

A Study of Surface Reactions on Steel Samples Using a Mass Spectrometer Probe

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This study presents a new probe to analyse the gas composition near a metal surface. The probe uses a mass spectrometric detector and is incorporated in an experimental reactor for the thermal treatment and surface formation of steel sheet samples. Steel samples were exposed to various oxidizing and reducing gas flows at pressures between ambient and 3 bar. The reaction product H_2O was measured with the MS-probe while reducing oxidized steel surfaces with H_2 as well as the consumption of H_2 as a function of the sample temperature. Similarly, the reaction products CO and H_2 were monitored during the oxidation of the bulk carbon with H_2O . The sample temperature was ramped linearly from ambient to 900 °C. From these measurements it was possible to evaluate the onset temperatures and the activation energies for the respective reactions. The in-situ monitoring of the gas phase near the steel surface within the experimental reactor allows controlling the formation of a layer of iron as a result of the iron oxide reduction. Similarly, the decarburization of steel can be followed up by measuring the time course of the CO concentration. It is expected that the MS-probe will become an efficient tool for the understanding and optimization of the annealing and formation processes during strip annealing before hot dipping.

Keywords: gas phase monitoring, galvanizing, mass spectrometer probe, preoxidation, reduction kinetics, steel surface reactions

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Introduction

The processes taking place when iron ores are reduced for the production of iron is still a matter of investigations, using gravimetric and chemical methods for analytical purposes [1]. The oxidation and reduction phenomena of steel are of considerable industrial interest. The rate constants for the formation of hematite and magnetite as a function of temperature and gas atmosphere were investigated as a part of the development of fuel cells [2, 3]. In this context, iron oxide pellets with various additives were tested for their applicability as hydrogen storage. The measurement of the reaction rates was carried out in an oven with controlled gas atmosphere via gravimetry.

The conditioning of steel products prior to hot dipping is crucial for the quality of the final product. It is generally recognized that, beyond steel grade and zinc bath chemistry, phenomena taking place during strip continuous annealing before hot dipping play an essential role [4]. The analysis of the chemical reaction mechanism taking place with iron oxide pellets is straightforward; however, the investigation of the oxidation and reduction processes on metal surfaces needs more sophisticated analytical methods. For the characterization of the reaction products formed on the metal surface as a function of the process parameters, various methods of surface analysis, such as GD-OES, SIMS, SAM and SEM, have been applied [5]. Besides those investigations at the final steel products, the in-situ observation of the whole annealing process would be desirable but is not available yet [6]. This applies particularly to the measurement of the composition of the gas phase within the reaction zone of simulation devices for

the evaluation of the optimum process parameters. In the same way the in-situ analysis of the gas phase within an industrial continuous annealing plant could be valuable for the process control.

Chatelain und Leroy [7] reported in 1986 about experiments on specially prepared steel coils to analyse the gas extracted from a hole drilled axially in the steel coil. The gas was transferred from this “micro reactor” with a volume of 80 cm³ into a mass spectrometer. During the experiments the concentrations of the components of interest, CO, CO₂, H₂O and hydro carbons reached after establishing equilibrium were as high as a few percent. As a result of this study, the process conditions were optimized in such a way that residues of the lubricating oil were completely eliminated from the steel strips. In contrast to the before mentioned experiments, under real process conditions, when relatively high gas flow rates occur, the gas concentrations to be measured will be much lower, since equilibrium concentrations cannot be established.

The present paper presents investigations using a mass spectrometer probe for the analysis of the gas composition surrounding a steel sample within an experimental reactor with temperature and gas flow control.

Experimental

An experimental device was developed to measure the gas composition near the surface of a steel sample. A scheme of the experimental reactor is shown in **Figure 1**. A steel sample is positioned within a quartz tube which can be evacuated and filled with various gases at definite flow rates. The sample temperature is measured with a thermocouple

