ON THE REDUCTION OF TEMPERATURE GRADIENTS WITHIN ALSI-COATED BLANKS WITH NON-CONSTANT SHEET THICKNESS FOR HOT PRESS FORMING APPLICATIONS

Friedrich Luther, Marc Debeaux and Frank Beier - Salzgitter Mannesmann Forschung GmbH, Germany

ABSTRACT

This study explores a modified AlSi coating concept for blanks with varying sheet thicknesses to minimise the temperature gradient within a blank and the hydrogen pickup during heating prior to press hardening. The approach used here is to form an iron rich layer on the AlSi coating surface by an adapted conversion treatment, which results in elevated heating rates.

Samples were produced by partly reducing the thickness of 22MnB5+AS150 blanks in a laboratory cold rolling process. The coating modification was applied before or after the cold rolling step. Additionally, a welded blank was produced in which only the thicker part was modified by a conversion treatment. The as produced samples were heated in a laboratory furnace, recording the heating rates of the thinner and thicker areas of each sample. Additionally, the amount of hydrogen pickup was analysed by thermal desorption mass spectroscopy (TDMS) from a separate set of samples.

It has been found that the temperature gradient within a blank can be reduced significantly for all modified samples compared to the unmodified reference material. This is due to a greatly increased heating rate of the thicker part of the sample. Therefore, the minimum furnace dwell time can be decreased, enlarging the process window and reducing the time-dependent hydrogen uptake during heating. Furthermore, hydrogen uptake is reduced by the conversion layer itself.

KEYWORDS

AlSi, temperature gradient, conversion treatment, surface modification, diffusion layer, hydrogen

INTRODUCTION

When heating steel blanks with different sheet thicknesses within prior to a hot press forming process, local heating rates may differ significantly. Therefore, the process window for heating the blanks is narrow, especially when aluminium-silicon (AlSi) coated material is used. The thicker part of the blank determines the minimum furnace dwell time for alloying of the coating to achieve sufficient paint adherence [1,2]. The thinner part, on the other hand, limits the maximum dwell time to ensure good spot weldability, because with increasing degree of alloying, welding current range decreases [3]. Additionally, when the heat treatment exceeds the process window, the amount of absorbed hydrogen may become detrimental [4,5]. It is known from literature that hydrogen absorption depends not only on material, dwell time, temperature and atmosphere but also increases with the degree of cold reduction [6-8].

Compared to uncoated material for hot press forming applications, AlSi coated blanks exhibit lower heating rates for the same material gauge and furnace conditions due to a higher surface reflectance. There are several approaches to increase the heat absorption of AlSi coatings, e.g. by an anodizing treatment [9]. However, none of them is intrinsically beneficial in terms of diffusible hydrogen pickup during heating. In contrast, this study deals with an AlSi coating modification that has a proven positive effect on both aspects.

1. ALSI COATING MODIFICATION

The developed coating modification is a multi-step cleaning and coating process. In the first step the AlSi surface is treated with a mild alkaline cleaner at pH 10.5 and 60 °C for several seconds to remove dust or traces of oil. The actual surface modification is carried out in the second step using a highly alkaline solution (0.7 M OH^-) of complexing dissolved Fe compounds at 45 °C. This conversion treatment can be carried out by spraying or dipping if a high shear rate at the interface is provided to remove hydrogen bubbles from the surface. The coating process is completed by thorough rinsing with DI-water, after the desired amount of Fe compounds has precipitated on the surface.

The AlSi coating before and after conversion treatment is shown in Fig. 1. The modified coating exhibits exposed silicon phases because aluminium is selectively dissolved during the process. Furthermore, a very thin iron rich layer forms on the coating surface, which can be proven by GDOES measurements (Fig. 1).

