Increasing the energy absorption of monolithic manganese boron steels in oxygen-free environment

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Abstract. The heat-treatable steel 22MnB5 is used in hot stamping processes to produce high-strength body-in-white components. In this process, sheet blanks are conventionally heated in roller hearth furnaces and then hot-stamped, whereby strengths of 1,500 MPa can be achieved. Disadvantages of this process are the low plastic deformation of the material in hardened state and the poor energy efficiency of roller hearth furnaces. In a new approach, these disadvantages are eliminated by combining edge decarburisation with resistance heating. Due to a diffusion-controlled removal of the carbon in the edge layer of the blanks heated in an oxygen-free atmosphere, the energy absorption in bending tests was improved by 61 % compared to customary hot-stamped 22MnB5. Furthermore, with a subsequent resistance heating in an oxygen-free silane atmosphere, the sheet can be heated and coated. A hermetically sealed heating chamber was developed which allows to heat the blanks up to 950 °C without scale formation. The coating during heating further improves the corrosion properties of the component. With this approach, hot-stamped components with improved properties and coated in an energy-efficient resistance-heated process can be manufactured.

1. Introduction

In the automotive industry, ultra-high-strength steels are used in safety-relevant areas of the passenger compartment to ensure the greatest possible protection of passengers and simultaneously reduce vehicle weight. Hot stamping is the established process for the production of such components as it combines both the shaping and the heat treatment of a sheet metal work piece in one process step [1]. Therefore, prior to the forming step, the blanks are heated up to a specific temperature in order to austenitise the steel material and subsequently quenched in a water-cooled forming tool. In industrial processes, the heating takes place in roller hearth furnaces [2].

The steel 22MnB5 with an aluminium-silicon coating (AlSi) has established itself in recent years as a suitable material for hot stamping. In the hardened state, 22MnB5 can achieve tensile strengths of up to approx. 1,500 MPa. However, in consequence of the hardening, the elongation at fracture decreases to 5%. [3]. In order to increase the crash performance, respectively the energy absorption, the mechanical properties can be specifically adjusted by applying tailored properties [4]. The approach of these varying methods is to avoid the formation of martensite in specific areas of a component in order to achieve a more ductile microstructure. In turn, this is accompanied by a significant loss of strength. Roll-cladded material systems like TRIBOND®1200 and TRIBOND®1400 developed by thyssenkrupp
Steel Europe combine a high-strength steel with a mild steel in a three-layer sandwich material. The arrangement of the mild steel as surface layer leads to a beneficial combination of both, strength and ductility, especially regarding bending load [5]. This study presents an approach by means of which a comparable distribution of the mechanical properties across the cross-section of a monolithic material can be achieved. Therefore, the surface of uncoated 22MnB5 is decarburised by a heat treatment in an argon-hydrogen atmosphere.

In order to prevent scale formation in hot stamping processes, the material either has to be coated or processed in an oxygen-free environment. The established AISi coating primarily serves as scale protection [6]. A major disadvantage associated with this coating is the limited heating rate. In order to prevent a melting of the coating, the blanks need to be heated up slowly, allowing the formation of intermetallic FeAl phases with a higher melting temperature [7]. This, respectively the formation of scale in general, represents one of the reasons why rapid heating processes, like resistance heating, have not yet become established in industrial production. By resistance heating, electric power is converted into heat by the current flow in the sheet and as a result of ohmic resistance. Due to the direct power conversion in the material, up to 74 % of the energy can be saved compared to roller hearth furnaces. Nevertheless, the hot-stamping temperature of 950 °C can be reached within seconds [8]. However, the AISi layer is unsuitable for this short process due to the duration of the formation of the intermetallic phase and due to the fact that scale is generated on uncoated sheets, as can be seen in Figure 1. Therefore, the development of a process chamber and suitable sheet coating for resistance heating in an oxygen-free monosilane-doped nitrogen atmosphere is the content of subproject A04 of the Collaborative Research Centre (CRC) 1368 “Oxygen-free production” [9]. For this purpose, an experimental chamber was developed in which resistance heating can be conducted in an oxygen-free silane atmosphere. Within this chamber, the blanks can be simultaneously braze-coated with the nickel-based alloy Ni700 (chemical composition 89% nickel + 11% phosphor), which is designed to bond with the sheet material within seconds and provides corrosive protection during the subsequent transfer to the forming tool. This creates an alternative process chain that allows to proceed the above-mentioned decarbonised material as well as customary uncoated 22MnB5 in an energy-efficient manner without scale formation.

