Original Article

Hydrogen absorption of ultra-high strength aluminum-silicon coated 22MnB5 steels

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ABSTRACT

The hot forming process allows to produce safety-relevant structural components in the automotive industry with strengths of 1500 MPa and higher. Generally, high strengths make material sensitive to hydrogen embrittlement. The heat treatment in the hot forming process chain is a potential source of diffusible hydrogen for hot-dipped aluminum-silicon coated boron-manganese steels. In the present work, the influence of different process gases and furnace dwell times during the heat treatment was investigated. Humidified process gases such as synthetic air, nitrogen, oxygen and carbon dioxide were used. The results of the thermal desorption mass spectrometry (TDMS) revealed a more pronounced hydrogen uptake for nitrogen and carbon dioxide gas atmosphere than for synthetic air and oxygen. Furthermore, different material conditions were investigated regarding their sensitivity to hydrogen absorption. The flat-rolled material tends to suffer a higher hydrogen absorption compared to the reference material when using humidified process gases. Materials being pretreated with dry synthetic air point at a relation between the duration time of the pretreatment and the content of absorbed hydrogen.

1. Introduction

To promote lightweight design and crash safety potential in the automotive industry, an increasing number of hot-stamped components with strengths of 1500 MPa and higher are used in car body constructions [1]. However, steels with high tensile strength reveal an increasing sensitivity to hydrogen embrittlement [2]. The mechanism of hydrogen uptake and diffusion processes were initially studied by Gräfen and Kuron [3] and Riecke [4]. Georges et al. [5] showed that the source of diffusible hydrogen is the humidity of the furnace atmosphere during the heat treatment in the hot forming process. Depending on the chemical properties of the metal coating and its condition (e.g., thickness), the potential for hydrogen generation, absorption and dissolution varies [6]. In direct hot forming of metal sheets, aluminum-silicon (AlSi)

coated 22MnB5 steels represent the most common material combination in the automotive industry. The heat treatment of the metal sheets is usually carried out at temperatures around 900 °C for 5—10 min in gas or electrical heated roller hearth furnaces [7]. During the heat treatment process, the bulk material transforms to austenite and iron diffuses from the bulk material towards the AlSi coating [8]. At around 575 °C, the coating partially melts and forms solid Al—Si—Fe intermetallic phases [9]. A thermochemical reaction between the AlSi-coating and oxygen, e.g., induced by water vapor of the furnace atmosphere, forms a thin aluminum oxide layer Al_2O_3. Caused by the oxidation reaction between aluminum and water vapor, atomic hydrogen evolves, is absorbed into the AlSi coating and eventually diffuses through the diffusion zone into the austenitic bulk material [10]. The possible thermochemical reaction for the hydrogen absorption is shown in detail in Fig. 1.

Jo et al. [6] showed that aluminum atoms of the coating react with water vapor molecules of the furnace atmosphere eventually generating atomic hydrogen on the surface (see Equation (1)). The transport mechanism of the generated hydrogen was proposed by Darley and Ruther in 1957 [12]. Hydrogen protons (H^+) diffuse through the Al_2O_3 layer towards the oxide-metal interface. In this case, the protons are reduced and the atomic hydrogen can diffuse into the coating layer. From the coating, the aluminum cations (Al^{3+}) diffuse to the atmosphere - oxide interface. After the hot forming process, the atomic hydrogen is dissolved within the bulk material. Furthermore, the diffusion zone of the AlSi coating acts like a diffusion barrier for the atomic hydrogen and eventually reduces its desorption ability [10].

The dew point of the furnace atmosphere is usually not controlled during the heat treatment of AlSi coated blanks. In special cases, hot forming production lines have a dew point control to reduce the diffusible hydrogen content [13]. The dew point and, therefore, the oxidation and hydration potential depend on the absolute humidity of the surrounding gas atmosphere [5]. Possible thermochemical reactions on the surface can be classified into dry and wet oxidation reactions being considered in the following equations [14]:

$$\text{Wet oxidation: } 2Al + 3H_2O \rightarrow Al_2O_3 + 6H_{ad} \qquad \text{(Equation 1)}$$