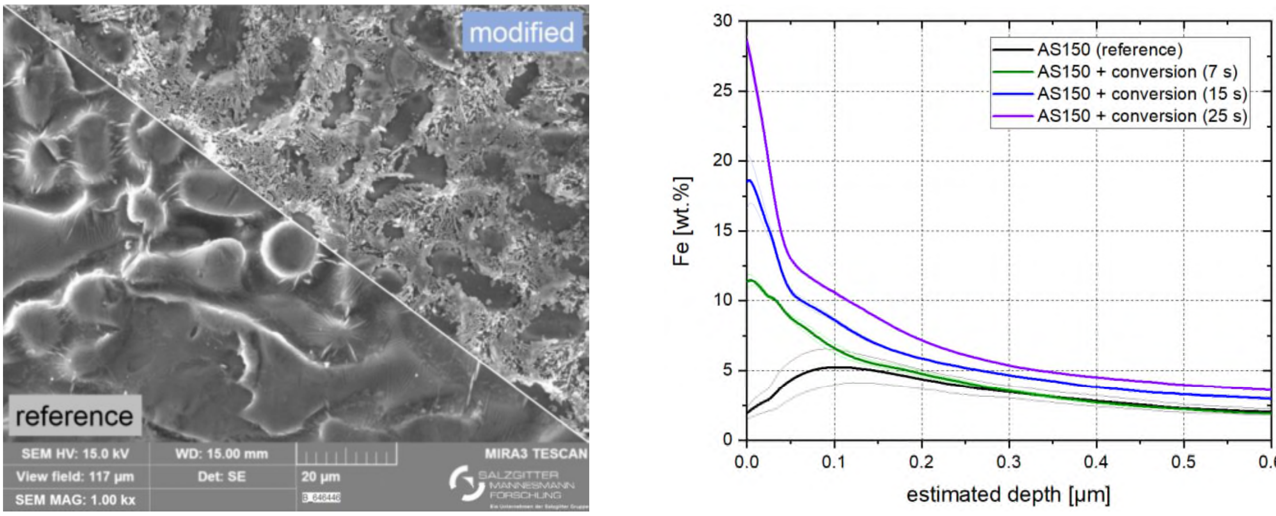

Fig. 1: SEM images and GDOES measurements of the AlSi coating surface before and after conversion treatment (prior to press hardening)

The modified surfaces exhibit an increased heat absorbance, which results in elevated heating rates. Fig. 2 shows measured heating curves for 1.5 mm AS150 material in the as delivered condition as well as modified with a conversion treatment in a laboratory furnace heated at 910 °C. Furthermore, the experiments have shown that after press hardening the coating morphology may change from a well-known quasi-continuous formation to a cluster-like formation of the intermetallic phases [1]. However, by reducing furnace zone temperatures, this effect can be avoided if necessary.

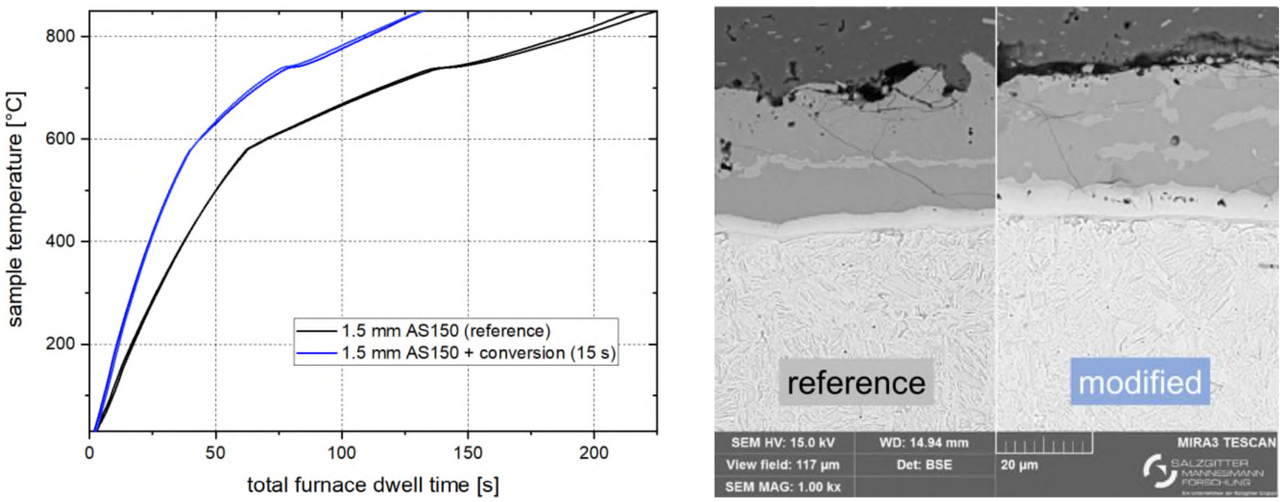

Fig. 2: Influence of 15 s conversion treatment on heating behaviour of 1.5 mm 22MnB5+AS150 at 910 °C furnace temperature (left); coating morphology with and without modification (right)