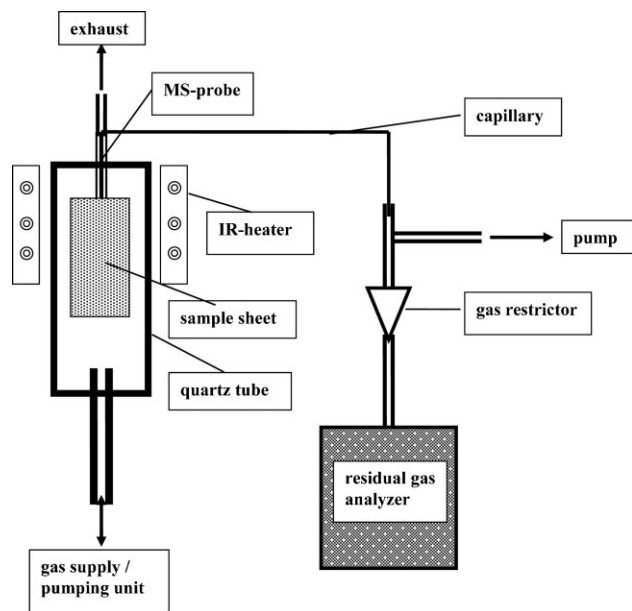


Figure 1. Scheme of the experimental reactor.

welded to the sample and the temperature controlled by an external infrared heater. **Figure 2** shows the experimental set-up while the infrared heater is removed and **Figure 3** depicts the sample together with the MS-probe (MS – mass spectrometer). The sample sheet and the MS-probe are attached to a rod, which can be moved from outside through a gas tight feed-through. The MS-probe consists of a ceramic tube, where an entrance capillary to the MS is inserted, ending in some distance from the tip of the ceramic tube. The gas to be investigated is sucked into the ceramic tube and is removed through the ring-shaped volume between capillary and ceramic tube. The entrance of the ceramic tube is directly positioned at the sample surface. This arrangement assures that the gas to be analysed reaches the MS capillary

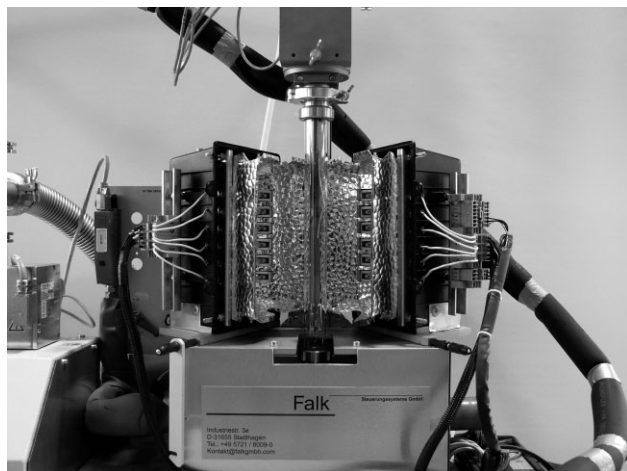


Figure 2. Photo of the experimental reactor with the infrared heaters opened.

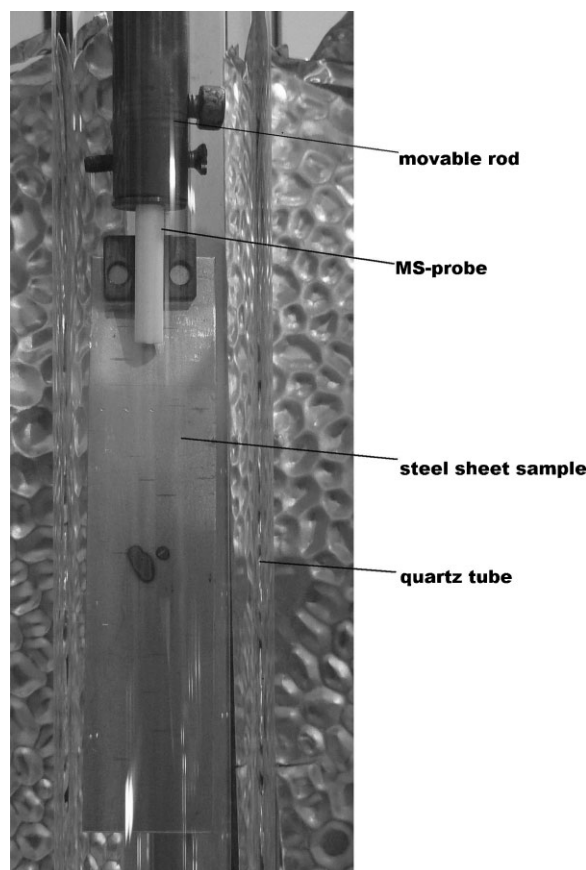


Figure 3. Photo of a steel sheet sample and MS-probe within the reactor.

unchanged with a negligible delay. The MS-probe from its entrance up to the MS is kept at a temperature above 80 °C.

