INFLUENCES OF MODERN AHSS-GRADES ON THE PICKLING, ANNEALING AND GALVANIZING PROCESS*

Francisco Morganti[1]
Fritz Brühl[2]
Caesar Sasse[7]

Abstract

Weight reduction is the main target of all carmakers, which results in a continuous development of new steel grades. Latest 3rdgeneration advanced high-strength steel grades (AHSS) are complex materials with special chemical compositions and multiphase microstructures. The pickling, annealing and galvanizing processes of these grades aresomewhatdifferent due to the changed chemical compositions and microstructures. Therefore, these innovative steel grades place new demands on the plant technology of pickling, annealing and galvanizing lines. The most significant challenges for the pickling process are sludge occurrence during pickling, varying pickling times, weld ability of the materials, changed visual appearance and required high surface qualities. The most important topic concerning annealing line is a precisely controlled and very flexible heating and cooling process in the furnace.One of the new requirements in galvanizing linesis the prevention of surface faults caused by bare spots, which can occur since these materials feature a higher content of alloying elements like silicon or manganese. Prevention is possible with the special pre-oxidation technologies.Due to the higher strength of the material also the mechanical equipment has to be designed differently in these lines. This paper describes the influences of the changed chemical composition and material characteristics of modern steel grades on the pickling, annealing and galvanizing process and gives an overview about the technical solutions.

Keywords: Pickling; Annealing; Galvanizing; High-strength steel grades.

[1] *Mechanical Engineer, Executive Vice President, Order Execution, SMS group Metalurgia do Brasil Ltda. Vespasiano, MG, Brazil*
[2] *Dr.-Ing. Metallurgy, Executive Vice President, Strip Processing Lines and Furnace Technology, SMS group, Düsseldorf, Germany.*
[3] *Technical Communications M.A., Technical Marketing Manager, Strip Processing Lines and Furnace Technology, SMS group, Hilden, Germany..*

1 INTRODUCTION

The main goal of all carmakers is to reduce weight and at the same time fulfill all necessary safety conditions, which results in development of several new grades (Figure 1). The pickling, annealing and galvanizing process of these grades is different and places new demands on the plant technology, especially due to the following characteristics:

- Higher contents of alloying elements
- Higher strength of the material
- More complicated microstructures

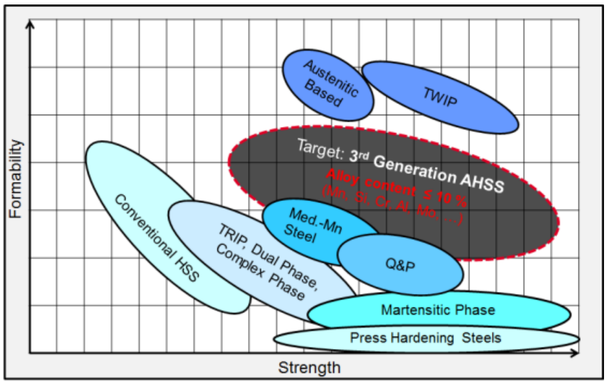

Figure 1. Development of the steel grades including 3rd generation grades advanced high-strength steel grades (AHSS) with higher alloying contents.

2 PICKLING PROCESS

The changed chemical composition of the material has certain influences on the production of pickled hot strip in pickling lines. Especially the higher contents of silicon and manganese have a critical impact on the production process. Further problems are caused due to the higher strength of the material. This leads to problems in conventional pickling lines and in some cases to necessary adaptation of the equipment.The most significant challenges are sludge occurrence during pickling, varying pickling times, weld ability of the materials, changed visual appearance and required high surface qualities. Due to the higher strength of the material also the mechanical equipment has to be designed differently in some ways (Figure 2).

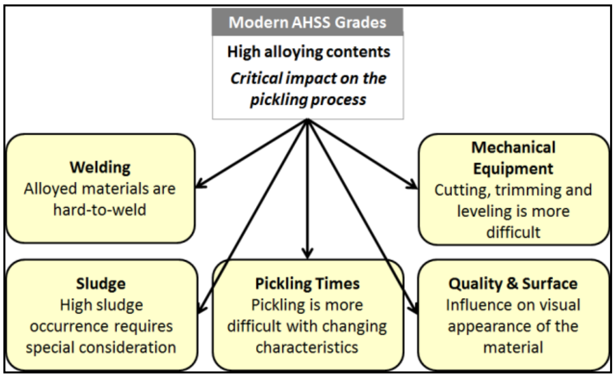

Figure 2. Influences on the production of pickled hot strip due to changed chemical composition.

