

# SURFACE CONDITIONING OF STEEL FOR GALVANIZATION CONTROLLED BY MASS SPECTROMETRY

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## ABSTRACT

The reactions taking place in the annealing atmosphere of a furnace simulator can be monitored with the help of a mass spectrometer probe positioned near to the steel surface [1]. The concentrations of water vapor and hydrogen near to the steel surface during the thermal cycle within the furnace are of particular interest, since they are changing as a result of the interaction with the alloying elements oxides on the steel sheet as well as those near to the surface. The concentrations of H<sub>2</sub>O, H<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub> and N have been measured via the mass spectrometer probe for studying the decarburization and nitriding processes. After the thermal treatment the concentration distributions of the relevant elements determined by GDOES within the surface near layer could be correlated to the measurements results of the gaseous species concentrations. These data allow controlling the surface conditions during the continuous annealing part of a hot dip galvanizing line by in-situ measurements and also a description of the metallurgical behavior of steel grades differing in their alloying concepts.

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

## INTRODUCTION

The zinc wettability of steels, particularly high strength qualities, depends in a critical way on the surface conditioning during the annealing steps before the contact with the molten zinc. The processes going on during the batch annealing treatment under various concentrations of hydrogen and water was studied with a laboratory hot dip simulator by Shastry et al. [2]. The resulting samples were investigated with different surface analytical methods such as SEM, XPS, GDOES and optical metallography. The selective oxidation of the alloying elements Mn, Si and Al could be interpreted by a theoretical model. The model assumptions about the concentration of water vapour near to the steel surface, which are essential for the theory, were not supported by measurements. This is a limitation of the investigations by Shastry et al. [2] since the water concentration differs at the surface from the value when the carrier gas is introduced into the reaction zone. The in-situ measurement of the gas phase near to the steel surface during the annealing provides data on the water vapour as well as other reactive gases [1]. The availability of the gas phase concentrations as a function of the sample temperature is a presupposition to controlling the annealing process. This applies for instance to the selective oxidation of sheet steels during annealing [3 - 8] or the interaction with NH<sub>3</sub>. In this paper we refer to a former publication of H. Falk and M. Falk [1] where the experimental set-up of a mass spectrometer probe (MS-probe) implemented into a thermal reactor was described. The oxidation, reduction, decarburization and nitriding of steel samples within the thermal reactor were studied.

## EXPERIMENTAL

A schematic of the MS-probe [1] is shown in Fig. 1. The sampling of the gases to be analyzed takes place in the vicinity of the sample surface where the carrier gas flow leaves the reactor through the ceramic tube which contains the entrance capillary of the mass spectrometer. Since the reaction products are collected near to the surface, the dilution by diffusion is minimized which results in low limits of detection.