$$\text{Dry oxidation: } 4Al + 3O_2 \rightarrow 2Al_2O_3 \qquad \text{(Equation 2)}$$
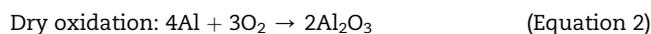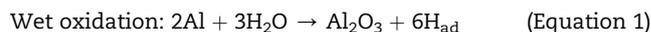
In the present work, the influence of the furnace atmosphere and its humidity on the absorption of the atomic hydrogen into the aluminum-silicon coated hot-dipped boron-manganese steel 22MnB5 was investigated. Besides, the same material after rolling to a degree of 50% was studied in order to understand the impact of the cold rolling process on the hydrogen content of the metal sheet. During the experiments different process gases with a dew point around 22 °C were used and the heat treatment duration was varied. The diffusible hydrogen content was analyzed by thermal desorption mass spectrometry (TDMS) [15,16]. In order to influence the ratio between wet and dry oxidation (see Equations (1) and (2)), humid nitrogen and oxygen gas atmospheres were employed. By using humid nitrogen gas, the oxidation of aluminum should be primarily caused by the reaction with water vapor molecules (see Equation (1)). Eventually, this should lead to higher diffusible hydrogen contents.
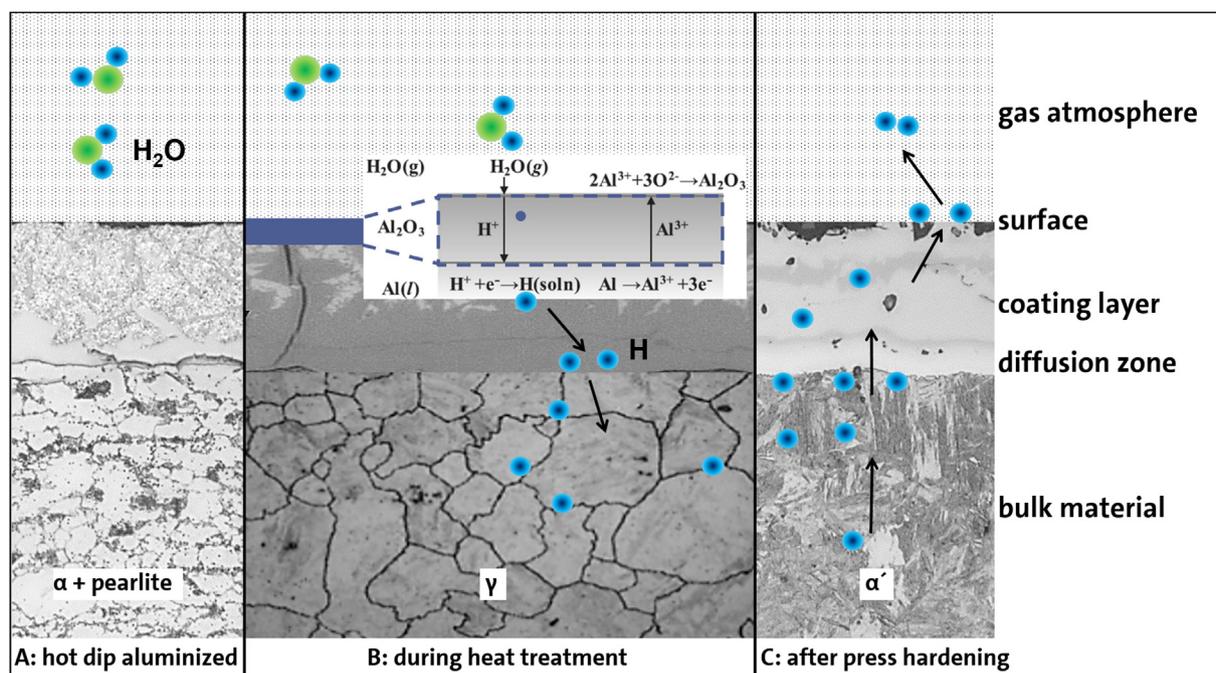

Fig. 1 — Schematic illustration of the hydrogen uptake caused by wet oxidation of the aluminum-silicon coated 22MnB5 steel. Modified after references [6,10,11].

Furthermore, by using humid oxygen gas, the contribution of the dry oxidation (see Equation (1)) should be higher than for humid synthetic air due to the higher oxygen partial pressure [14], i.e., the diffusible hydrogen content should be lowered for humid oxygen treated samples. In addition to nitrogen and oxygen atmospheres, the impact of carbon dioxide gas was also studied as carbon dioxide is released into the furnace atmosphere due to burner defects of gas-heated furnaces [17]. Finally, flat-rolled and pretreated samples were studied regarding their hydrogen absorption ability in humid synthetic air atmosphere.