2. Methodology and Results

In this chapter, the procedure and results of the investigations are described. First, the heat treatment of the surface decarburisation of uncoated 22MnB5 blanks and the plate-bending tests conducted are described. Subsequently, the developed process chamber is presented in which uncoated 22MnB5 blanks can be heated by resistance heating in an oxygen-free silane atmosphere and can simultaneously be coated with Ni700.

2.1. Decarburisation

The decarburisation of carbon steel can be performed by means of heat treatment in ambient air [10] or in a protective atmosphere containing hydrogen [11]. The latter offers the great advantage, that a simultaneous oxidation of the steel surface is avoided. A certain amount of water residue in the hydrogen atmosphere, which is inevitably generated in open conveyor-belt furnaces, is necessary to ensure decarburisation. The water reacts with the carbon to form gaseous carbon monoxide. For that, the carbon atoms dissolved in the steel must migrate from the bulk to the surface, which is a diffusion-controlled process. Therefore, process temperature and time are the dominant parameters for controlling the decarburisation depth achievable.
Investigating appropriate process parameters for the edge decarburisation of 22MnB5 steel (thickness 1.5 mm), sheet specimens were heat-treated in a conveyor-belt furnace (HTE 1200–200/80–1500, Kohnle GmbH, Birkenfeld, Germany) using an argon-based process gas mixture with 20 vol.-% hydrogen ratio. Two different temperatures in the heating zone, 860 and 960 °C, were combined with two different dwell times, 25 min and 40 min (controlled by the speed of the conveyor belt) for a parameter study within application-suited limits for continuous heat treatment of 22MnB5. The water residue in the process gas measured by a dew point sensor (DMT152, Vaisala Oyi, Finland) amounted to (60±10) ppm during all measurements. The resulting temperature curves of the samples that had been instrumented with thermocouples for temperature detection are shown in Figure 2.

Sheet samples heat-treated in this way were prepared metallographically and examined under an optical microscope. For this purpose, the metallographic cross sections were suitably etched [12] beforehand to visualise carbon-containing microstructural constituents. The micrographs displayed in Figure 3 show that the microstructure of the specimens heat-treated at 860 °C is finer-grained than that of the sheets treated at 960 °C. This is due to the higher degree of recrystallisation, which is accompanied by more pronounced grain coarsening at higher temperatures. Generally, the carbon-containing phases show up in the form of a pearlitic microstructure, dark grey phases as well as row-like arrangements in the microstructure. The transition to the lower-carbon edge layer, which is fine grained ferrite with only few fraction of perlite, is smooth. The transition area is marked by dashed white lines in the micrographs. The decarburisation depth for the specimens heat-treated at 860 °C is thus about 50 µm, while the specimens treated at 960 °C reached about 90 µm. With respect to the different treatment times (25 min and 40 min dwell time in the annealing zone) at the respective temperatures, no significant difference in the decarburisation depth was observed.

Corresponding to a conventional hot-stamping process, sheet specimens were heated up to 950 °C in a chamber furnace (N161/S, Nabertherm). After a dwell time of 360 s, the specimens were quenched in a water-cooled plate tool. Surface-decarburised and subsequently hot-stamped plates were also subjected to metallographic examination to investigate the extent and effect of decarburisation on the hardened microstructure. In this case, the transverse sections were first etched in ethanolic nitric acid, which reveals the martensitic microstructure in the form of brown, marbled areas shown in Figure 4.