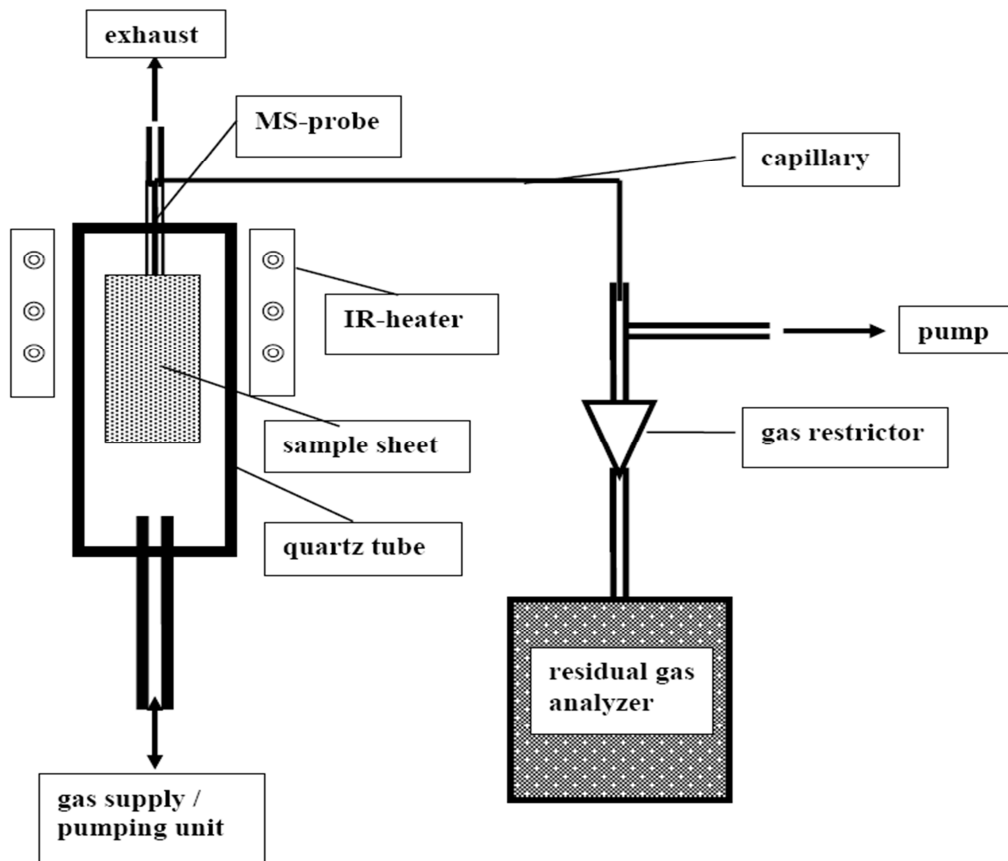


Fig. 1. Scheme of the experimental reactor [1].

The reactions of interest are displayed in Tab. 1. From this can be deduced that the most important species are  $H_2$ ,  $H_2O$ ,  $CO$ ,  $N_2$  and  $NH_3$ . For the measurement of  $CO$  the presence of  $N_2$  has to be avoided, since those molecules have coinciding masses. Therefore, Ar was used as the carrier gas. To study the interaction of steel with  $NH_3$  the carrier gas Ar was also applied, allowing the observation of  $N_2$  as a dissociation product of  $NH_3$ . The hydrogen, stemming from the dissociation, according to (6) in Tab. 1. can be distinguished via the  $N_2$  concentration.

Besides the species of interest mentioned above their fragments O, OH, N and C were detected too. A deviation of the concentration ratio between fragments and parent molecule from that which has to be expected is a hint at the interference by a third molecule.

**Tab. 1. Gas phase reactions at the surface of a steel sample.**

Process	reaction	No.
hematite oxidation/reduction	$3 \text{ H}_2 + \text{Fe}_2\text{O}_3 \leftrightarrow 3 \text{ H}_2\text{O} + 2 \text{ Fe}$	(1)
hematite oxidation/reduction	$\text{H}_2 + 3 \text{ Fe}_2\text{O}_3 \leftrightarrow \text{H}_2\text{O} + 2 \text{ Fe}_3\text{O}_4$	(2)
magnetite oxidation/reduction	$4 \text{ H}_2 + \text{Fe}_3\text{O}_4 \leftrightarrow 4 \text{ H}_2\text{O} + 3 \text{ Fe}$	(3)
bulk carbon oxidation/reduction	$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$	(4)
nitriding	$2 \text{ NH}_3 \leftrightarrow 2 \text{ N} + 3/2 \text{ H}_2$	(5)
dissociation	$2 \text{ NH}_3 \leftrightarrow \text{N}_2 + 3/2 \text{ H}_2$	(6)

The oxidation of the steel samples was carried out using air as well as water vapor. The thermal programs used for the experiments are shown in Tab. 2 while the chemical composition is presented in Tab. 3. Sheet samples of DP, High Mn, TRIP Al and TRIP Si with dimensions 80 x 20 mm<sup>2</sup>, thickness: 1 to 1.5 mm have been used.

**Tab. 2. Experimental conditions for the thermal treatment of the steel samples. Gas pressure: approx. 1.3 bar.**

	gas	T1; R1 (°C; K/s)	T2; t2 (°C; s)	R2; T3 (K/s; °C)	T3; t3 (°C; s)
oxidation	air	100; 10	500; 3 - 20		
oxidation	H <sub>2</sub> O	100; 10	300; 20	1; 900	900; 1 - 500
reduction	Ar-H <sub>2</sub> ; 95-5	100; 10	300; 20	1; 900	
nitriding	Ar; NH <sub>3</sub> 0.5 – 4.5 %	100; 10	300; 20	1 - 6; 750 - 900	750 – 900; 1 - 200

**Tab. 3. Chemical composition of the different steel probes**

Steel probe	element (mass-%)				
	C	Si	Mn	Al	Cr
DP	0.07	0.1	1.4	0.05	0.5
High Mn	0.3	0.2	22	0.01	0.1
TRIP Al	0.2	0.1	1.6	1.55	0.1
TRIP Si	0.16	1.5	1.6	0.05	0.02

## RESULTS

### *OXIDATION BY WATER VAPOR*

The progress of the oxidation at the surface and the layers beneath can be followed up via the concentrations of hydrogen, CO and sometimes CO<sub>2</sub>. Fig. 1 shows the partial pressures of H<sub>2</sub>, CO and CO<sub>2</sub> at the surface of DP and High Mn steels as a function of the sample temperature. The samples were oxidized in wet Ar at a dew point of 30 °C. From Fig. 1 one can see that the delay of about 16 s of the readings of the partial pressure measured by the MS-probe and that of the temperature can be neglected at a temperature ramp rate of 1 K /s as applied in this experiment.