2.1 Sludge

As mentioned above the high silicon contents increase the occurrence of silica sludge significantly. The turbulence pickling system by SMS (Figure3) has certain advantages concerning sludge compared to other pickling systems. First of all the high-turbulence in the pickling tanks avoids any sludge settlement within the pickling tank itself. The turbulence removes also silica particles from the surface. Since fast changes of the turbulence and the temperature are possible, the process can be easily adapted to the different material characteristics. One special feature is the optional semi-automatic rinsing system with alkaline solution (sodium hydroxide) to clean the circulation piping.

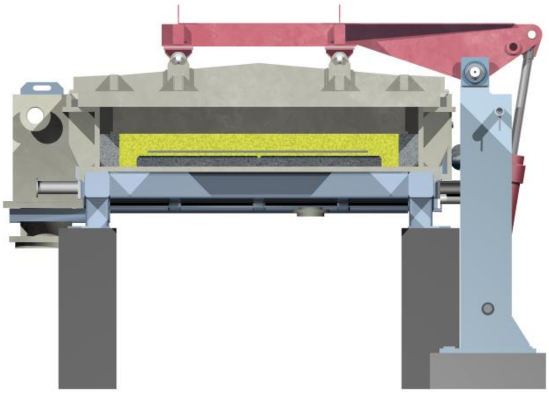

Figure 3. Racks of nozzles are constantly spraying heated hydrochloric acid into the shallow pickling channel and generate an extremely high turbulence which ensures maximum contact between the acid and the strip surface by continually forcing fresh acid into the scale layer cracks.

One important characteristic of silicon sludge is that the particles are very small. The diameter of the majority of the particles is less than 10 micrometer (Figure4). There is no economical filtration system available for these fine particles. Therefore, a sedimentation system has to be implemented in the lines.

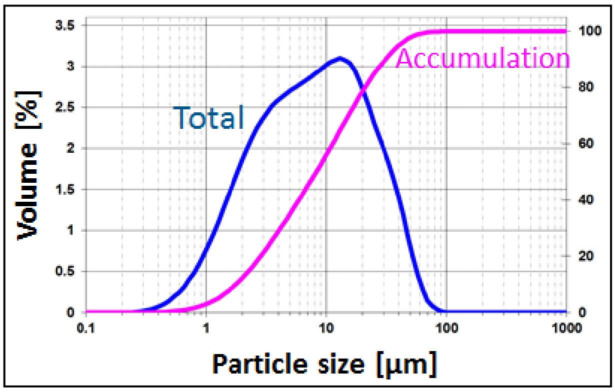

Figure 4. Investigations have shown that the particle size of silicon sludge is very small.

Further investigations have demonstrated that the settling period of the particles within an acid tank is very long. Settling of silica sludge takes several hours due to the small particle size (Figure 5).

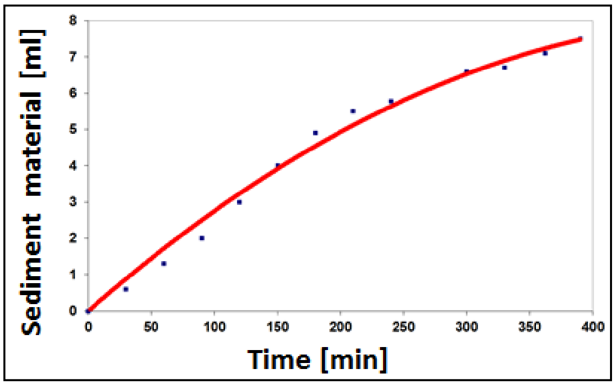

Figure 5. Settling of the sediment material takes several hours.

SMS group has huge experience with electrical silicon steel grades with high silicon contents. The proven two tank system can be used for sludge removal in carbon steel pickling lines, too. Furthermore, a settling tank should be included before the waste acid flows into the regeneration system. This increases the efficiency of the acid regeneration and helps to remove the silica content out of the process.