Lab scale experiments with batch-wise modified AS150 blanks have been performed to evaluate the modified coating approach in comparison to standard-AlSi material in press hardened condition. Fig. 3 shows cross sections of the surface near region of the coating as well as the results of welding tests for different conversion treatment times. The modified coating shows a thickened Al-oxide layer, which may result from an accelerated Al_2O_3 growth due to the precipitated iron, affecting O and/or Al transport rates [10]. However, up to 10 s conversion treatment time, no effect on welding current range was noticeable. For longer treatment times, the welding current range becomes smaller due to a higher degree of alloying caused by increased heating rates as well as the thickened oxide layer. Additional tests for evaluation of adhesive bonding and corrosion resistance (corrosion creep, stone ship resistance) show comparable results.

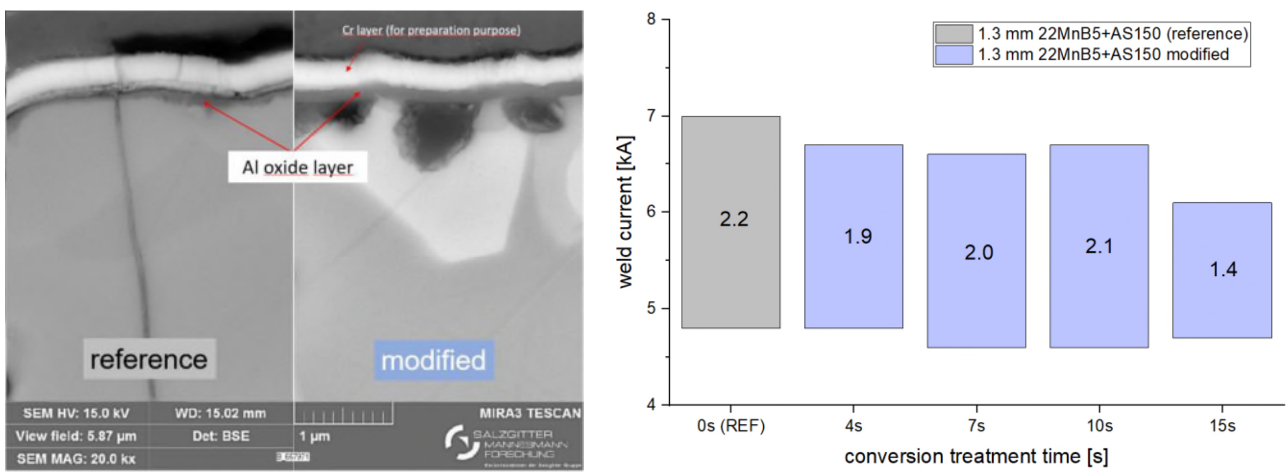

Fig. 3: SEM images of cross sections from AlSi coatings in the surface near region after hot forming with and without conversion treatment (left); welding current range (SEP 1220-2) for different conversion treatment times after hot forming (930 °C furnace temperature, 360 s total furnace dwell time)

2. EXPERIMENTAL

For this contribution 22MnB5+AS150 blanks with dimensions of gauge 1.5 mm were used as well as 0.75 mm blanks produced from 1.5 mm AS150 blanks by rolling in a laboratory cold rolling mill. In the first part of this study, the influence of conversion treatment time and cold reduction on iron layer weight and resulting heating rates was determined. Therefore, cleaned samples with dimensions 200 x 300 mm^2 were dipped in alkaline solution (0.7 M OH^-) of complexing dissolved Fe compounds at 45 °C according to Table 1, followed by rinsing with DI-water. The as produced samples were analysed by optical emission spectrometry (ICP-OES). Additionally, samples with spot-welded thermocouples were used to measure heating curves in a laboratory furnace pre-heated to 930 °C under ambient atmosphere.