2. Experimental

2.1. Measurement setup and heat treatment

For performing resource-efficient and flexible experiments with high precision, a custom-built measurement setup for heat treatment of metals was constructed (see Fig. 2). An electric chamber furnace was used in order to ensure a precise temperature control and to avoid formation of combustion gases, which could distort the measurement results due to the presence of water. To establish a stable, laminar gas flow and a well-defined homogenous humidity distribution, a self-designed quartz glass tube was chosen as reaction chamber. The metal samples were placed through a flexible opening ($\approx$ 40 mm in diameter), while both other openings ($\approx$ 10 mm in diameter) were used for gas injection and dew point monitoring. The humidity of the gas atmosphere was set by using a bubbler system from *Carl Roth GmbH + Co. KG* and controlled by the dew point measurement system *Optidew* from *Michell Instruments Limited*. After the dwell times had been attained, the metal sheets were quenched in liquid nitrogen to enforce martensitic transformation and to avoid further reactions on the metal surface. In order to prevent hydrogen desorption, all samples were immediately stored in a Dewar vessel filled with liquid nitrogen.

The temperature-time curves of the heat-treated metal samples were measured by using a thermocouple of type K. The total heating ti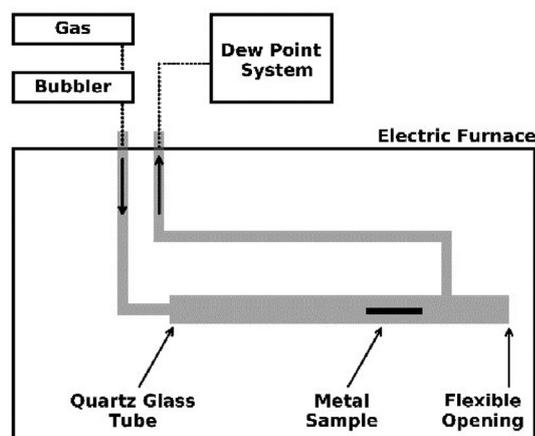me of the metal here is defined as the dwell time during the experiment (see Fig. 3). Measurements were performed at a furnace temperature of about 912 °C and dwell times between 30 s and 10 min for different humid gas atmospheres, i.e., synthetic air, nitrogen, oxygen, and carbon dioxide atmosphere. Before the experiments, the reaction chamber was flushed with the respective gas for several hours in order to promote a stable humidity level. The dew point of the atmosphere was measured continuously during the experiments, and amounted to 22 $\pm$ 3 °C. Furthermore, pretreated samples were investigated concerning their hydrogen absorption ability in humid air and humid nitrogen gas atmosphere, respectively. The metal samples were heated up to 912 °C in dry synthetic air for 3, 6 and 10 min in order to reduce the hydrogen absorption. After quenching in liquid nitrogen, the hydrogen content was determined by using one part of the metal sheet sample. Then, all pretreated samples were heated up for a second time for 6 min using humid synthetic air or humid nitrogen gas atmosphere. Based on this approach, it was studied whether the hydrogen formation and its subsequent absorption into the metal sheet is affected or even hindered after a pretreatment due to an already existing oxide scale layer and gradually formed intermetallic phases leading in turn to a different solubility and diffusibility of hydrogen atoms [10].

2.2. Material composition and sample preparation

In the experiments, the most common hot-dipped aluminum-silicon coated (AS60/60, i.e., at least 60 g of AlSi coating per side and m^2 metal sheet) 22MnB5 steel used in the automotive industry was studied. For comparison, a flat-rolled version being characterized by a thickness reduction of 50% (FR 50%) was applied in order to analyze the impact of a reduced AlSi coating thickness on the hydrogen absorption. The material compositions of both materials and their coating thicknesses (AlSi10Fe3) are listed in Table 1. The sample sizes for hydrogen measurements were about (32 x 25) mm^2 with a metal sheet thickness of 1.5 mm for dwell times of 3 min or longer. For furnace dwell times below 3 min, the metal samples had a size of (26 x 18) mm^2 due to a specific sample holder in order to prevent a sticking at the quartz glass tube being caused by the liquefaction of the AlSi coating during heating.