2.2 Pickling times

The high alloying contents cause different scale layer characteristics. In general, the pickling times are significantly higher and vary a lot more. The hot rolling and coiling temperatures have to be considered more strongly, since they have a major impact.
Again, the turbulence pickling system has certain features to deal with the varying and increasing pickling time. It is the most flexible pickling technology. It is possible to change the line speed, the acid temperature and the turbulence very fast. This way, the pickling efficiency can be adjusted easily based on the materials to be pickled using an efficient process control via level 2 models.
A special feature is the ECO-production pickling model. This model considers all production related parameters, calculates the optimized coil sequence, the optimized pickling parameters and the transition behavior from coil to coil (Figure 6). The model sets the parameters in a way that maximizes yield and process speed and minimizes temperature and turbulence. Thus, the model generates several operational savings.

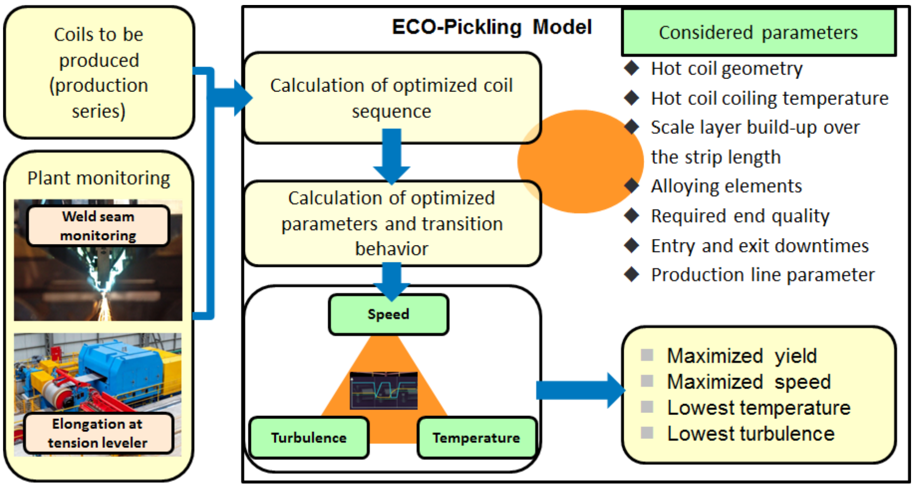

Figure 6. All key pickling process parameters are actively controlled and perfectly adjusted to the requirements of each hot strip coil considering all production related parameters.

2.3 Quality and surface

Homogeneous high surface quality is required for downstream processing of 3rd generation AHSS materials. Minimal quality deviations can cause significant problems while finishing (e.g. wettability of zinc coatings). The turbulence pickling system in combination with the ECO-pickling and production models ensures homogenous surface quality. The turbulence technology removes the silicon oxides and other residuals from the surface during the pickling process.
It is important to note that alloying elements are influencing the visual appearance of the material. The surface appearance after pickling is darker if the manganese content is high, but this is not a quality problem. The technological quality of the surface is the same even if it is darker.

2.4 Welding

High alloying contents do also have an influence on the weld ability of the materials. Welding of these materials is often not possible with conventional flash butt welding machines or laser welding machines. During welding of these materials a high proportion of tough martensitic material is produced. The ductility of the weld seam is very low and therefore the risk of weld seam breaks during processing and rolling increases.
One major advantage of the X-Pro® laser welder by SMS group is the patented inductive pre- and post-heat-treatment of the weld seam. The machine allows an individual softening process of the hardened weld seam. This gives the weld seam the necessary ductility for further processing. Since every material combination is different, the distances between the inductive heaters and the seam as well as the power are variable. This means, the treatment time and temperature are adjusted flexibly in the most suitable way for each weld seam. This allows welding of hard-to-weld materials with high alloying contents. In the pickling line/tandem cold mill of Hyundai Steel in South Korea, for instance, grades with high silicon contents were successfully connected and cold rolled.
The X-Pro® laser welder features numerous further technological highlights. The welder convinces by the automatic adaptation of the welding parameters. With this system new material pairings can be welded without extensive testing. It uses level 2 data for cast analysis and thickness to calculate carbon equivalents and features a database with suitable welding parameters.The integrated automated weld-seam quality assurance system with two cameras evaluates the whole process. The first camera positions the welding head on the middle of the joint. The second camera checks and rates the quality of the welded seam. If everything is ok, the system automatically approves.A further convincing feature of the machine is its cycle time of less than 60 seconds which makes it the fastest machine on the market. Also the set-up time for the two knife cartridges in the shear are very short. They can be changed in well below less than 15 minutes.Since the welding source is freely selectable, the carbon dioxide laser used so far can be exchanged. Tests have already been carried out successfully with a fiber laser source in this welder.
Several X-Pro® laser welders are already successfully in operation or ordered for different hot-strip processing lines worldwide (Figure 7).