Table 1: Parameters for sample preparation

material	cold reduction	sample gauge	conversion treatment time
	%	mm	s
22MnB5+AS150 (1.5 mm)	0	1.5	0
			7
			11
			15
			25
			50
	50	0.75	0
			7
			11
			15
			25
			50

In the second part of this study, the influence of conversion treatment and cold reduction on the amount of diffusible hydrogen was analysed by thermal desorption mass spectroscopy (TDMS). Therefore, cleaned samples with dimensions 800 x 200 mm^2 were treated in an adapted laboratory degreasing line according to Table 2 (spray conversion, alkaline solution as in the first part of this study). Two samples for each condition with dimensions 20 x 200 mm^2 were heated in a laboratory furnace preheated to 930 °C for 320 s total furnace dwell time followed by press hardening in a flat die (ambient atmosphere, dew point +4 °C). Immediately after hardening, 6 subsamples with dimensions 20 x 40 mm^2 for each condition were stored in liquid nitrogen and subsequently analysed by TDMS at a heating rate of 0.33 K/s from 40 to 450 °C.

Table 2: Parameters for sample preparation (CR=cold reduction; CL=conversion layer)

material	treatment A	treatment B	sample gauge	condition
			mm	
22MnB5+AS150 (1.5 mm)	-	-	1.5	1.5 mm reference
	conversion (10 s)	-	1.5	1.5 mm CL
	cold reduction (50 %)	-	0.75	0.75 mm CR reference
	cold reduction (50 %)	conversion (10 s)	0.75	0.75 mm CR+CL
	conversion (10 s)	cold reduction (50 %)	0.75	0.75 mm CL+CR

In the final part of this study, samples were produced by partly reducing the thickness of 800 x 200 mm^2 22MnB5+AS150 blanks from 1.5 down to 0.75 mm in a laboratory cold rolling process. A 15 s spray conversion treatment was applied in the adapted laboratory degreasing line before or after the rolling step (alkaline solution as before). Additionally, a welded blank was produced in which only the thicker 1.5 mm part was modified. The produced samples were cut down to dimensions of 600 x 200 mm^2, whereby the thickness transition was in the middle of the specimen. Fig. 4 illustrates the preparation of the different sample types.

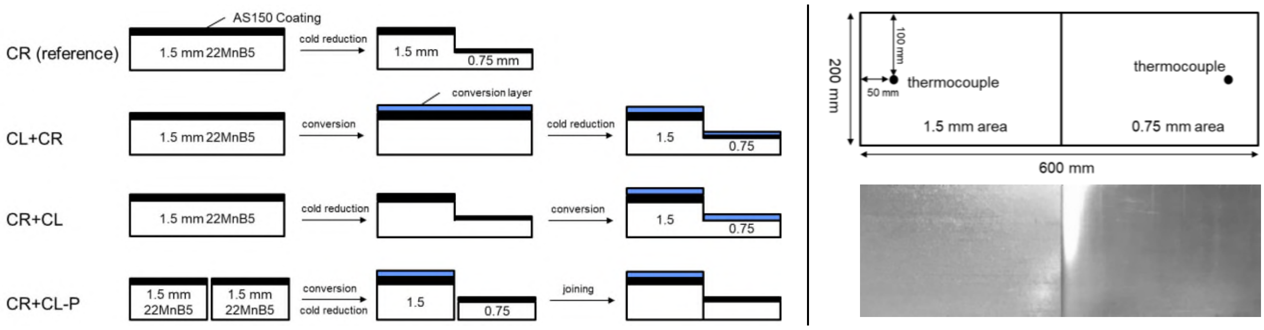

Fig. 4: Sample preparation (CL-P=conversion layer partially applied)

The as produced samples were heated in a laboratory furnace preheated to 920 °C with 300 s total furnace dwell time. The heating rates of the thinner and thicker areas for each condition were simultaneously recorded by spot welded thermocouples (see Fig. 4), followed by natural cooling in air (no hardening was applied due to the spot-welded thermocouples). Additionally, the diffusion layer thickness in both areas of each sample was determined from cross sections, taken from the immediate vicinity of the thermocouples.

3. RESULTS AND DISCUSSION

The influence of conversion treatment time and cold reduction on iron layer weight and resulting heating rates is shown in Fig. 5. With increasing conversion treatment time, the resulting iron layer weight increases as well. However, regarding the necessary furnace dwell times of the samples to reach 850 °C, an improvement could only be observed up to 15 seconds treatment time. While short conversion treatment times of 7 and 11 s lead to comparable iron layer weight on the 0.75 and 1.5 mm samples, cold rolled 0.75 mm samples show a lower iron layer weight at longer treatment times of 15, 25 and particularly 50 s, indicating a self-limiting process.