Figure 2: Temperature curves of 22MnB5 sheet specimens heat-treated in a conveyor-belt furnace in Ar+ 20 vol.-% H₂ atmosphere with different furnace temperatures and dwell times.

Figure 3: Micrographs of 22MnB5 sheet specimens after decarburisation in Ar/H₂ atmosphere. Decarburisation depth is approximately at the dashed lines (transition from a linear microstructure with increased pearlitic structure to a fine grained ferrite structure with lower perlite contents).
Relevant micrographs are shown in Figure 4. It can be seen that the heat treatment carried out in this case under atmosphere has resulted in a peeling iron oxide layer on the sheet surfaces. This is followed by a narrow region consisting of ferritic microstructure (light grey crystalline microstructure) which, as expected, is much more pronounced in the specimen decarburised at 960 °C than in the sheet treated at 860 °C. A comparison of the extent of these edge zones with the results from Figure 4 shows that in both cases a comparable part of the ferritic edge structure (approx. 30-40 µm) was obviously oxidized, so that the decarburised edge thickness was to some extent reduced by the hot-stamping process. Nevertheless, in both cases a ferritic surface layer remained, suggesting a more ductile edge region.

2.2. Plate-bending Test
Plate-bending tests have been conducted according to VDA 238-100 [13] in order to investigate the effect of the decarburisation on energy absorption and bending angle. Additionally, customary 22MnB5+AS, TRIBOND®1200+AS and TRIBOND®1400+AS have been used as comparative samples. After austenitising at 950 °C for 360 s, all samples were hot-stamped and subsequently cut to 60 mm x 60 mm samples by water jet. The samples were bent in a bending device without lubricants and supported on pivoted rollers, until a drop in the force of 30 N was detected after the maximum force had been reached. The force is measured with a load cell and the traverse path with an inductive path transducer. For the analysis, the energy as well as the bending angle were calculated via the force-displacement curve. TRIBOND®1200 and TRIBOND®1400 were tested in 0 ° and 90 ° rolling direction, while the remaining samples were tested in 90 ° to rolling direction. The classification of the specimens is shown in table 1.

| Nomination | Surface decarburization | Rolling direction in [°] | Quantity [-] |
|------------|--------------------------|--------------------------|--------------|
| 22MnB5     | none                     | 90                       |              |
| TRIBOND®1200 | none                   | 0                        | 3            |
| TRIBOND®1200 | 860, 25 min            | 90                       |              |
| TRIBOND®1400 | 960, 25 min            | 0                        |              |
| Sample 1   | 860, 25 min             | 90                       | 1            |
| Sample 2   | 860, 40 min             |                          |              |
| Sample 3   | 960, 25 min             |                          |              |
| Sample 4   | 960, 40 min             |                          |              |

The bending energy determined and the bending angle can be seen in figure 5. In this comparison, customary 22MnB5 achieves the lowest values with regard to a determined bending energy of 41 J and a bending angle of 42 °. The highest bending energy with 97 J and a bending angle of 121 ° was detected.
for TRIBOND®1200 for a rolling direction of 0 °, with only slightly lower values for a rolling direction of 90 °. A more pronounced anisotropy was determined for TRIBOND®1400 with a bending energy between 70 J to 87 J. For the decarburised samples, the determined bending energy varies between 68 J and 76 J. Compared to customary 22MnB5, the energy absorption can be increased by 44 % for sample 2 and even by 61 % for sample 4 and thus, achieve values in the range of a TRIBOND®1400. This shows that surface decarburisation decisively improves the material behaviour with respect to crash potential under bending stresses.