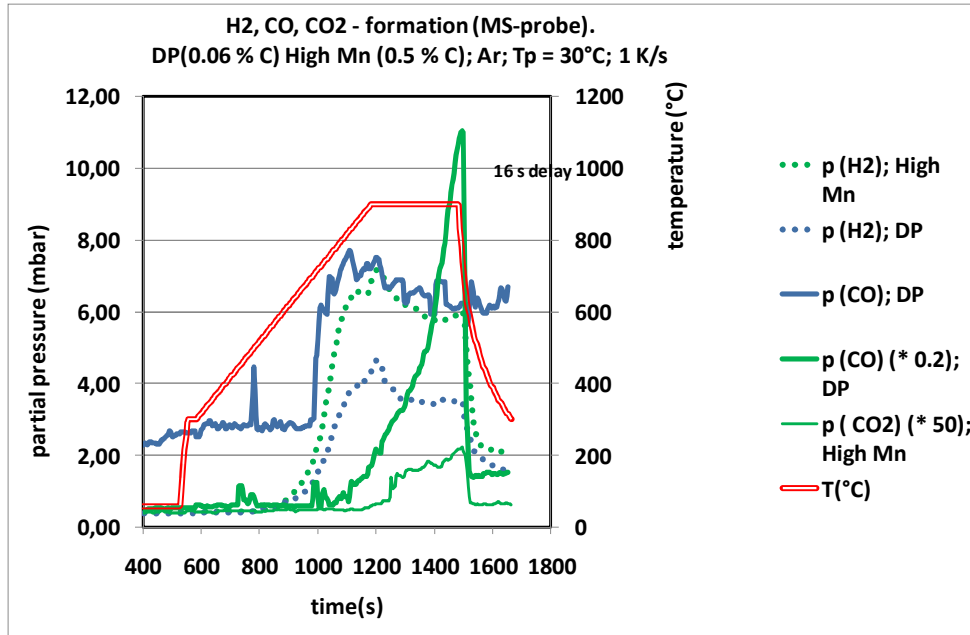


Fig. 1. Partial pressures of the reaction products formed during the thermal treatment of DP and High Mn steel samples in wet Ar at the dew point of 30 °C. Note that the signals from High Mn of CO and for CO<sub>2</sub> were multiplied by the factors of 0.2 and 50, resp.

Whereas the partial pressure of H<sub>2</sub> for High Mn is twice that for DP, the CO pressure for DP starts at lower temperature and is 7 times lower as for High Mn. A small CO<sub>2</sub> peak was observed for High Mn only. It is obvious, that the surface oxidation of the High Mn sample starts at much lower temperature than the decarburization, which latter depends on the temperature characteristics of the diffusion coefficient of carbon.

The carbon concentration as a function of the sample depth within two samples exposed to wet Ar at 900 °C for 200 and 500 s, resp. were determined by GDOES, which is shown in Fig. 2. Additionally, there are the H<sub>2</sub> and CO pressures measured during the thermal treatment.

