Calibration of Mass Spectrometric Measurements of Gas Phase Reactions on Steel Surfaces

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Abstract

The sampling of the surface-near gas composition using a mass spectrometer (MS-Probe) is a valuable tool within a hot dip process simulator. Since reference samples with well characterized surface coverage are usually not available, steel samples can deliver quantifiable amounts of the process relevant species H_2O, CO and H_2 using the decarburization reaction with water vapour. Such "artificial calibration samples" (ACS) can be used for the calibration of the MS-Probe measurements. The carbon release rate, which is governed by the diffusion law, was determined by GDOES, since the diffusion coefficients of carbon in steel samples are usually not known. The measured carbon concentration profiles in the ACS after the thermal treatment confirmed the validity of the diffusion model described in this paper. The carbon bulk concentration > 100 ppm is sufficient for the use of a steel material as ACS. The experimental results reported in this paper reveal, that with the MS-Probe the LOQ of less than one monolayer of iron oxide can be achieved.

Keywords: Mass spectrometer probe, steel surface reactions, gas phase monitoring, galvanizing, calibration.

1   Introduction

For continuous hot dip steel galvanization production lines the zinc wettability of steels depends in a critical way on the surface conditioning during the annealing steps before the contact with the molten zinc. The steel surface is exposed to the surrounding gas atmosphere consisting of nitrogen with various concentrations of hydrogen, water vapour and oxygen during the annealing steps while passing the production line. The concentrations of the reactive components of the gas phase are influenced by the chemical interaction with the surface of the steel strip, e.g. the consumption of water by the oxidation of iron, alloying metals or carbon. During the reduction process, water vapour will be released from the surface. The oxidation and subsequent reduction of the steel strip while passing the production line are often applied process steps as part of the conditioning of the surface before the contact with the molten zinc. Typical oxide layer depths range between 50nm and several hundred nanometer, where a surface layer of 100nm depth corresponds to a surface coverage of 520 mg * cm^-2 .

For the understanding of the processes going on in continuous hot dip steel galvanization lines, Hot Dip Process Simulators (HDPS) are used [1, 2]. A limitation of these measurements is the fact that the actual concentrations of the reactive gases near to the steel surface are not known. Such information can be obtained by the introduction of a mass spectrometer probe (MS-Probe) into the thermal reactor of the HDPS [3].

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The availability of the gas phase concentrations as a function of the sample temperature is a presupposition to controlling the annealing process [4].

This paper refers to the experimental setup described in former publications [5, 6]. Such a setup allows the monitoring and measurement of the near-surface concentrations of all relevant gaseous species during the thermal treatment of a steel sample within the simulator. Because of the multitude of impacts of local conditions such as gas flow rate, diffusion coefficients, heating rate etc., on the data observed from the MS Probe the quantitation is not straight forward. Further, certified reference materials with defined surface coverage are not available. Therefore, an alternative calibration method for the measurements with the MS-Probe within a thermal was developed, which is the subject of this paper.

2   Calibration method

2.1   Basic considerations

The main processes going on in the gas atmosphere surrounding the steel sample are shown in Fig. 1. Because of the various parameters involved while measuring the release of surface species in the thermal reactor, a calibration with reference samples is obligatory. There are basically two options for the calibration:

Use of a reference standard with well-defined elemental concentrations at the surface, which has to be replaced for the next experiment. Or alternatively use of an "artificial calibration standard" (ACS), based on a known bulk content of a reference sample delivering predictable amounts of the relevant gaseous species from the sample surface.

Since reference materials with known surface coverage are not available, in the following only the "artificial standards" will be considered here.

The ACS should fulfill the following conditions:

The ACS sample should exactly simulate the surface processes of a „real" measurement.

The bulk concentration of the relevant elements within the ACS is sufficient for the release of the relevant species.

ACS should permit separation of „external" (adsorption at the sample surface, incomplete sample preparation, etc.) from „intrinsic" influences (fluctuation of the gas composition or sample temperature or capillary temperature or MS-detector background).

The ACS should be stable over long periods, and readily available to other researchers.

Instead of the surface process the decarburisation process can be used, according to the reaction:

$$C + H_2O \rightarrow CO + H_2 \qquad\qquad (1)$$

Reaction (1) involves the three most interesting species: H_2O, CO and H_2. While the concentration of H_2O is decreased, that of CO and H_2 will increase. Since these species are resulting from the reaction at the surface, they undergo the same processes as those in the oxidation or reduction reactions on the sample surface, e.g. according to:

$$3 H_2 + Fe_2O_3 \leftrightarrow 3 H_2O + 2 Fe \qquad\qquad (2)$$
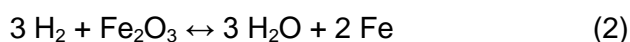
If the amount of carbon, which was released during a measurement cycle, can be determined independently, the corresponding amount of the species H_2O, CO and H_2 can be calculated via stoichiometry according to reaction (1). For the determination of the amount of carbon released from the sample surface one can exploit the diffusion of carbon from the bulk to the surface during the thermal treatment based on a theoretical model.