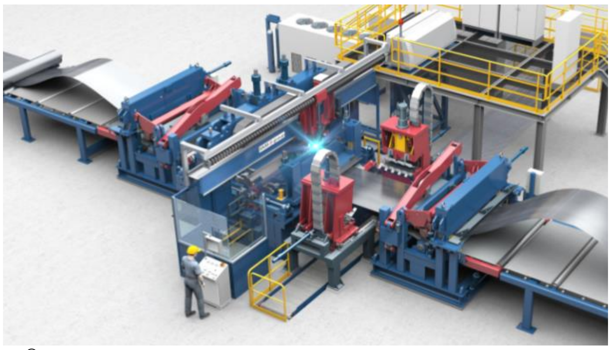

Figure 7. The X-Pro® laser welder allows an individual softening process which gives the weld seam the necessary ductility for further processing and makes it an ideal machine for welding of materials with high alloying contents.

3 ANNEALING PROCESS

The previously described material development leads to adapted annealing and galvanizing processes. The furnace technology has to be adapted to the new processes. A comparison of typical annealing curves for different steel grades including high-strength materials shows that processing furnaces for cold strip must offer considerable flexibility with regard to heat treatment (Figure 8). In particular, the following characteristics are different compared to conventional cold strip processing lines:

- High heating temperatures (e.g. MS, Q&P)
- High cooling capacity (e.g. DP, MS, Q&P)
- Reheating of the material (e.g. DP, Q&P)
- Time for partitioning (e.g. Q&P)

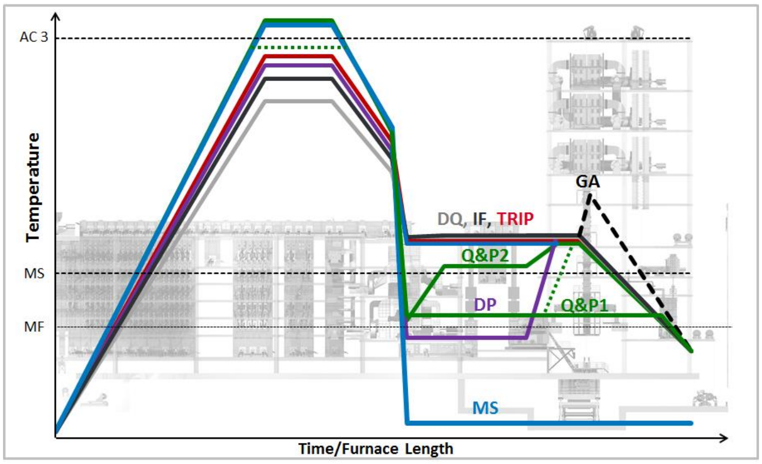

Figure 8. Annealing curves with 3rd generation AHSS grades (examples).

3.1 Ultra fast cooling with gas

High strength steel grades can be produced by a combination of alloying elements and cooling rate. The higher the cooling rate the less alloying elements can be used. When applying high cooling rates, conventional systems consume a lot of resources. With the ultra fast cooling system (Figure 9), cooling rates of up to 150 kelvin per second per millimeter can be achieved due to the injection of pure hydrogen into the cooling chamber limiting the diffusion of hydrogen into the adjacent chambers (patented).

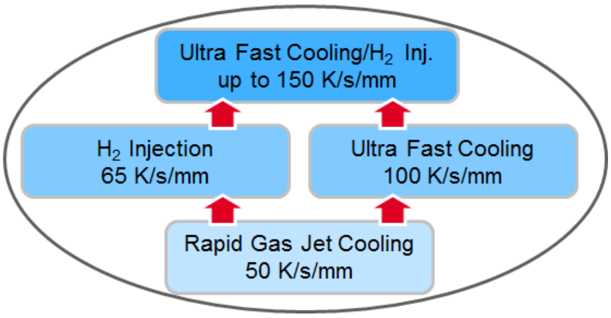

Figure 9. **Development from rapid gas jet to ultra fast cooling with hydrogen injection.**

Regarding combustion gas, electrical energy, hydrogen and nitrogen significant savings are possible. Further savings are generated due to reduced consumption of alloying elements. The cooling gas is applied to the strip via nozzles with transverse slots to ensure uniform cooling over the full strip width, thickness, and length. The distance between the strip and nozzles can be infinitely varied between 40 and 120 millimeters. Despite the high flow rate, the special design of the cooling chamber safeguards great strip stability with a minimum of vibrations.