2.3. Analyzing techniques

Thermal desorption mass spectrometry (TDMS) was utilized to determine the diffusible hydrogen content of the heat-treated metal samples. The TDMS consists of a gas control unit *G8 Galileo* and an infrared heater *IR07* from *Bruker Corporation* as well as a mass spectrometer from *InProcess Instruments*. During the measurements, a quartz glass tube was flushed with nitrogen gas and the metal samples were heated up to 300 °C isothermally between 7 and 14 min. Metallurgical investigations were performed using the optical microscope *ZEISS Axio Imager 2* from *Carl Zeiss AG*. Heat-treated metal samples were embedded into a black epoxy resin by using the hot mounting press *OPAL 465* from *ATM* at a temperature of 180 °C and a pressure of 130 bar for 8 min. Afterwards, the resulting polymer pucks were ground and polished with a *SAPHIR 550* machine from *ATM*. Grinding was performed by

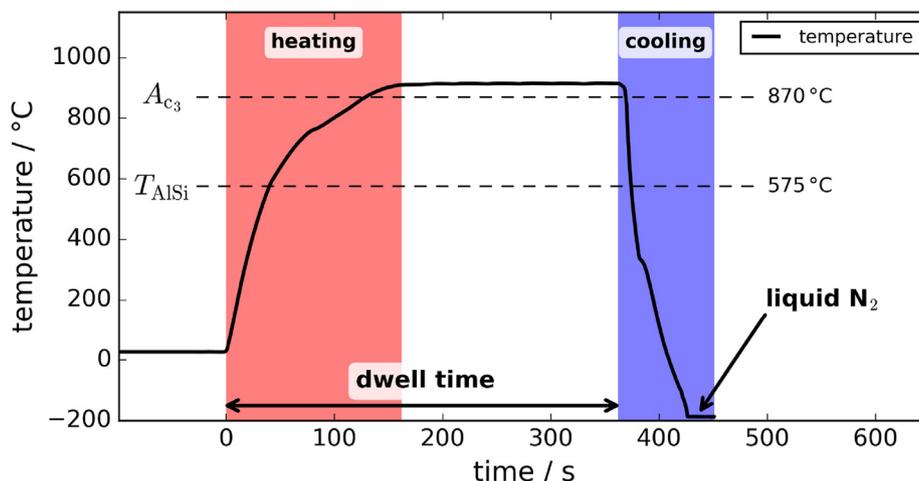Fig. 2 — Schematic illustration of the applied measurement setup.

Fig. 3 − Characteristic temperature-time curve of a heat-treated metal sample with a dwell time of 6 min.

using SiC grinding papers and polishing was conducted with different synthetic cloths (Alpha, Iota and Omega from *ATM*). All pucks were cleaned with ethanol between each step. For subsequent optical investigations, the ground surfaces were slightly etched with 3% concentrated nitric acid in ethanol (nital solution).

3. Results and discussion

### 3.1. *Hydrogen absorption in different gas atmospheres*

Figs. 4 and 5 present the experimentally determined absorption curves of diffusible hydrogen as a function of the furnace dwell time for different humid gas atmospheres. It is clearly visible that the flat-rolled material condition AS60/60 FR50% (see dashed lines in Fig. 5) shows a much more pronounced hydrogen absorption compared to the classical material coating system AS60/60 (see solid lines in Fig. 4), most probably being caused by the reduced coating thickness of the flat-rolled material. The hydrogen absorption already starts during heating and is characterized by the strongest relative hydrogen uptake within the first 3 min due to the reaction processes between water molecules from the surrounding gas atmosphere and the metal surface of the aluminum-silicon coating. Experiments with dry gas atmospheres have led to hydrogen values lower than 0.1 ppm and, therefore, confirm this kind of reaction, i.e., the necessary presence of water for hydrogen uptake into the metal. Most relevant molecular mechanisms and model systems explaining the hydrogen absorption into the material are shown in Fig. 1 and have already been presented by Draley and Ruther [12] or Cho et al.

[10], respectively. For longer furnace dwell times, the hydrogen absorption becomes less pronounced probably caused by saturation effects of the bulk material and the oxide layer formed on the coating surface. Independent of the material coating system AS60/60 and AS60/60 FR50%, the experiments demonstrate impressively that both the humid carbon dioxide and the humid nitrogen gas atmosphere strongly promote hydrogen absorption compared to humid synthetic air or humid oxygen gas atmosphere. After typical industrial dwell times of 5−6 min, the content of diffusible hydrogen reaches values well above 1.5 ppm for the flat-rolled material AS60/60 FR50% when a humid nitrogen or humid carbon dioxide gas atmosphere is present (see Fig. 5). Even the classical material coating system AS60/60 shows values between 0.75 ppm and 1.25 ppm for the same gas atmospheres (see Fig. 4). The reason for the more pronounced hydrogen absorption ability in humid nitrogen and humid carbon dioxide atmosphere might be a missing competitive oxidation process as illustrated in Equations (1) and (2). By using a humid oxygen and a humid synthetic air atmosphere, respectively, two possible competitive oxidation reactions are enabled, i.e., wet and dry oxidation: On the one hand, between Al atoms of the coating surface and the water vapor molecules H_2O (wet oxidation) as well as, on the other hand, between Al atoms and oxygen molecules O_2 (dry oxidation) from the surrounding gas atmosphere [10].