2.2   Concentration of carbon at the sample surface

Steel samples, which have been exposed to air, show a carbon concentration in the near surface layer exceeding the bulk concentration, as the result of the reaction with carbon dioxide. If the decarburization according to (1) takes place, the carbon concentration within the surface-near layer will be reduced below the bulk concentration. If the sample temperature is sufficiently high, the carbon losses at the surface will be compensated by the carbon diffusion from the bulk to the surface. The calculation of the diffusion controlled carbon supply to the surface will be explained below.

The carbon concentration within a thin steel sheet sample can be considered as only depending on the x-coordinate perpendicular to the sample surface. In this case the diffusion is governed by the one-dimensional 2nd Fick's law:

$$\partial c / \partial t = D * \partial^2 c / \partial x^2 \qquad (3)$$

where $c = c(x, t)$ – concentration of carbon (kg * m^-3); x – coordinate perpendicular to the sample surface (m); t – time (s); D – diffusion coefficient (m^2 * s^-1).

The solution of equation (3) can be written as:

$$c(x,t) = cs + (co - cs) * erf(x / xd) \qquad (4)$$

where cs – surface concentration; co – bulk concentration;

$$xd = 2 * (D * t)\text{^}0.5 \qquad (5)$$

The diffusion coefficient for carbon in steel is temperature dependent according to:

$$D = Do * exp(- E_D / (R * T) \qquad (6)$$

where Do – material dependent constant (m^2 * s^-1); ED – activation energy (J * mol^-1); R – gas constant (J * mole^-1 * K^-1); T – temperature (K).

The mass flow of carbon jC (kg * m^-2 * s^-1) released from the surface is proportional to the concentration gradient at the surface, and by differentiating equation (4) one gets:

$$jC = (co - cs) * (D / (\pi * t))\text{^}0.5 \qquad (7)$$

jC decreases with the root of the time and can be calculated for any time interval, if the carbon concentration and the diffusion coefficient are known. From (6) reveals that the carbon loss rate will decrease when D is decreased or the process time increases. Consequently, if the ACS is kept at a temperature which causes a low diffusion coefficient, the carbon loss rate will become almost constant. In this case, the release rates of H_2O, CO and H_2 stay nearly constant too.

3   Experimental results and evaluation

3.1   Mass spectrometer probe

The partial pressures of H_2O, CO, H_2 and CO_2 were measured using the setup shown in Fig. 1. An example showing 12 repetitions of the same heating cycle from 500 to 760°C is displayed in Fig. 3. Despite of the first peaks of H_2O, CO and H_2 resulting from the surface coverage, the following peaks are fairly constant, as to be expected in case of a low release rate of carbon. Since the H_2O is consumed by the reaction (2), the corresponding peaks are negative, causing only a small variation of the initial level. The experiment shown in Fig. 3 was repeated but using the 20 °C higher maximum temperature of 780°C, which can be seen in Fig. 4. The increase of the CO and H_2 peaks by the higher temperature is remarkable. The amount of CO_2 is negligible relative to CO.

At a given set of conditions, the addition of a few percent of hydrogen to the carrier gas Ar, which is common in the hot dip galvanization process, led to an increase of the CO and H_2 signals by a factor of more than 5. This corresponds to an enhancement of the carbon

release as a result of the addition of hydrogen and thus the increase of the decarburized layer of the sample.

The repeated heating procedure allows controlling the accuracy of the baseline for the measurement of the partial pressure. For the quantitation, the measured peaks and the background intervals before and after the peak were integrated over the same time interval (see Fig. 5). The net peak integral is a measure of the amount of the respective species which was released into the gas phase surrounding the sample. A typical example can be seen in Tab. 1, which refers to the same measurements as displayed in Figs. 4 and 5. The stability of the pressure background is satisfactory.

A quantitative comparison of the carbon release from the sample surface at different experimental conditions can be done by considering the respective peak integrals. Such an example is displayed in Fig. 6 which shows that at high carbon release rate the amount of CO follows a power function with a power of approximately 0.5. This functionality can be expected according to equation (6).

3.2   GDOES concentration profiles

After decarburization in the thermal reactor some samples were analyzed with GDOES. The depth distribution of the carbon concentration is of particular interest for the determination of the amount of carbon lost during the thermal treatment. Fig. 7 shows the carbon distribution together with some other elements for the case of a very weak decarburization. The high carbon concentration in the depth of less than 1 µm is due to the reaction with CO_2 caused by the air exposure. The increase of the process temperature and the addition of hydrogen to the carrier gas both result in a thicker depletion layer for carbon, as can be seen in Fig. 8 (please note the larger abscissa scale in comparison with Fig. 7). For the repeated heating at high release rate the carbon depletion layer may exceed 100 µm.