With the help of the infrared heater the temperature of the sheet sample can be kept at any desired value between ambient and 1000 °C or heated with ramp rates up to 20 K/s. The sample temperature below the MS-probe was uniform within some °C.

A residual gas quadrupole mass spectrometer (Stanford QMS 100) designed for the process monitoring was used for the experiments. Typically, 10 masses have been scanned during a cycle time of 3 s and unit mass resolution. The time constant of the MS-probe was essentially determined by the capillary and ranged between 5 and 30 s (10 to 90%). The pressure reduction factor between the entrance of the probe and the mass spectrometer was about $3 \cdot 10^6$, $2 \cdot 10^8$ and $1 \cdot 10^8$ for H₂, H₂O and N₂, respectively.

Since the temperature ramp rate applied was 1 K/s, the temperature error resulting from the time behaviour of the MS-probe was below 30 °C.

Results

MS monitoring of surface reactions. The steel samples were heated up and exposed to an air flow within the reactor such that a definite oxide layer had to be formed at

the surface. Subsequently the oxidized sample were exposed to a flow of a reduction gas (95% N₂, 5% H₂), cleaned at 300 °C and heated at a constant heating rate of 1 K/s up to 900 °C. The partial pressures of various masses of interest were continuously recorded with the MS-probe.

The relevant chemical reactions which take place at the steel surface are shown in **Table 1**.

Consequently, the monitoring of the partial pressure of water near the steel surface during the heating up process allows following up the reaction rate of the reduction process. The activation energy *E_a* [J] can be evaluated from the Arrhenius-plot according to

$$k(T) = A \cdot \exp(-E_a / (k \cdot T)) \quad (4)$$

where *A* is formation constant [cm³ molecule⁻¹ s⁻¹], *k* is Boltzmann constant [J/K] and *T* is temperature [K].

The main components of the steel samples investigated in this study are listed in **Table 2**. The experimental conditions can be seen in **Table 3**. An example for the time dependence of the partial pressures for some masses of interest near an oxidized steel sample exposed to reduction gas can be seen in **Figure 4**. The evaluation of the measurements from Figure 4 is shown in **Figure 5** for OH and H₂O. The activation energies evaluated from the partial

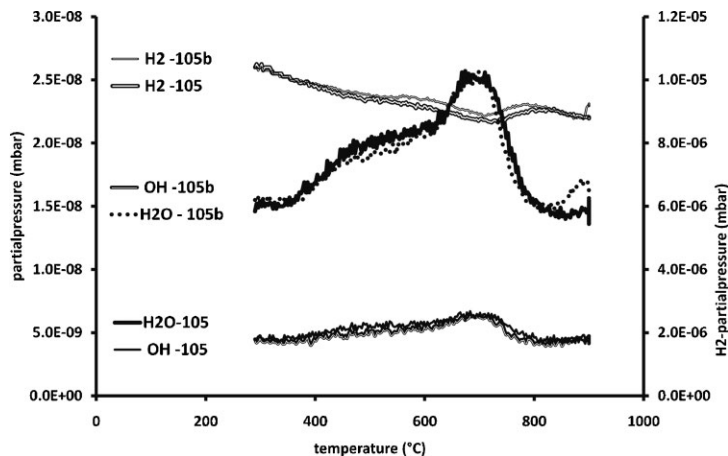
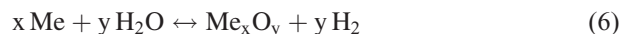


Figure 4. Partial pressures of H₂, H₂O and OH measured in two runs (105 and 105b). Oxidized sheets of Mn/Cr-DP steel in reducing atmosphere (95% N₂ and 5% H₂), temperature ramp rate: 1 K/s.

pressures of H₂O and OH, respectively, agreed satisfactorily. Because of the lower absolute value of OH compared to H₂O, the statistical error of OH was higher. Some activation energies for the reduction of the surface oxide are shown in **Table 4**.

Mass spectrometric monitoring of bulk reactions.