3.2 Water-spray cooling

Cold strip processing lines with water-spray cooling systems are specifically designed to produce the ultra-high-strength steel strip needed for interior components over the entire car area. Generally, this system is used while manufacturing martensitic grades or dual phase steels with a tensile strength of up to and greater than 1,700 MPa. These materials are mainly used to produce crash-proof structural parts in the passenger compartment.
Following austenitization of steel strips in the furnace, the water-spray system for fast cooling may attain cooling rates that are much higher than those achievable by a gas cooling system. Due to the high specific heat capacity of water it is possible, within a short period of time, to discharge a high amount of heat energy by spraying (Figure 10). The cooling rates obtainable are above 1,000 kelvins per second and millimeter strip thickness.

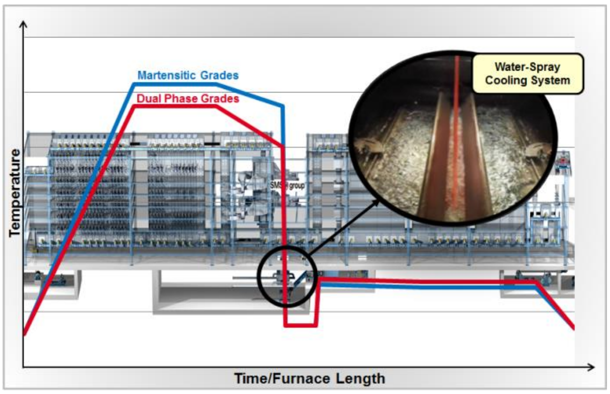

Figure 10. Exemplary heating curves for martensitic and dual phase grades in a continuous annealing line, which are cooled very fast via water-spray cooling.

In the water spray section, the strip is immersed in demineralized water. During this procedure, both sides are sprayed with water by special nozzles. This continuous spraying action is accomplished under high pressure and generates turbulences

which ensure the heat energy is rapidly discharged. In the nozzle chamber, over a distance of merely 700 millimeters, a one-millimeter-thick steel strip is cooled down within a very short time from more than 800 degrees Celsius, for instance, to less than 300 degrees Celsius which is below martensite final temperature.
In the past few years, SMS group has put on stream three continuous annealing lines including water-spray cooling systems. These lines are producing high-strength steel grades such as DP1180 and MS1700. A factor deserving particular notice is the excellent flatness results achieved.

3.4 Quench and partitioning

The quench and partitioning process is more often applied in modern cold-strip processing line to produce for example martensitic steel grades with enhanced levels of retained austenite. These grades are characteristic by high tensile strength and more often used for automotive applications.
Quench and partitioning foresees heating of the material above Ac3 and subsequent down cooling with high cooling rates to a temperature in the range between Ms and Mf, which results in a partially martensitic and austenitic microstructure. Partitioning takes place via holding the material at a higher temperature (below or above Ms) in the so called two-step process. Thus the material has to be heated up very fast which is executed via induction heating device (Figure 11). The partitioning step leads to a partial carbon depletion of the martensite and carbon diffusion to the austenite, which results in carbon stabilized austenite. This austenite remains stable in the microstructure after final quenching to room temperature.

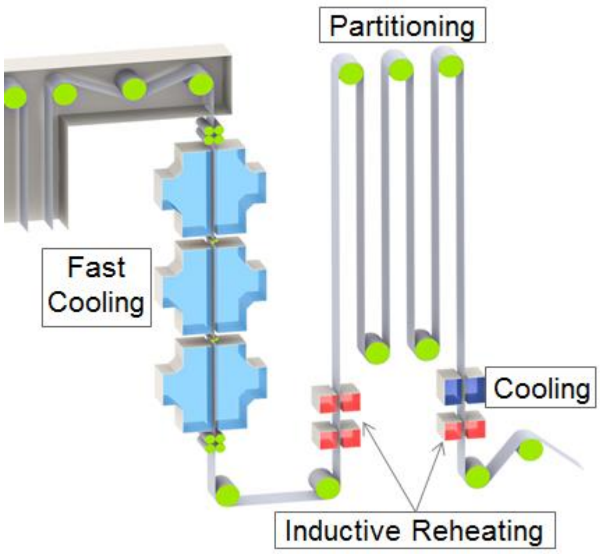

Figure 11. Possible layout of a quench and partitioning section in a continuous galvanizing line with fast cooling, two inductive reheating options, and additional cooling options in front of the galvanizing section.