The concentration distribution measured by GDOES can be compared with a simulation according to equation (4). Fig. 9 shows two examples, where the diffusion coefficient was chosen such, to get the best fit between the normalized curves from GDOES and equation (4). The concentration measurements can be approximated satisfactorily by the model calculations, if the diffusion coefficient and the process duration are appropriate. This presupposition will be discussed below.

4   Limits of quantitation and discussion

4.1   LOQ of the carbon concentration in the sample

For the use of a material as an ACS its carbon concentration has to be sufficient, as mentioned previously. The carbon concentration in the sample, which allows sufficiently high signals of H_2O, CO and H_2, resp., for the quantification, can be determined by

$$c(LOQ; C) = c(C; bulk) * 10 * SD(background\ integral)\ /\ peak\ integral \qquad (8)$$

where c(LOQ; C) – carbon concentration at the limit of quantification; c(C; bulk) - carbon concentration within the sample; SD(background integral) - standard deviation of the background integral (see Fig. 5). Since the signals from the MS-Probe depend on the instrumental parameters, such as gas supply and temperature program, c(LOQ; C) holds true only for a given set of parameters. Therefore, LOQ's in Tab. 2 should be considered as examples. As a rule, c(LOQ; C) will increase, if the process temperature and/or process time are decreased and vice versa.

4.2   LOQ of the gaseous components

The absolute amount of H_2O, CO and H_2 (in kg * m^-2) can be calculated from the carbon loss of the sample using the stoichiometric relationship shown in equation (1). Basically, the carbon loss can be calculated with the help of equation (7) provided that the process duration

and the diffusion coefficient are known. The process time is sufficiently well defined, if the temperature program provides short heating and cooling times relative to the hold time at maximum temperature. The diffusion coefficient of carbon in steel depends on the steel grade and its microscopic structure and is usually not known. At a temperature of 780°C as applied in this study, for steels with body-centered cubic and face-centered cubic structures diffusion coefficients of 5E-11 and 3.3E-12 $m^2 * s^{-1}$, resp., are reported [7]. Data on the influence of hydrogen on the decarburization rate at steel surfaces in the presence of water as a function of the temperature could not be found in the literature. Consequently, the actual carbon loss after the thermal treatment with the used experimental parameters for the calibration has to be measured with a reference method, e.g. GDOES. If a given sample material has been characterized once by the reference method, it can be applied as the ACS without additional analyses. This information can be used also to determine the diffusion coefficient of carbon for the respective material and experimental conditions as will be demonstrated below (see Fig. 9).

If the H_2O, CO and H_2 signals from the MS-Probe are calibrated in absolute amounts (in kg * m^{-2}), the H_2O peaks measured in a reduction process can be attributed to a certain layer thickness of Fe_2O_3 using equation (2). The same procedure can be applied while attributing the hydrogen peak caused by the surface oxidation of iron with water to the thickness of the iron oxide layer, removed from the surface. However, the contribution of the decarburization, if observable via the CO signal, has to be taken into account.

With the known signal-to-noise ratio of the calibrated H_2O and H_2 peaks, resp., it is possible to calculate the LOQ for the determination of the thickness of the iron oxide during the oxidation or reduction processes. Tab. 3 shows the LOQ's for two cases of a very low carbon release rate (measurement No. 222_2 in Fig.3 and 7) and a high carbon release rate (measurement No.   C – 9 in Fig. 9), resp. For the calculation it was assumed, that the density of the bulk iron oxide is also valid for the layer at the surface. At a low carbon release rate the LOQ is below 1 monolayer of the iron oxide. The LOQ increases with rising carbon release rate, since the signal-to-noise ratio of the measured partial pressure increases less than proportional to the carbon release rate.

5   Conclusions

Steel samples with known carbon bulk concentration can be used for the calibration of surface reactions at steel surfaces in hot dip process simulators. These "Artificial Reference Samples" (ARS) are based on the decarburization reaction of the sample with water at elevated temperatures. The species H_2O, CO and H_2, which are relevant for the hot dip simulator are involved in the decarburization reaction.

Although the diffusion determined carbon release rate can be satisfactorily described by a theoretical model, usually the carbon depletion layer has to be determined by an independent method, e.g. by GDOES.

If the decarburization rate is sufficiently low, it stays essentially constant in the course of a large number of repeated simulator experiments. This means that a steel sample for which the diffusion coefficient is known can be used for the investigation of a multitude of instrumental parameter settings of the MS-Probe and for the quantitation of the surface reaction measurements of unknown samples as well.