When a humid nitrogen or a humid carbon dioxide gas atmosphere is present, there is a higher probability for water vapor molecules to find an appropriate reaction partner, i.e., a reduction of water to hydrogen is promoted. In this case, the metal of the coating surface does not react with oxygen atoms and, therefore, hydrogen absorption is not prevented. Hence,

Material	Coating thickness (AlSi10Fe3)/μm	C	Si	Al	Mn	Cr	Ti	B
22MnB5 + AS60/60	25−30	0.22	0.27	0.031	1.21	0.18	0.032	0.003
22MnB5 + AS60/60 FR 50%	≈15	0.22	0.23	0.034	1.10	0.18	0.027	0.003

Table 1 − Chemical composition of the bulk material 22MnB5 in mass%. The measurement was performed by optical emission spectroscopy. FR 50%: thickness reduction of 50%.
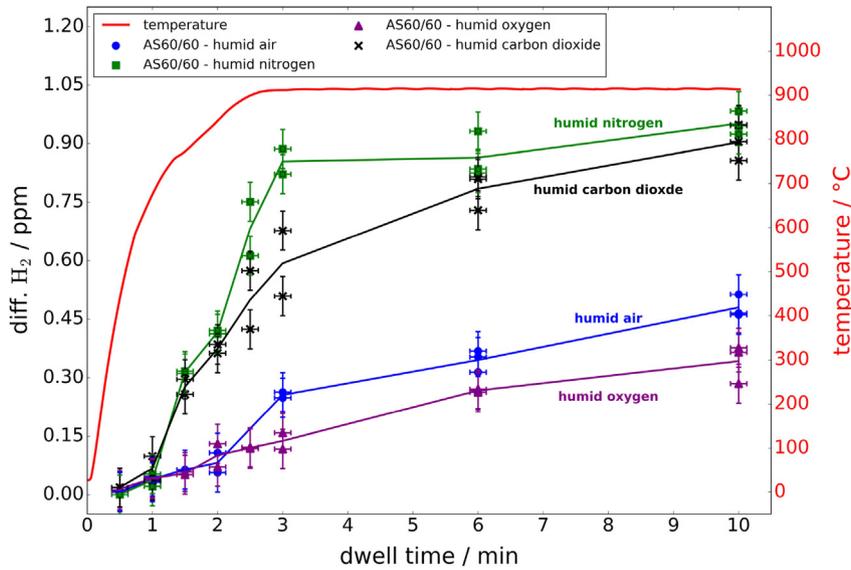
Fig. 4 − Evolution of diffusible hydrogen curves for the AS60/60 coated 22MnB5 steel as a function of the dwell time and the corresponding heating curve. The gas atmosphere consisted of humid synthetic air, nitrogen, oxygen and carbon dioxide, respectively, with a dew point around +22 °C. The final furnace temperature was about 912 °C.

due to the missing competitive dry oxidation process, the slopes of the hydrogen absorption curves for humid nitrogen and humid carbon dioxide gas atmosphere are steeper, finally leading to higher diffusible hydrogen values compared to humid synthetic air or oxygen gas atmosphere.

### 3.2. Influence of coating characteristics on hydrogen absorption

Due to the flat rolling processes, the material coating system AS60/60 FR50% shows a damaged and interrupted diffusion zone. In order to analyze the relation between the hydrogen uptake and the damage level of the diffusion zone, several micrographs were acquired by optical microscopy and are depicted in Fig. 6a−f. The metal samples were heated up within time intervals between 0.5 and 3 min under humid synthetic air atmosphere.