The concentration of the bulk elements will be changed as a result of the surface reactions, if the bulk elements have a sufficient mobility within the material. This applies e. g. to the oxidation of carbon in steel, according to Table 1. Parallel to the reaction (5), the oxygen-affine elements like Mn, Cr and Si, as described by Maitaigne et al. [4], will be selectively oxidized according to the mechanism:



where “Me” stands for metal. Furthermore, Van den Eynde et al. [9] as well as T. Van de Putte et al. [10] have postulated that the carbon dissolved in the steel matrix should be able to effectively reduce the oxides of iron and other elements while undergoing the hot annealing process. For this, the

Table 1. Chemical reactions between steel sample and gas phase.

Process		No.
Hematite reduction	3 H ₂ + Fe ₂ O ₃ ↔ 3 H ₂ O + 2 Fe	(1)
Hematite reduction	H ₂ + 3 Fe ₂ O ₃ ↔ H ₂ O + 2 Fe ₃ O ₄	(2)
Magnetite reduction	4 H ₂ + Fe ₃ O ₄ ↔ 4 H ₂ O + 3 Fe	(3)
Bulk carbon oxidation	C + H ₂ O ↔ CO + H ₂	(4)

Table 2. Main components of the steel samples investigated in this study.

Steel grade	Chemical composition (mass-%)				
	C	Si	Mn	Al	Cr
Mn/Cr-DP	0.07	0.1	1.4	0.05	0.5
MnAl-TRIP	0.2	0.1	1.6	1.55	0.1

Table 3. Experimental conditions applied for surface reactions. T1-start temperature [°C], R1-ramp rate [K/s], T2-hold-temperature [°C], t2-hold-time [s], R2- ramp rate [K/s], T3-final temperature [°C].

	Gas	Gas pressure bar	T1; R1 °C; K/s	T2; t2 °C; s	R2; T3 K/s, °C
Oxidation 1	air	1	100;10	500;3	
Oxidation 2	air	1	100;10	500;10	
Oxidation 3	air	1	100;10	500;20	
Reduction	N ₂ -H ₂ ; 95-5	1	100;10	300;20	1;900

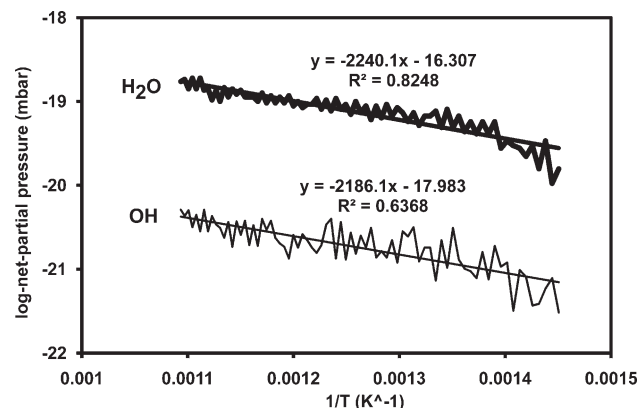
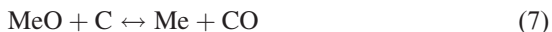


Figure 5. Arrhenius plots derived from measured partial pressures of OH and H₂O after background subtraction. Same experiment as in Figure 4, temperature range: 416 to 641 °C.

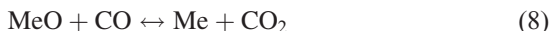
Table 4. Examples for the determination of activation energies from Arrhenius plots.

Sample	Measurement-No	Oxidation 1 T ₁ ; R ₁ °C; K/s	Oxidation 2 T ₂ ; t ₂ °C; K/s	Temperature range °C	Activation energy E _a kJ/mol
Mn/Cr-DP	p-T-99	100;10	500;10	413 - 662	21.1
Mn/Cr-DP	p-T-102	100;10	500;10	420 - 653	27.6

following reaction has been assumed:



If the reaction (4) is included as well, another mechanism becomes likely:



Because of the reactions (4 and 6–8) and the high mobility of carbon in the steel matrix, the carbon concentration near the surface will be reduced. The concentration in the bulk will be reduced according to the temperature depending diffusion coefficient of the carbon. Consequently, the amount of CO released from the surface depends in a complex way on the carbon concentration within the material, the speed of the diffusion and the reaction rate of carbon with the water vapour. The latter is a function of the density of the water vapour near the steel surface. In addition to the processes just mentioned, the reactions (1) and (3) with the oxidation and reduction of iron will take place at the surface, too. Moreover, these reactions will influence the ratio of the water and hydrogen concentrations near the steel surface. Therefore, the material balance within the gas phase depends on various mechanisms, meaning that a simple temperature dependence as in the case of the above mentioned surface reactions is not to be expected.