The ARS concept allows estimating the limit of quantitation of the thickness of surface layers while interacting with the surrounding gas within a hot dip process simulator. Iron oxide layers below one monolayer (or 0.4 nm thickness) are measurable. With typical oxide layer thicknesses in the hot dip process line above 50 nm, the detection capability of the MS-Probe is sufficient for the monitoring of the gas phase reactions taking place in a hot dip process simulator.

Literature

[1] M. Norden, Heterogene Glühgas/Metall-Reaktionen in der Schmelztauchveredelung höherfester Mehrphasenstähle, Thesis; RWTH Aachen, Shaker Verlag Aachen, ISBN 978-3-8322-9652-0, Aachen (2010) 56 – 59.
[2] C. R. Shastry, J. A. Totole and T. W. Kaiser, Characterization of selective oxidation of alloying elements in an advanced high strength steel from theoretical and experimental viewpoints, Galvatec '07 (2007) 403 - 408.
[3] A. Bulanova, R. Gburik, J. Hunady, P. Zimovcak, Optimization of continuous annealing process on hot-dip process simulator, Metal 2008 13. – 15.5.2008 Hradec nad Moravici.
[4] B. C. De Cooman, The surface and sub-surface structure of continuously annealed sheet steel: implications for galvanizing and galvannealing, Trans. Indian Inst. Met. Vol. 59 No. 5 October 2006 769 – 786.
[5] H. Falk, M. Falk, Investigation of gas phase reactions during the thermal pretreatment for the galvanization of steel samples, Steel Research Int. 81 (2010) 4 320 – 324.
[6] H. Falk, M. Falk, M. Norden, F. Huber, W. Bleck, Surface conditioning of steel for galvanization controlled by mass spectrometry, Galvatec '11 (2011) paper no. 16.
[7] Physikalische Werkstoffeigenschaften, IFW Dresden, Kap. 8 Diffusion (2013).

Legends to the figures

Fig. 1. Schematic of the main transport processes near to the sample surface within a thermal reactor with MS-Probe [5].

Fig. 2. Normalized carbon concentration at a high reaction rate at the surface (cs = 0) with the parameter duration, as calculated according to equation (4). Diffusion constant D = 5E-11 m^2 * s^-1.

Fig. 3. Partial pressures measured using the MS-Probe while repeated heating of the steel sample (TRIPAL; 1400 ppm C; sample 222_2) from 500 to 760°C. Heating rate: 5 K/s; hold time at 760°C: 20 s; Ar flow rate: 3 l/min; dew point: 10°C. The H_2 peaks are wider compared to the CO peaks because of the H_2 contribution of the iron oxide formation.

Fig. 4. Same as Fig. 3, but 20°C higher maximum temperature of 780°C (TRIPAL; 1400 ppm C; sample 222_4).

Fig. 5. Evaluation of the partial pressure measurements using the MS-Probe. Steel sample (TRIPAL; 1400 ppm C; sample 222_4) heating from 500 to 780°C. Heating rate: 5 K/s; hold time at 780°C: 20 s; Ar flow rate: 3 l/min; dew point: 10°C.

Fig.6. CO peak integrals evaluated from repeated heating. Steel sample (TRIPAL; 1400 ppm C; samples 222_2, 222_4, 222_9). Heating rate: 5 K/s; hold time at Tmax: 20 s; Ar flow rate: 3 l/min; dew point: 10°C. 222_2: 500 to 760°C; 222_4: 500 to 780°C; 222_9: 500 to 780°C, Ar + 3% H_2.

Fig. 7. GDOES concentration profiles of steel samples (TRIPAL; 1400 ppm C; sample 222_2) after thermal treatment. Heating 12 times from 500 to 760°C. Heating rate: 5 K/s; hold time at 760°C: 20 s; Ar flow rate: 3 l/min; dew point: 10°C.

Fig. 8. GDOES concentration profiles of Steel samples (TRIPAL; 1400 ppm C; sample 222_7 and 222_9) after thermal treatment. Heating rate: 5 K/s; hold time at 780°C: 20 s; Ar + 3% H_2, flow rate: 3 l/min; dew point: 10°C. Curves Al; Mn; C; O: heating once from 500 to 780°C. Curve C _9: heating 12 times from 500 to 780°C.

Fig. 9. Comparison of the carbon distribution measured by GDOES and simulations using equation (4) (dotted curves). C (222_2) – conditions from Fig. 7; C (222_7) – conditions from Fig. 8; Sim 1 – D = 1.8E-13 m^2 * s^-1 t = 20 s; Sim 2 – D = 6 E-12 m^2 * s^-1 t = 20 s.