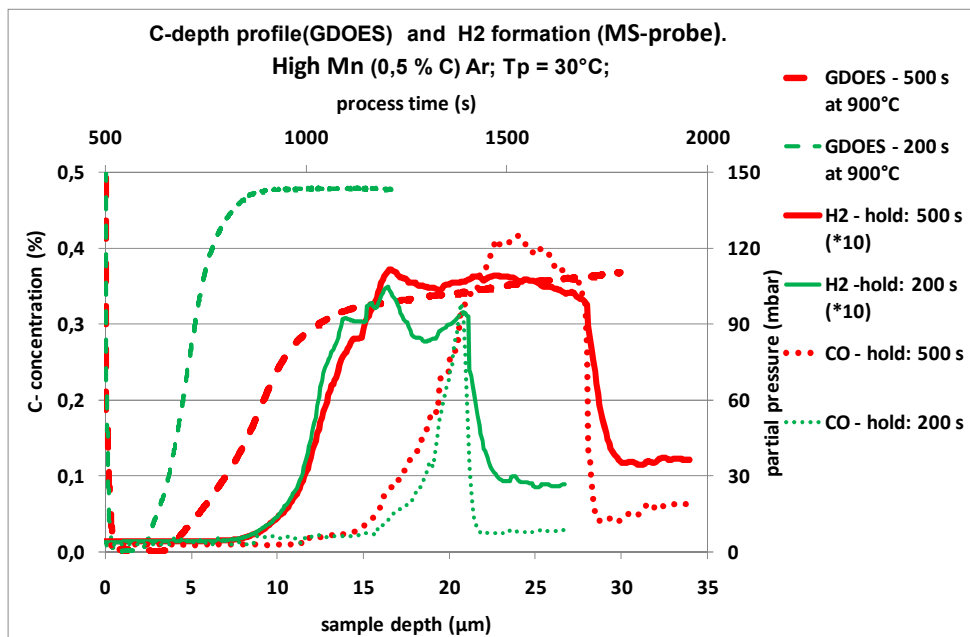


Fig. 2. Carbon concentration as a function of the sample depth determined by GDOES for High Mn samples exposed to wet Ar at 900 °C for 200 and 900 s, resp. H<sub>2</sub> and CO pressures for those samples measured during the thermal treatment by the MS-probe are shown as well.

The CO amount released during the thermal treatment represented by the integral over the CO peak is a measure of the degree of the decarburization of the sample. Since the first part of the H<sub>2</sub> formation is governed by surface oxidation because of the missing CO formation, the rising edge of the H<sub>2</sub> peak can be evaluated via the Arrhenius-plot. From Fig. 2 the resulting activation energy is 92 kJ/mole, which was also found within  $\pm 10$  kJ/mol for other steel grades. This finding suggests the formation of magnetite according to eq. (3) from Tab. 1 with the activation energy  $\Delta H(800^\circ\text{C}) = -97.7$  kJ/mole as reported by Hacker et al. [9].

### REDUCTION OF OXIDIZED STEEL SURFACES

An example for the water vapor formed during the thermal treatment of two samples from different steel grades is shown in Fig. 3. Both samples were oxidized under air at 1100 mbar and heated up from 300 to 550 °C with the heating rate of 1 K/s. Nevertheless, there are significant differences of the appearance temperatures and the activation energy, the latter evaluated via Arrhenius-plot. This implies that the chemical composition of the oxides formed at the surface of TRIP Al steel is different from that of High Mn steel. For both samples the removing of the oxide was completed before the end of the thermal treatment process applied, meaning that the process could be stopped, when the water vapor signal disappears.

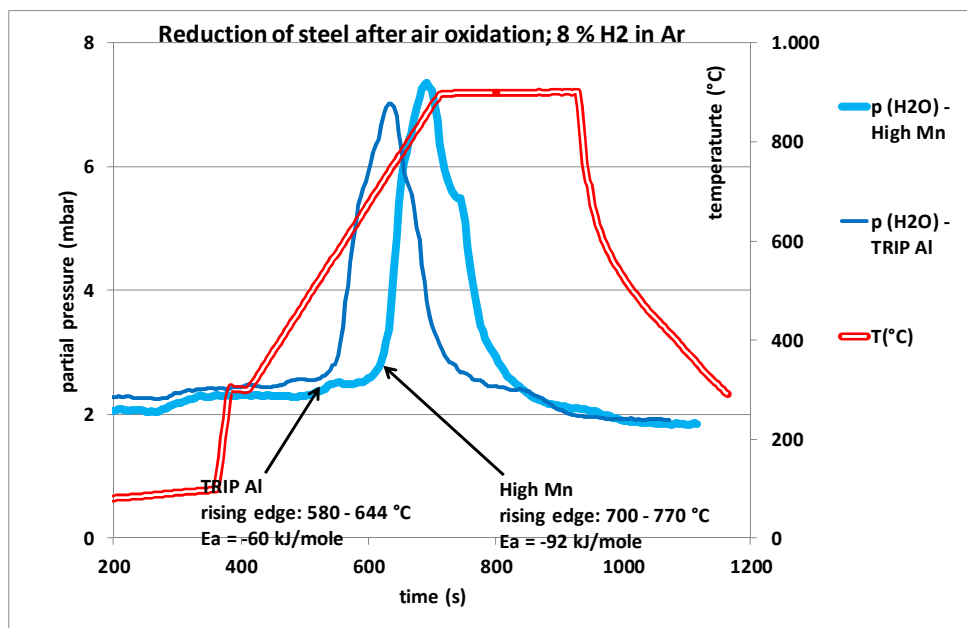


Fig. 3. Partial pressures of water vapor during reduction of (air) oxidized TRIP Al and High Mn steel samples, resp. Heating rate: 2 K/s; pressure: 1300 mbar; 8 % H<sub>2</sub> in Ar.

