrogen contained inside the specimens after hot forming (920 °C, 5 min.). The figure extends measurements already reported in Ref. [10]. As can be seen, there is a well pronounced difference between standard AS and AS Pro coated samples. Up to a dew point of 15 °C, the hydrogen content is below 0.2 ppm whereas in standard AS these values are at least 60% higher, depending on the actual dew point.

The results of the hot strip drawing tests are summarized in Fig. 5. For AS Pro specimens, a slightly lowered friction coefficient was detected compared to standard AS. This difference increases with higher drawing temperature (cf. Figure 5). However, the significantly different oxidation behavior does not require technical modifications in the hot stamping setup. The surface formation after hot forming in microstructural

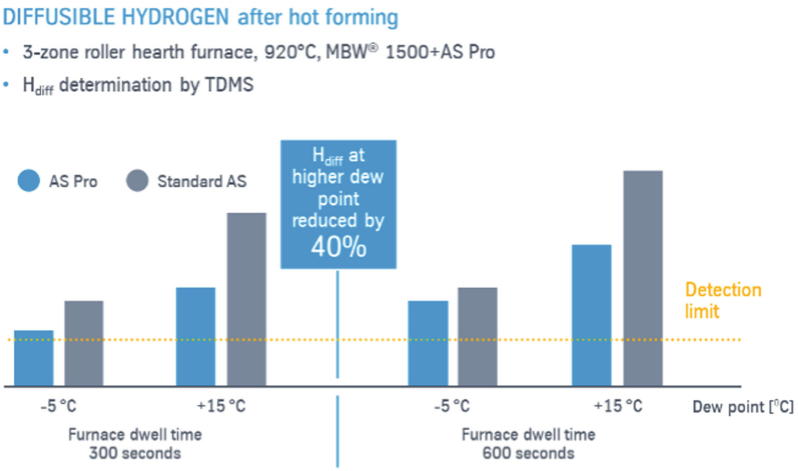

Fig. 3. Diffusive hydrogen content after hot forming vs. furnace dew point.

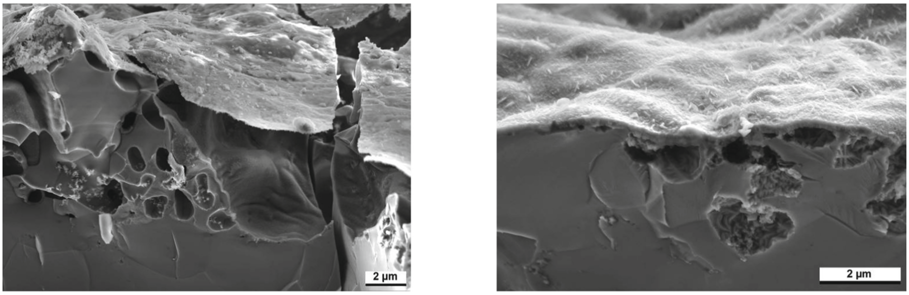

Fig. 4. SEM of broken up surface after hot forming of AS (left) and AS Pro (right).

evaluation was investigated after 300s dwell time. The overall coating thickness with 35–40 μm and the inter-diffusion layer thickness of 10μm were comparable with the conventional coating.

GDOES measurements (see Fig. 2) have shown a nearly homogeneous magnesium distribution over the coating thickness after the hot dip aluminizing process. After hot forming magnesium enrichment was detected in surface near areas.

Additionally, SEM investigation was conducted on hot formed samples to confirm the assumption of modified oxidation behavior and magnesium oxide layer formation. Therefore, samples were broken open under liquid nitrogen. The AS Pro sample featured a covering oxide layer whereas the conventional AS coating had a fault block like oxygen layer (see Fig. 4). To confirm the magnesium enrichment a SEM element mapping was conducted.

Regarding the forming behavior, no significant differences were detected. Additional tests were conducted with a hat profile and a B-pillar mid segment. The processability of the modified coating was comparable to series AS coated material.

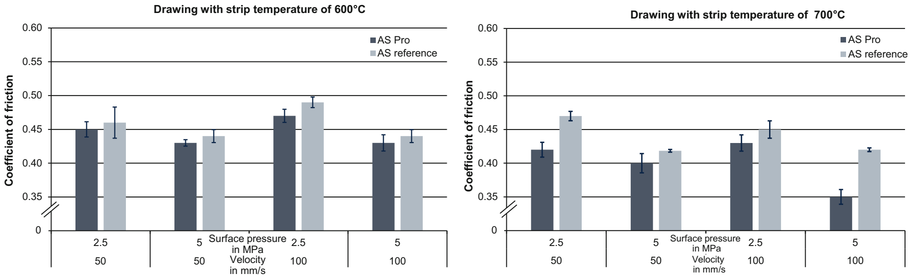

Fig. 5. Coefficient of friction for different drawing parameters (hot strip drawing test [12]).

Despite the different oxidation behavior, the resistance spot welding tests showed a comparable processability for both AS and AS Pro coated material. Both types of specimens exhibited nearly the same range of applicable welding current. During electrode lifespan tests, no welding splatters were observed on neither coating type. These tests were run up to 2000 welding spots. Metal active gas (MAG) welding tests proved good processability of both coating types as well.

Paint adhesion tests yielded a cross cut value of GT 0 without corrosion exposure. After 10 cycles of alternating climate test, this value was still at GT 1. It can be concluded that the addition of magnesium to the standard AS coating does not hamper welding or corrosion behavior of the material.