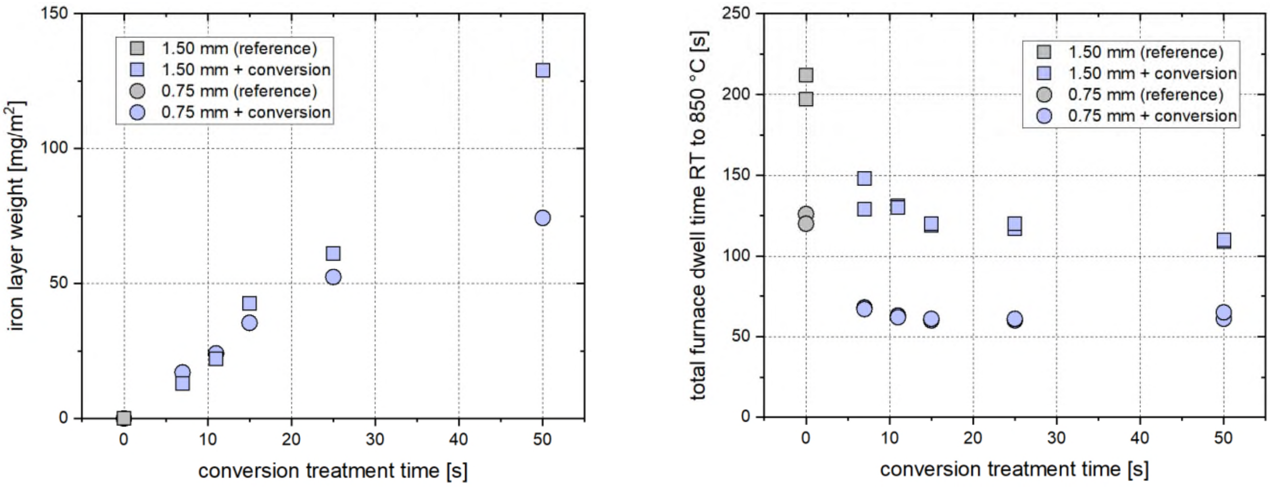

Fig. 5: Iron layer weight and total furnace dwell time (RT to 850 °C) as a function of conversion treatment time

This unexpected behaviour of the cold rolled AlSi surfaces is probably caused by the segmentation of the Si phases in the coating as a result of the cold rolling step. Si phases are important for the conversion reaction as preferred sites of hydrogen generation, accelerating the iron deposition rate.

For the cold rolled samples, this reaction is inhibited after a period of time, which was veryfied by in situ analysis of the conversion reaction on rolled and non-cold rolled AlSi coatings shown in Fig. 6. This is most likely due to the reason that the small Si-phase segments are covered by the iron layer and subsequently are no longer available as sites for hydrogen generation.

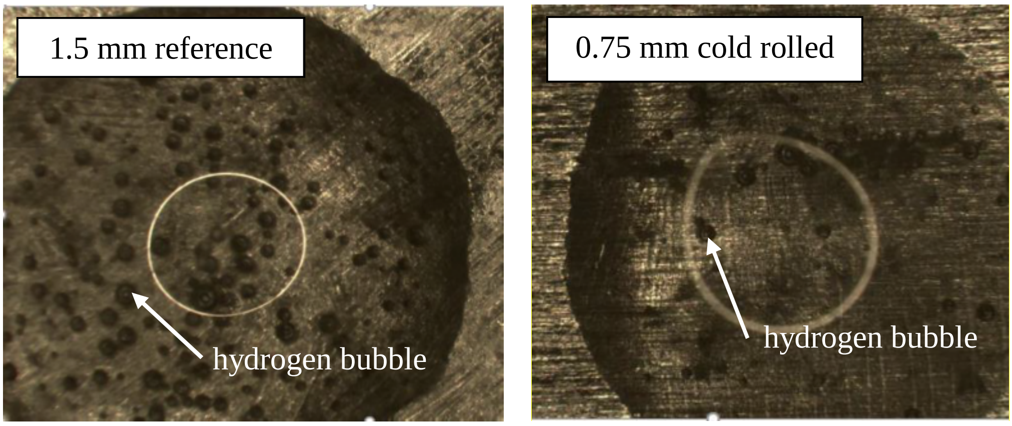

Fig. 6: LOM images of ongoing conversion treatments in droplets on AlSi coatings (left: 1.5 mm AS150 reference; right: 0.75 mm AS cold rolled (produced from 1.5 mm AS150)

The developed conversion treatment reduces diffusible hydrogen pick up during heating, which can be verified by TDMS measurements, presented in Fig. 7. In order to interpret these results, it should be noted that the heating rates and dwell times at high temperature were significantly higher for the modified samples. Therefore, the difference in hydrogen pickup should be more pronounced for comparable heating curves but these tests could not be carried out due to technical limitations. The best results were achieved for the cold rolled samples, when the conversion treatment was applied after the cold rolling step (CR+CL).