**Figure 5:** Determined bending energy (a) and bending angle (b) resulting from conducted plate-bending test.
2.3. Oxygen-free silane resistance heating

In order to heat uncoated 22MnB5 blanks, such as surface-decarburised 22MnB5 blanks, without scaling, an experimental chamber was developed in CRC 1368 "oxygen-free production" in subsection A04. Within an oxygen-free silane atmosphere, blanks can be heated by resistance heating and simultaneously coated, in order to prevent the formation of scale during the subsequent transfer to the forming tool. The experimental chamber is shown in figure 6. On the left, the chamber is open and the main components, consisting of the oxygen and temperature measurement, the process gas flow, the sheet with the different areas and the high temperature insulation for regulating the atmosphere and the coating process can be seen. The pass of the sheets into the experimental chamber and the experimental chamber itself are sealed with a smooth inorganic non-conductive high-temperature insulation to compensate for the rapid temperature fluctuations. The gas is distributed into the experimental chamber through a piping system. An oxygen-measurement system collects process gas directly above the metal surface of the sheet and measures the oxygen concentration. For this purpose, an automated measurement recording and evaluation system (developed in subproject S01 of the CRC) was implemented on the basis of a commercial oxygen-measurement system (Mesa Industrie-Elektronik GmbH, Marl, Germany) in order to record the residual oxygen content prevailing in the process chamber in situ. On the right side in figure 6, the closed chamber is displayed during a heating process. The electrodes, located outside on the left and right of the chamber, clamp the sheet and transmit the current for heating. The viewing windows in the chamber are used for visual assessment of the coating process and for temperature measurement by means of a pyrometer, which is mounted outside the chamber due to the temperatures of up to 400 °C inside.

![Figure 6: Structure of the process chamber for oxygen-free resistance heating](image)

The process gases nitrogen and silane are used to suppress the formation of scale. The chamber is first evacuated with nitrogen to remove the air from the chamber. At an oxygen concentration of 0.001 vol. %, silane is added and heating is started. During heating, the blank can be coated with a plastic-coated nickel powder. The plastic ensures adhesion to the blank in advance and protects the powder from oxidation. The plastic coating decomposes at a temperature of 200 °C and has completely evaporated when the hot-stamping temperature is reached. The process window of the coating is in the
range of 850 °C, where it starts to become liquid, and about 1000 °C. The properties can be adjusted with the heating temperature and holding time of a few seconds.

Figure 7 shows a cross-section of a resistance-heated sheet metal coated on one side in an oxygen-free silane atmosphere at a heating temperature of 973 °C and a holding time of 31 s. The 50 µm thick Ni700 coating (grey) metallurgically bonded to the 1.5 mm thick 22MnB5 sheet (light blue), exhibits a loadable joint between the coating and the parent metal. It can be seen that neither in the upper area of the coating nor on the bottom, scale was formed. This shows that heating in an oxygen-free silane atmosphere suppresses the formation of scale and that the Ni700 coating protects the surface of the blank from corrosion in the environment after removal from the chamber. Scale-free heating and coating of uncoated 22MnB5 is thus possible.

3. Conclusion

In this study, oxygen-free atmosphere was used in order to improve the mechanical properties of hot-stamped components with respect to crash performance, and the hot-stamping process itself regarding process time and energy consumption.

By means of surface-layer decarburisation, an increase in crash performance could be determined in plate-bending tests. By decreasing the carbon content in the surface layers, the specimens achieved higher bending angles and higher energy absorption. With the parameters used in this study, it was possible to increase the bending energy by up to 61 % compared to customary 22MnB5. The energy absorption of the surface-decarburised 22MnB5 samples could be increased to the range of a TRIBOND®1400.

In order to process uncoated sheet blanks in hot stamping, a test chamber was developed. Within this test chamber, the sheet blanks are heated by resistance heating in an oxygen-free silane atmosphere and can simultaneously be coated to prevent the formation of scale during the subsequent transfer to the forming tool. First results presented in this study show a homogeneous distribution of the applied Ni700 coating without any formation of scale.