The as-rolled reference material shows a severely damaged diffusion zone being highlighted by red lines (see 0 min, Fig. 6a). The same surface conditions following a dwell time of 0.5 min can be seen in Fig. 6b. This is due to the low actual temperature of around 460 °C (see Fig. 7). After a dwell time of 1 min (see Fig. 6c), the temperature is increased to approximately 685 °C, eventually exceeding the coating
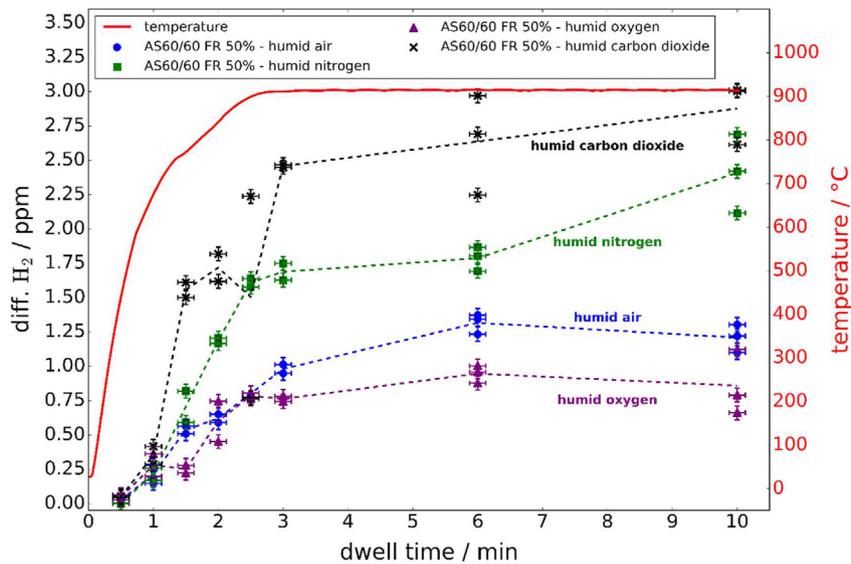
Fig. 5 − Evolution of diffusible hydrogen curves for the AS60/60 coated FR50% 22MnB5 steel as a function of the dwell time and the corresponding heating curve. The gas atmosphere consisted of humid synthetic air, nitrogen, oxygen and carbon dioxide, respectively, with a dew point around +22 °C. The final furnace temperature was about 912 °C.
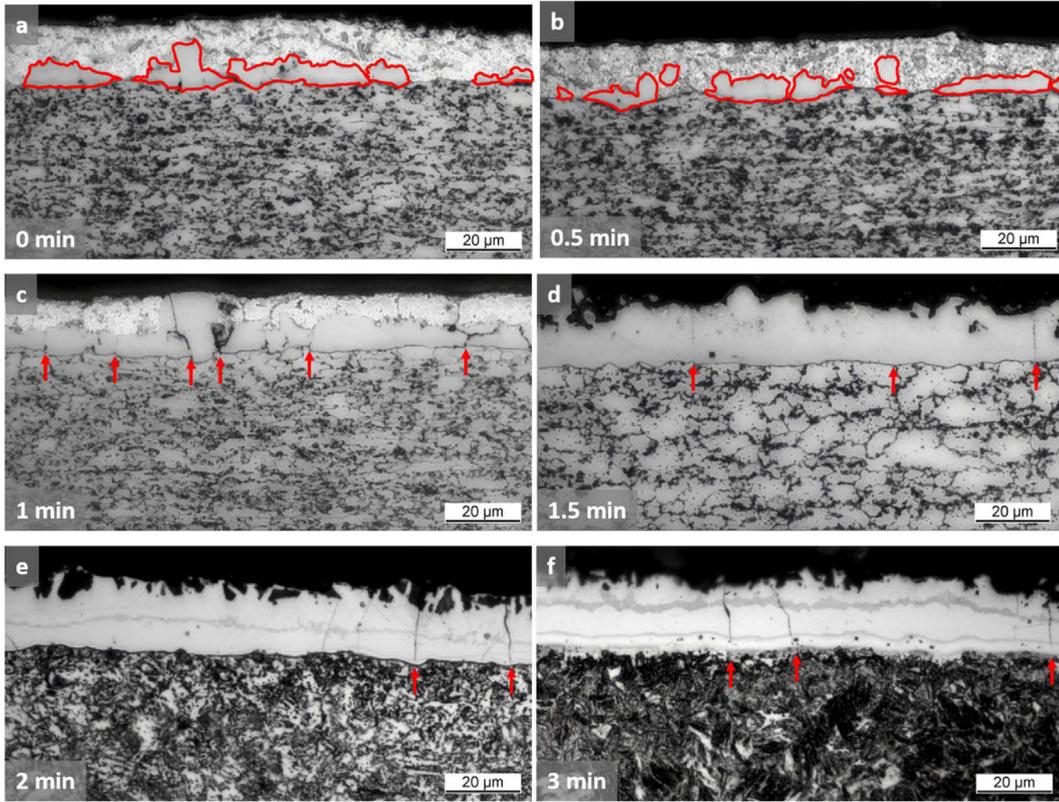
Fig. 6 — Optical micrographs detailing the healing process of the damaged diffusion zone (red frames highlighted in a,b) of the flat-rolled material condition AS60/60 FR 50%. The dwell times were set between 0.5 and 3 min and the gas atmosphere consisted of humid synthetic air. Remaining defects of the coating are labeled by red arrows (in c to f). See text for details.