Furnace concepts for quenching and partitioning of steel grades have been developed. The furnace comprises of high-speed cooling systems and subsequent heating modules, preferable by high-frequency induction. In continuous galvanizing line also cooling and heating devices can be integrated in front of the galvanizing section to adjust the temperature before galvanizing in case of a deviation of the partitioning temperature to the galvanizing temperature.

3.5 I-FURNACE

The I-Furnace (Intelligent Furnace) is a smart furnace process and production optimization model. The combination of various tools leads to an optimized heat treatment and production process. It combines furnace control, online strength measurement and a model to predict the material properties after the treatment. This intelligent combination of efficient tools is a great step forward towards an autonomously working furnace (Figure 12).

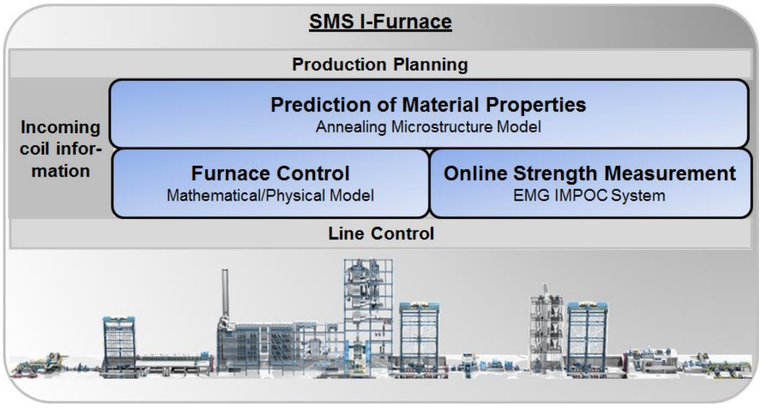

Figure 12. A powerful combination of three tools leads to optimized coil heat treatment.

The I-Furnace creates several advantages concerning line operation:

- A capacity increase up to 15 percent is possible due to a better utilization of the furnace capacity as well as an efficient production planning and transition behavior
- Energy savings can be realized due to a better temperature control close to its lower limit
- Special sophisticated grades can be produced more easily
- Improved material characteristics – especially for coils with deviations

For example, the changes in mechanical properties over the coil length showed a systematic behavior for some coils which resulted in a typical "camel" shape (Figure 13.1). In order to improve the quality of the steel parameters have been evaluated that can be changed fairly quickly and can change the IMPOC value. From the metallurgical analysis and the linear models, the temperature after slow cooling was identified as a good way to improve the quality of the steel (Figure 13.2). Changing the slow cooling strip temperature is better than changing the annealing temperature, because it is possible to change it more quickly. By using the temperature at the exit of the slow cooling it is possible to compensate the "camel" shape profile of the DP 600 coils. The higher temperature after slow cooling will cause that relatively more austenite is retained before rapid cooling. This austenite will transform into martensite. Thus the higher temperatures lead to a higher martensite fraction, which gives a higher tensile strength. During some trials this behavior could be verified and on optimized annealing curve for this kind of coils could be found (Figure 13.3).

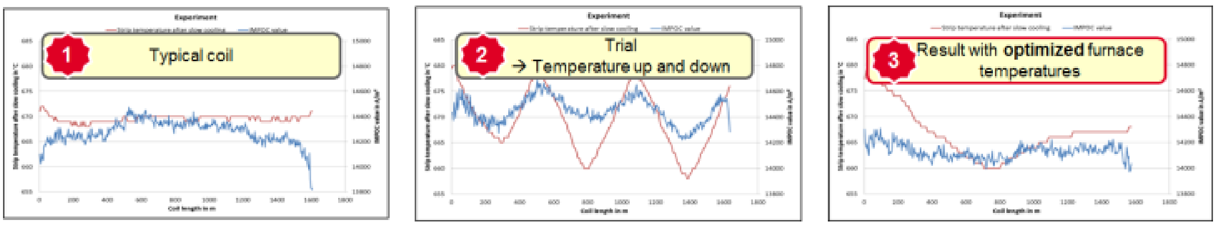

Figure 13. The typical coil shows a "camel" shape curve of the IMPOC value in blue and the strip temperature at the exit of the slow cooling in red, via several trials the effect of a changed slow cooling temperature was tested, and eventually the slow cooling temperature has been optimized and thus the "camel" shape has been eliminated.