The time dependence of the partial pressures of various gaseous components above a steel sample while a wet argon flow was introduced into the experimental reactor is shown in **Figure 6**. A temperature ramp rate of 1 K/s was applied. **Figure 7** shows the same results but with linear ordinate to make the signal changes clearer. As expected, the increase of the CO signal with temperature between 500 and 600 °C could not be approximated by an exponential function with one single activation energy. The same applies to H₂ and to the decrease of the concentration of H₂O. The CO signal shows a steep rise between 690 and 760 °C and then levels off. The first phase is determined by the activation energy of the CO formation, whereas the second phase represents the limitation of the carbon concentration at the surface as a result of its diffusion through the bulk material.

A further example for the course of the gaseous concentrations measured with the MS-probe is shown in **Figure 8**. In this case, compared to Figures 6 and 7, the dew point was higher by 10 °C and the temperature program was extended by a hold time of 90 s at 900 °C.

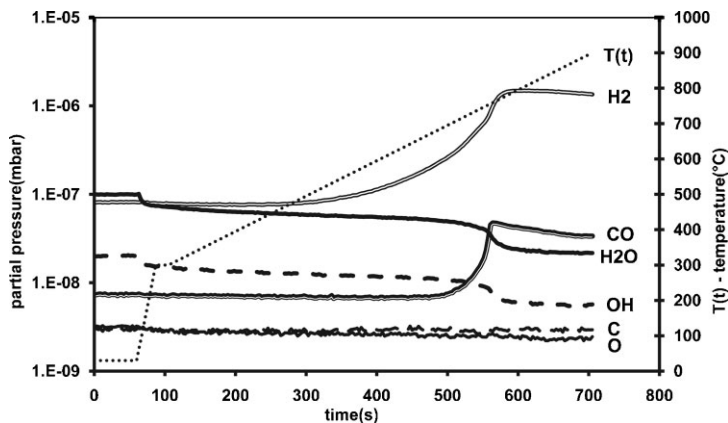


Figure 6. Partial pressures of various gaseous species near a steel sample (Mn/Al-TRIP; 0.22% C) using the MS-probe. Ar at 2022 mbar; water dew point: 20 °C; temperature ramp rate: 1 K/s; temperature range: 300 to 900 °C.

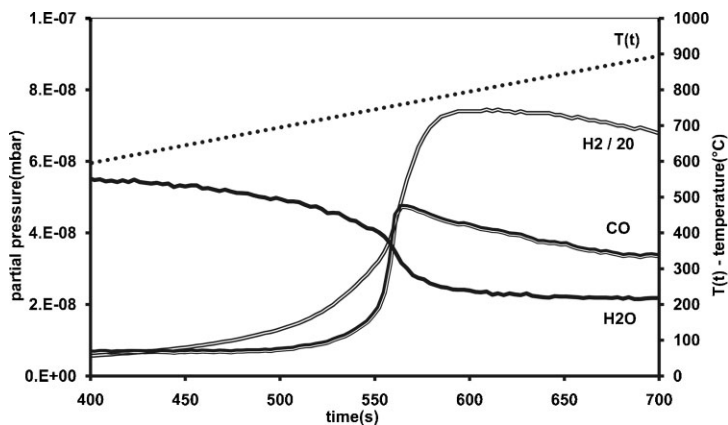


Figure 7. Details of Figure 6. with linear ordinate.

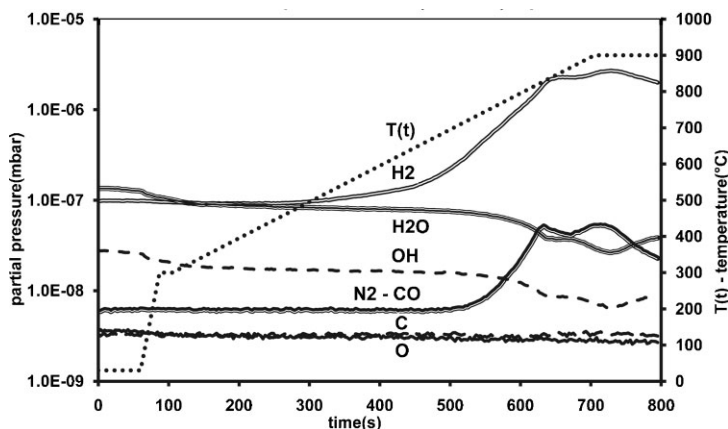


Figure 8. Partial pressures of various gaseous species near a steel sample; same experimental conditions as in Figure 6 but water dew point: 30 °C; hold time at 900 °C: 90 s.