melting point of 575 °C leading to a partial liquefaction of the AlSi layer [9]. This in turn supports diffusion processes and the previously damaged diffusion zone starts to heal. Only a few remaining defects can be identified and are labeled by red arrows (see Fig. 6d—f). The diffusion zone is fully healed and closed after a furnace dwell time of 1.5 min (see Fig. 6d) and a maximum actual temperature of around 770 °C (see Fig. 7).

Intermetallic phases within the AlSi coating occur after heating for 2 and 3 min (see Fig. 6e—f).

The hydrogen absorption curves in Fig. 5 clearly demonstrate the most pronounced hydrogen increase within the first 3 min of heating. However, the absorption behavior does not correlate with the damage level of the diffusion zone being healed and closed after a dwell time of 1.5 min (see Fig. 6d).
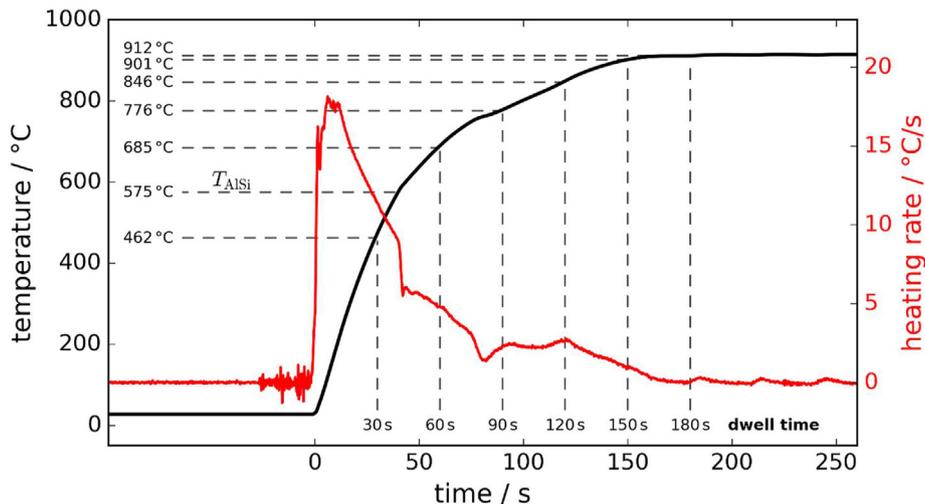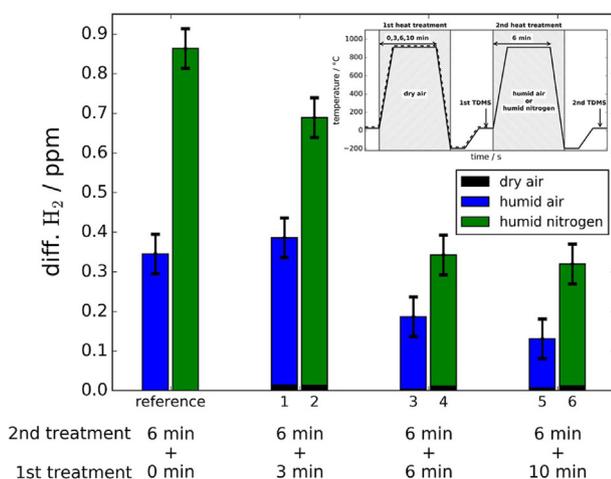

Fig. 7 — Characteristic heating curve and the corresponding heating rate of a heat-treated metal sample.

Here, the hydrogen uptake still is much more pronounced compared to the classical coating system AS60/60 (compare Figs. 4 and 5). Eventually, it seems to be the case that the thickness of the AlSi coating (see Table 1) has a stronger influence on the hydrogen absorption than the damage level of the diffusion zone. Moreover, the influence of the grain boundaries has to be taken into account. Due to the flat rolling process, the microstructure of the bulk material is affected considerably compared to the initial condition, i.e., the classical material coating system AS60/60. It is expected that rolling-induced changes of the microstructure have a pronounced impact on the hydrogen absorption as the grain boundaries of the austenite phase typically serve as reversible traps for absorbed hydrogen atoms. This already has been shown by Riecke [4] and Erdmann-Jesnitzer and Wessel [18].