A more comprehensive quality improvement is possible with a consideration of the upstream data, since the quality deviations are often influenced or caused by upstream parameters. One example has been the modelling of steel quality for DP 800 based on measurements taken at the hot strip mill and the galvanizing line.
When using the data from the hot strip mill (e.g. slab temperature going into the rougher, slab temperature going into the finishing mill and coiling temperature) and the galvanizing line (e.g. strip temperature after heating, strip temperature after soaking, strip temperature after slow cooling, line speed and slow cooling time) the quality of the produced galvanized cold strip could be predicted well (Figure 14). Of course, a precise knowledge of the resulting strength distribution after the heat treatment allows more efficient compensations of possible deviations.

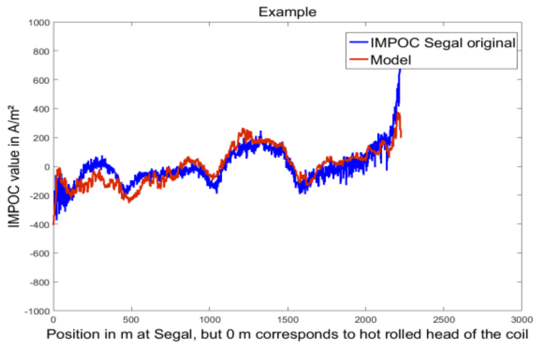

Figure 14. Comparison of modeled (red) and real measured (blue) development of the tensile strength within a DP 800 coil (trials made at Segal galvanizing line).

With the inverse function of the above mentioned data driven model it is also possible to determine the strip temperature after slow cooling using upstream data and a reference IMPOC value. In the online model an optimum slow cooling temperature can now be calculated for each segment of the strip and is monitored by the IMPOC.
For all DP steel grades this online model is applicable and can easily adopted for other AHSS grades.

4 GALVANIZING PROCESS

The newly developed materials lead also to an evolution of the galvanizing process. With increased speed and thinner strips it gets even more important to stabilize the strip. Increased alloying contents lead to wettability problems which can be solved with pre-oxidation technology. New coating systems are used nowadays. Most lines must be able to apply different coatings.Concerning the mechanical equipment of a galvanizing line there have to be made provisions to cut, level or temper steel grades with increased tensile strength. An overview about the most important components and main technical data is given below (Figure 15).

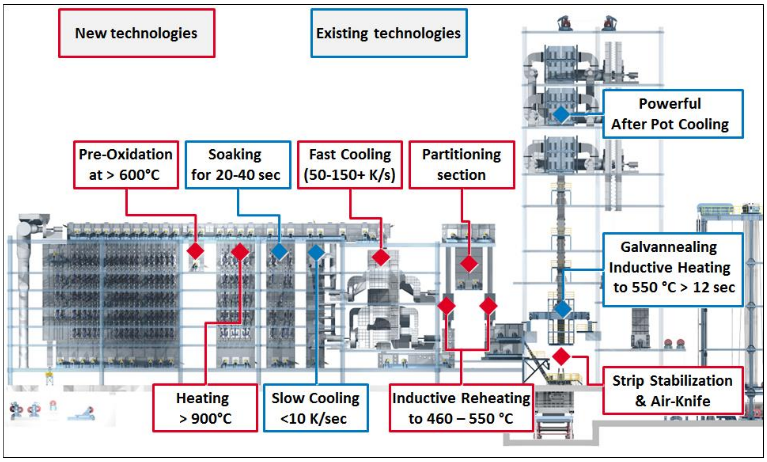

Figure 15. Comparison of modeled (red) and real measured (blue) development of the tensile strength within a DP 800 coil (trials made at Segal galvanizing line).

4.1 Pre-oxidation of high-alloyed grades

Coating problems incurred in conventional hot-dip galvanizing processes can be prevented by a specific oxidation and reduction process for which SMS group offers the PrOBOx®-technology. For this purpose, the strip surface is subjected to targeted oxidation during the annealing process at temperatures between 600 and 700 degrees Celsius. The Wagner model shows which dew point (defined as the ratio between hydrogen and water partial pressures) is needed for total oxidation to take place and to stop further migration of the alloying elements (Figure 16).