### NITRIDING

According to eq. (5) in Tab. 1 the measurement of the H<sub>2</sub> partial pressure using the MS-probe served as the indicator for the nitrogen concentration within the surface layer of steel samples. Fig. 4 shows an example for DP steel exposed to different NH<sub>3</sub> concentrations in Ar applying the same thermal treatment.

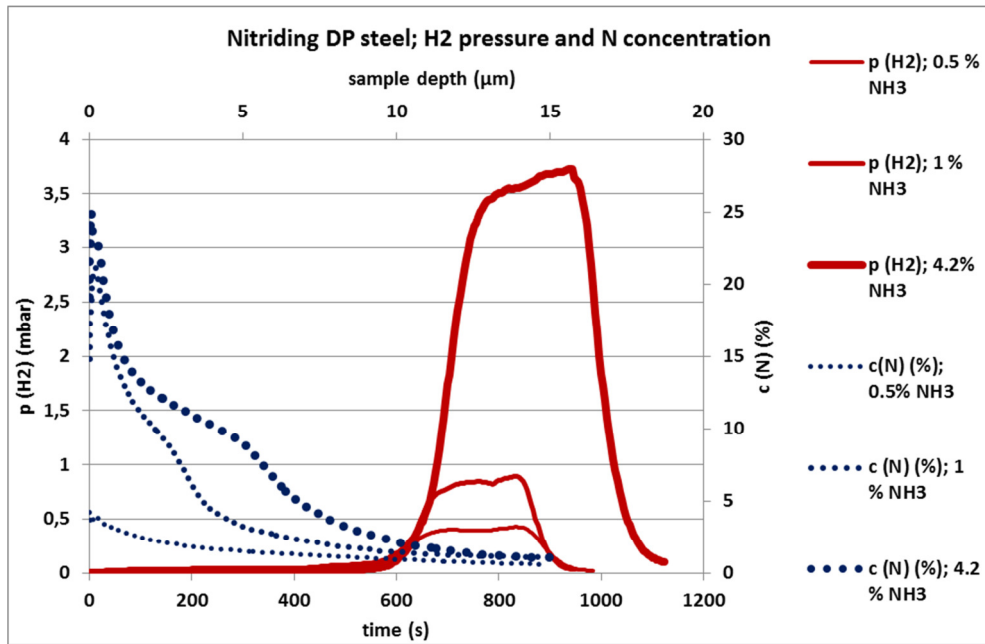


Fig. 4. H<sub>2</sub> pressure (left scale) measured via MS-probe during nitriding of DP steel and N concentration (right scale) after thermal treatment determined with GDOES. Ar with 0.5; 1; 4.2 % NH<sub>3</sub>, resp. ramp rate: 1 K/s.

The H<sub>2</sub> partial pressure integrated over the time interval of the thermal treatment is essentially proportional to the NH<sub>3</sub> concentration in the carrier gas. The resulting N concentration integrated over the sample depth increased with the NH<sub>3</sub> concentration, but less than linear. In this context it has to be noted, that NH<sub>3</sub> is partly transformed into N<sub>2</sub>, according to equation (6) in Tab. 1, during the thermal treatment. This fraction of the NH<sub>3</sub> introduced was observed via the MS-probe. At least, there exists a monotone relationship between the H<sub>2</sub> formation measured and the resulting N amount penetrating into the steel. Consequently, the H<sub>2</sub> partial pressure allows controlling the nitriding process.

## CONCLUSIONS

The in-situ measurement of the partial pressures released near to a steel surface during the thermal treatment using the MS-probe delivers valuable information on the processes involved. These data allow controlling the surface conditions during the continuous annealing part of a hot dip galvanizing line by in-situ measurements and also metallurgical behavior description of steel grades differing in their alloying concepts. Experiments with different steel grades revealed the specific reaction rates of the materials. Essentially the same procedure is applicable exploring the thermal treatment of steel while oxidizing, reducing or nitriding the material. By evaluating the activation energy for oxidation or reduction one gets a hint at the chemical compounds involved. The quantification of the released gaseous species, e.g. of CO during decarburization, allows estimating the reaction depth within the material. This relationship could be confirmed by measuring the resulting concentration distributions of the relevant elements using GDOES. The experiments on the thermal treatment as a part of the annealing process have shown that the different steps of the temperature program as well as the composition of the reactive gases can be optimized with the help of the MS-probe in a straightforward manner.

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