3.3.   Hydrogen absorption of pretreated materials

Fig. 8 presents the hydrogen absorption ability of pretreated materials and clearly demonstrates the necessity of water molecules being present for hydrogen uptake into the metal sheet. By using dry synthetic air for the first heat treatment of 3, 6 and 10 min, the hydrogen content remains below 0.05 ppm. The second heat treatment was performed under humid synthetic air or humid nitrogen gas atmosphere for 6 min with a dew point range between 15 °C and 20 °C in each case (see inset of Fig. 8). After treatment with humid synthetic air, the diffusible hydrogen content reaches a value of around 0.4 ppm (sample 1) being similar to the reference material without any pretreatment (see Fig. 4). For longer treatments under dry gas atmosphere, the hydrogen content is halved after the second treatment to values below 0.2 ppm (sample 3 and 5). The same trend applies to the experiments considering humid nitrogen treatment. After a pretreatment of 3 min, the hydrogen value is around 0.7 ppm (sample 2) and, therefore,

much higher than for sample 1 because of the missing oxidation reaction during the second heat treatment step, eventually leading to the generation of hydrogen atoms. However, for a longer pretreatment time with dry synthetic air atmosphere, the hydrogen absorption ability decreases during the second heat treatment and only reaches values of around 0.35 ppm (sample 4) and 0.3 ppm (sample 6). The reason for the attenuated hydrogen absorption is thought to be caused by the formation of intermetallic phases and their chemical composition, however, most importantly by the grown oxide scale layer, which becomes thicker for longer pretreatments. This layer most probably impedes wet oxidation processes, i.e., hydrogen generation at the coating surface. The conducted experiments simulate a hot forming process with an inhomogeneous gas atmosphere, e.g., dry gas atmosphere conditions at the furnace entry and humid gas atmosphere conditions at the center or end of the furnace. The predominant sources of water are burner defects and combustion of natural gas, respectively. Obviously, it is important to monitor the dew point inside the whole furnace and not only at the furnace entry where the aluminum-silicon coating is liquefied.

4.   Conclusion and summary

The present study investigated the hydrogen absorption of ultra-high strength AlSi coated 22MnB5 steels under different gas atmospheres. Metal samples were heat-treated at 912 °C for different furnace dwell times in various humid gas atmospheres. The diffusible hydrogen content was measured by thermal desorption mass spectrometry (TDMS). The main results of the present work are:

1. The most pronounced hydrogen uptake already takes place within the first 3 min of the heating process.
2. Flat-rolled materials show higher hydrogen contents than the classical aluminum-silicon coated 22MnB5 steel, most probably caused by a reduced coating thickness.
3. The hydrogen uptake is much more pronounced for humid nitrogen and humid carbon dioxide gas atmospheres in direct comparison to humid oxygen or humid synthetic air. The reason for the strongly promoted hydrogen absorption ability is a missing competitive dry oxidation between metal atoms of the aluminum-silicon coating and oxygen molecules from the gas atmosphere. Thus, in case of humid nitrogen or humid carbon dioxide atmosphere treated metals, the oxide layer is primarily formed by a wet oxidation process. Hence, there is a higher probability for a formation of atomic hydrogen leading to a stronger penetration into the material. However, further investigations have to be considered in order to analyze the hydrogen absorption and oxide formation on the atomic scale more precisely.
4. The results of the present work imply consequences to the gas injection in classical hot forming production lines being heated by the combustion of natural gases. Experiments confirmed that burner defects, i.e., release of water vapor due to the combustion of methane, result in a strong hydrogen absorption. In this case, production series with

Fig. 8 — Diffusible hydrogen contents of pretreated samples (sample number depicted below each single column) with the material coating system AS60/60. The pretreatment was performed under dry synthetic air atmosphere (black column). The second heat treatment took place under humid synthetic air (blue column) or humid nitrogen (green column) gas atmosphere (see inset).

dry nitrogen gas injection are much more sensitive to hydrogen uptake than dry air because of the released water and carbon dioxide. Due to the missing competitive dry oxidation and the resulting more pronounced hydrogen uptake, it should be questioned whether a dry nitrogen gas atmosphere should be used further for heat treatments of AlSi coated ultra-high strength steels in industrial hot forming production lines.

5. Materials being pretreated with dry synthetic air for 6 or 10 min and afterwards exposed to a humid gas atmosphere, exhibit an attenuated hydrogen uptake being probably caused by the grown oxide scale layer and the resulting inhibition of wet oxidation reactions at the coating surface.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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