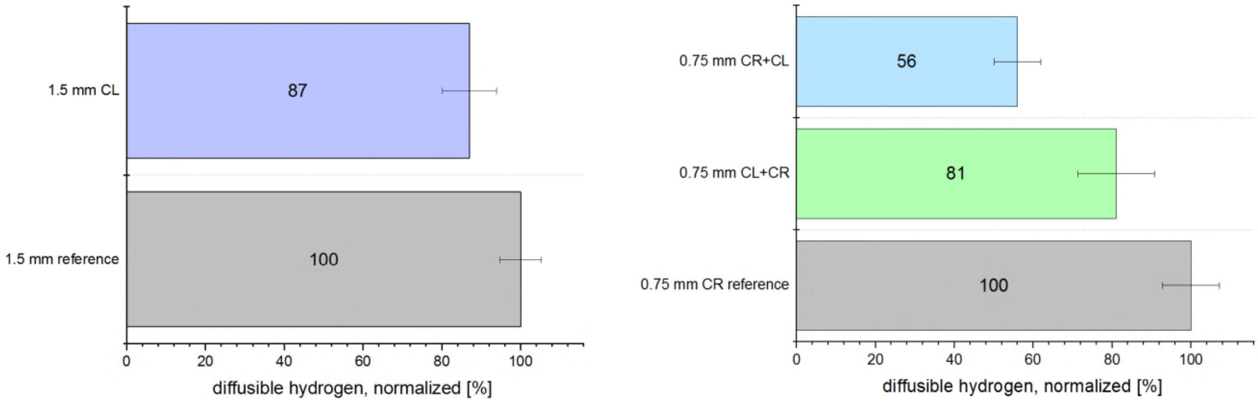

Fig. 7: Diffusible hydrogen content of AlSi coated samples in different conditions after hot forming (930 °C furnace temperature, 320 s total furnace dwell time, dewpoint +4 °C)

Fig. 8 shows the average heating curves of the partly cold rolled 22MnB5+AS150 samples in the thinner and thicker area for each condition. In addition, the resulting mean temperature difference between the thinner and thicker area ($T_{0.75mm}$-$T_{1.5mm}$) is shown for each condition as a function of the total furnace dwell time. Compared to the reference material CR, all modified samples exhibit higher heating rates in both areas and a significant reduction of the temperature gradient. The variant with a conversion treatment before the cold rolling step (CL+CR) shows the best result with the lowest temperature gradient, because here, the effectiveness of the conversion treatment in the thinner sample area has obviously been significantly reduced by the cold rolling step. However, the variant with a modification after the rolling step (CR+CL) also shows a lower temperature gradient, because the conversion treatment is less effective in the thinner cold rolled area. In case of the welded blank, where only the thicker 1.5 mm part was modified (CR+CL-P), this area heated up even faster than the untreated thinner part of the sample.