Nevertheless, the results presented in this study need to be validated in further tests. With regard to surface decarburisation, more parameter combinations need to be investigated. It is furthermore planned to process the decarburised sheet in the developed test chamber, in order to prevent the formation of scale. The resistance heating system is also being modified on the basis of the shown experimental chamber. The focus is on shortening the cycle time as well as further developing coating powders and powder application processes. In the next step, the electrodes are to be integrated in the process chamber so that the entire sheet can be heated and coated without scaling under an oxygen-free silane atmosphere. The coating powder is being further developed for hot stamping and corrosive protection. The behaviour of the coating from 200 to 850 °C for hot stamping is in focus and will be described by means of a model.

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References

[1] A. Bardelcik, M.J. Worswick, S. Winkler 1, M.A. Wells (2012) „A strain rate sensitive constitutive model for quenched boron steel with tailored Properties“, pp. 49-62, 2012 DOI:10.1016/j.ijimpeng.2012.06.007

[2] H. Karbasian, A.E. Tekkaya, “A review on hot stamping” Journal of Materials Processing Technology 210 (2010) 2103–2118, DOI:10.1016/j.jmatprotec.2010.07.019

[3] L. Wolf, M. Diekamp, Th. Gretzki, F. Nürnberg, F.-W. Bach, D. Rodman, J. Moritz, J. Schrödter, S. Hübner, B.-A. Behrens (2014) „Hot stamping and subsequent spray cooling: A new manufacturing approach“, Plastic Deformation of Metals (pp.36-55)

[4] Bernd-Arno Behrens, Anas Bouguecha, Christoph Michael Gaebel, Jörn Moritz, Jens Schrödter (2014) “Hot stamping of load adjusted structural parts”, DOI:10.1016/j.proeng.2014.10.227

[5] D Rosenstock, J Banik, T Gerber, S Myslowicki (2019) “Hot stamping steel grades with increased tensile strength and ductility - MBW-K 1900, tribond 1200 and tribond 1400”, DOI:10.1088/1757-899X/651/1/012040

[6] C. Couto, I. Costa, M. Colosio, J. L. Rossi, Z. Panossian und L. P. Barbosa (2018) „Characterization of 22MnB5 steel metallic coated with either hot-dip AlSi or electroplated ZnNi before and after hot stamping“, SAE Technical Paper Series, 27th. SAE Brasil International Congress and Exhibit, 03 09 2018, DOI:10.4271/2018-36-0074

[7] R. Veit, H. Hofmann, R. Kolleck und S. Sikora (2011) „Investigation of the Phase Formation of AlSi-Coatings for Hot Stamping of Boron Alloyed Steel“, AIP Conference Proceedings, 27 01 2011, DOI:10.1063/1.3552543

[8] B.-A. Behrens, S. Hübner, J. Schrödter and J. Uhe (2015) „Conductive Heating Opens Up Various New Opportunities in Hot Stamping“, International Conference on Accuracy in Forming Technology

[9] Holländer, U., Wulff, D., Langohr, A., Möhwald, K., Maier, H.J. (2020) “Brazing in SiH4-Doped Inert Gases: A New Approach to an Environment Friendly Production Process.” Int. J. of Precis. Eng. and Manuf.-Green Tech. 7, 1059–1071, DOI:10.1007/s40684-019-00109-1

[10] Zhao, F. Zhang, C.L., Liu, Y.Z. (2016) “Ferrite Decarburization of High Silicon Spring Steel in Three Temperature Ranges.” Archives of Metallurgy and Materials. 61. 1369-1376. DOI:10.1515/ammm-2016-0252, DOI:10.1515/ammm-2016-0252

[11] Grapke, H.J.; (1975) „Kinetik und Mechanismen der Oberflächenreaktionen bei der Auf- und Entkohlung und Auf- und Entstickung von Eisen in Gasen.“ Arch. Eisenhüttenwes.46, Nr.2, DOI:10.1002/srin.1975030989

[12] Petzow, G., (1994) „Metallographisches, keramographisches, plastographisches Ätzen, 6. Auflage“, Gebrüder Bornträger, Berlin, Stuttgart, DOI:10.1002/maco.19940451212

[13] VDA 238-100: Plättchens-Biegeversuch für metallische Werkstoffe, (VDA 238-100-12:2010)