In addition to the reported standard tests, we performed cold rolling tests prior to hot stamping in order to evaluate if AS Pro coated material would be suitable for additional cold rolling processes to obtain locally adapted blank thicknesses. Literature generally suggests in this context, that with increasing degree of cold reduction an increasing amount of hydrogen will be found in the material after hot stamping [10, 15]. As mentioned before, sheets of an initial thickness of 2.0 mm were coated in an industrial process and exposed to cold rolling to 30% prior to hot stamping. Figure 6 exemplarily shows polished cross sections of these specimens. As can be seen, the rolling process significantly stretches the coating and reduces its thickness. After hot stamping, the comparatively brittle ternary alloy layer breaks and opens up. Nevertheless, in all observed cases, the coating still covered 100% of the sheet surface completely – also when magnesium was added to the standard AS coating.

The TDMS measurements after cold rolling and press hardening are presented in Fig. 7. For standard AS, these measurements confirm the above-mentioned indications from literature with an increasing hydrogen content resulting from a higher degree of deformation. Nevertheless, this is not the case for AS Pro, where a higher degree of deformation does not harm the material by means of increased hydrogen intake. Therefore, it can be concluded that AS Pro might be even more suitable for flexible rolling processes combined with subsequent hot stamping than standard AS.

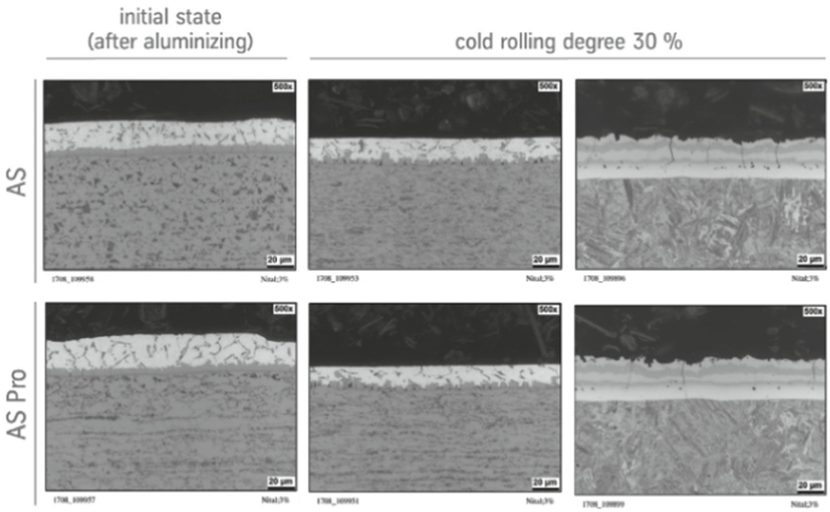

Fig. 6. Cross sections of AS and AS Pro as delivered, after cold rolling and after press hardening.

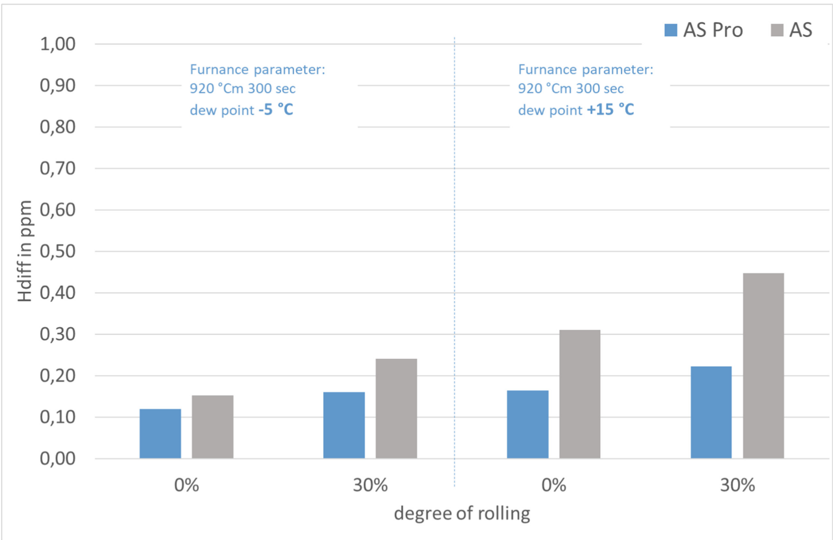

Fig. 7. Diffusive hydrogen content after cold rolling and press hardening (920 °C annealing temperature).

4 Conclusion

The reduction of diffusive hydrogen in coated press hardened steels is an important issue concerning aspects like delayed fracture of crash relevant automotive components. This contribution reports on experimental work, which shows that modifying the standard AlSi-coating by adding small amounts of magnesium significantly reduces hydrogen uptake into material during the hot forming process. The difference in hydrogen uptake can even exceed values like 60% depending on the particular processing conditions, e.g. the atmosphere during annealing. Besides this significant impact on the hydrogen issue, it turned out that there are no drawbacks of the novel AS Pro coating regarding key processing properties of the material like welding, corrosion behavior and paint adhesion. Cold rolling experiments prior to hot stamping indicate that AS Pro is even less susceptible for increased hydrogen intake during hot forming. Therefore, AS Pro coated material could be much more suitable than standard AS for thicknesses adapted blanks when these are subsequently combined with hot stamping after cold rolling processes. The notice about lower hydrogen intake of AS Pro renders complex technologies for atmosphere control during annealing unnecessary and thus leads to significant saving regarding complexity in production as well as energy consumption.

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