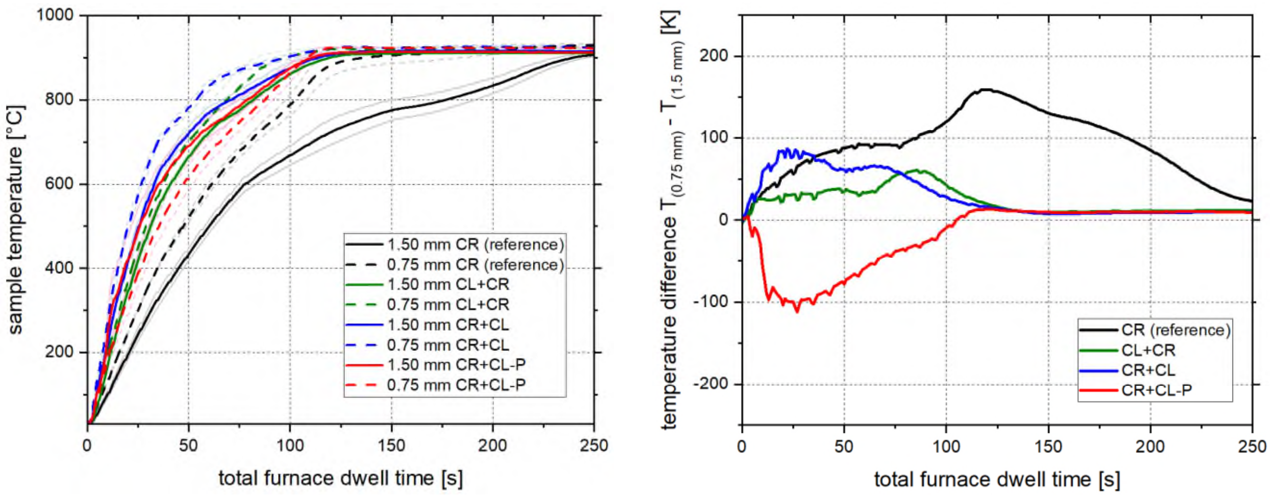

Fig. 8: Average heating curves of each sample type in the 1.5 and 0.75 mm area and resulting mean temperature differences (920 °C furnace temperature, furnace gradient +10 K for thermocouple of thinner sample area)

The analysis of the AlSi layer structure with regard to the diffusion layer thicknesses in the thicker and thinner areas of each sample confirms the effectiveness of the modification treatments carried out, see Fig. 9. While the diffusion layer thicknesses differ considerably in the reference samples (CR), they are at the same level for the modified blanks, taking into account the furnace gradient of +10 K for the thermocouple of the thinner sample area.

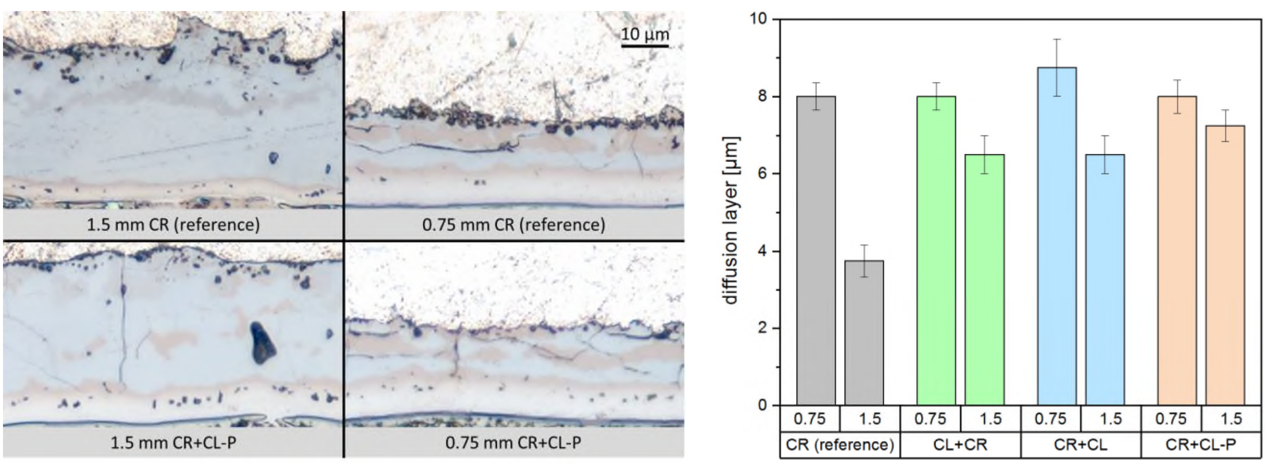

Fig. 9: Diffusion layer thickness in the 1.5 and 0.75 mm area (920 °C furnace temperature, 300 s total furnace dwell time, furnace gradient +10 K for thermocouple of thinner sample area)

4. CONCLUSIONS

The developed conversion treatment for AlSi coated material is suitable to enlarge the process window for hot press forming of blanks with non-constant sheet thickness by significantly reducing the temperature gradient between thicker and thinner areas within a blank. The modification can be applied before or after a cold reduction step of the coated material as well as locally, if welded blanks are considered. Due to the substantial increase of the heating rate particularly in the thicker areas of a blank, the required minimum total furnace dwell times can be reduced, which lowers costs and as a side effect decreases time-dependent hydrogen uptake in the furnace. Furthermore, hydrogen uptake is reduced by the conversion layer itself.

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