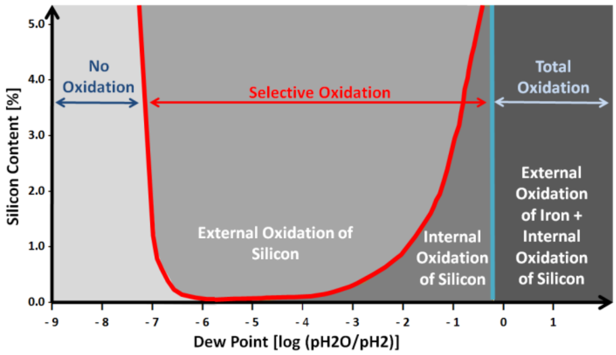

Figure 16. The Wagner model for binary iron-silicon alloy shows based on the temperature in the annealing furnace and depending on the silicon content at which dew points the elements oxidize and when internal or external oxidation.

Due to the total oxidation a uniform iron oxide layer of a thickness between 150 and 200 nanometers is created. After leaving the pre-oxidation chamber, the uniform iron oxide is reduced in the atmosphere with a lower dew point to a homogenous and slightly porous iron sponge layer prior to the galvanizing process in the radiant tube furnace. As the strip is running through the zinc bath, on this layer a very thin coat of iron-aluminum is formed which is required for the hot-dip galvanizing process and serves as adhesion promoting layer. In the further course of the process, a uniform zinc layer is thus created which meets even highest demands (Figure 17).

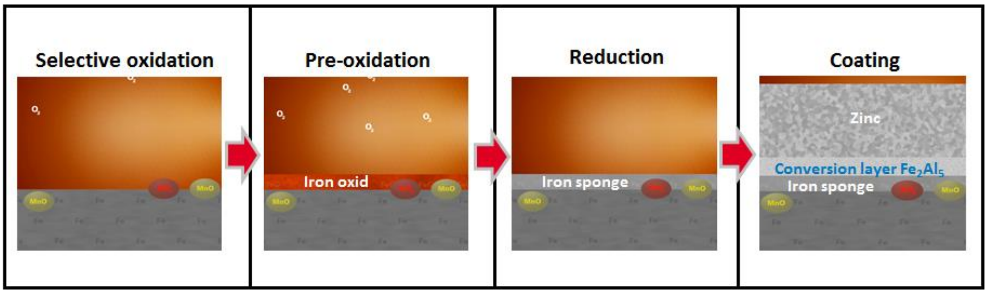

Figure 17. Schematic representation of the layers generated in a galvanizing process with pre-oxidation-technology.

In particular, the technology is characterized by the very precise formation and continuous determination of the layer thickness. Another highlight is the strip's maximized uptake of oxygen. Applying this technology means that the major portion of the oxygen added migrates into the strip surface. A further benefit is that the furnace atmosphere is prevented from pollution by excessively escaping oxygen.
Exact settings of gas temperature and volume as well as a specific nozzles design are essential to attain the high degree of oxygen uptake.

4.2 Air knife system and strip stabilization

Hot-dip galvanizing lines for automotive exposed applications are capable of producing best surfaces (C-surfaces). What mainly determines excellent surface quality is an outstanding air knife system. Also significant here is zinc pot equipment tailored to the special requirements of the process. Another important feature is the electromagnetic strip stabilizing system that guarantees smooth strip travel and superb coating precision (Figure 18). Special features of the stabilization system are the high cross-bow interaction and the independent scan/skew function. Modern stabilization systems are integrated into the air knife for most advanced stabilization results.

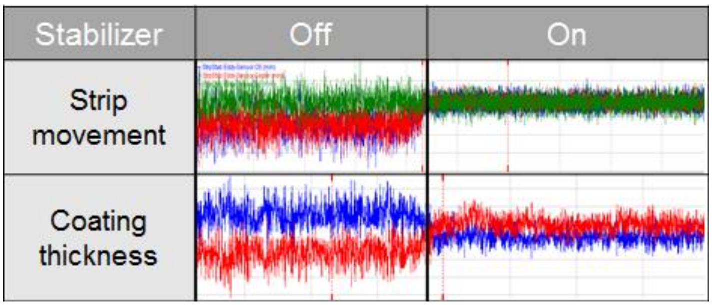

Figure 18: Change of strip movement and coating thickness with active and inactive stabilizer system.

5 CONCLUSION

This paper has shown that the operators of pickling, annealing or galvanizing lines are facing several challenges when it comes to modern advanced high strength steel grades of the 3rd generation (AHSS). A comprehensive portfolio by SMS is available for customers to deal with these challenges. Many of the shown technologies are already implemented and in operation. Various other technologies will be implemented soon in a way that the steel industry can make full use of SMS's ongoing further developments.