During the first 20 s of the hold time the CO concentration remains almost constant but then it starts to drop significantly. This can be interpreted as a depletion of the carbon content of the sample.

Conclusions

The MS-probe enables the in-situ observation of gas phase processes taking place at steel surfaces during annealing and surface conditioning. The temperature dependences of the chemical reactions between steel surface and reactive gases can be quantified, which is a basis for the understanding of the underlying mechanisms. One example is the determination of activation energies, which can be attributed to the corresponding chemical reactions. Furthermore, the measurement of the gas components near a metal sample is very helpful to find the optimum process parameters, such as the temperature program or gas composition, e. g. for the surface formation by oxidation and reduction steps [11] or to achieve the necessary degree of decarburization.

The activation energies for the oxidation and reduction of iron or other steel components as known from the literature [2, 3] have been determined using granulates or powders. It has to be expected that activation energies determined for thin layers, e. g. an oxidized steel surface, will differ from those reported in the literature for compact or powdered material. But for the process control during annealing and surface formation the characteristics of the thin surface films is of foremost interest.

Another benefit of the in-situ measurement with the MS-probe compared to other methods of surface analysis consists in the avoidance of the surface contamination by air exposition, which causes for instance a very high carbon concentration within the surface-near volume of some 100 μm depth. Process relevant surface films are also in the thickness range of some 100 μm . If these films would be contaminated by air exposition, the interpretation of surface measurements would be hampered.

Whereas the evaluation of the final result of the annealing and formation processes within a reactor needs many successive experiments, the in-situ observation with the help of the MS-probe delivers many process data during one single run of the reactor. Consequently, the latter allows for a considerable reduction of the optimization time.

Acknowledgements

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References

- [1] M. I. Nasr, A. A. Omar, M. H. Khedr, A. A. El-Geassy: *ISIJ Int.*, 35 (1985), No. 9, 1043–1049.
- [2] H. Y. Lin, Y. W. Chen, C. P. Li: *Thermochimica Acta*, 400 (2003), No. 1-2, 61–67.
- [3] V. Hacker, R. Vallant, M. Thaler: *Ind. Eng. Chem. Res.* 46 (2007), 8993–8999.
- [4] B. Schumacher, T. Heller, M. Steinhörst, W. Warnecke: Recent development of high strength steels with zinc or zinc alloy coating in Europe, Conf. Proc. GALVATEC 2007, p. 397.
- [5] J. M. Maigne, M. Lamberigts, V. Leroy: Selective oxidation of cold rolled steel during recrystallisation annealing, in: Development in the annealing of sheet steels, Ed. R. Pradhan and I. Gupta, The Minerals, Metals & Materials Society, pp. 511–528, 1992.
- [6] B. C. De Cooman: *Trans. Indian Inst. Met.*, 59 (2006), No. 5, 769–786.
- [7] B. Chatelain, V. Leroy: *Steel Research*, 57 (1986), No. 1, 13–17.
- [8] J. M. Maigne, M. Lamberigts, V. Leroy: Selective Oxidation of Cold-rolled Steel During Recrystallization Annealing, Conf. Proc. TMS Fall Meeting 1991, p. 511–528.
- [9] X. Vanden Eynde, J. P. Servais, M. Lamberigts: Surface oxide maturation and self-reduction: a new process to ensure TRIP steel hot dip galvanizing, Conf. Proc. Galvatech 2004, p. 367–372.
- [10] T. Van De Putte, J. Fenning, S. Claessens, Z. Zermout, D. Loison: “Surface analysis of the selective oxidation during austenitic annealing of CMnSi high strength steel”, Galvatech '07 Conference Proceedings, pp. 415–420, 2007.
- [11] G. Angeli, A. Jarosik, A. Muhr, H. Burger, T. Haunschmied, J. Angeli: Hot dip galvanizing of high strength steel: Reduction after preoxidation, Conf. Proc. Galvatech (2007), p. 427–432.