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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 vapor. 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.

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 50 nm and several hundred nanometers, where a surface layer of a 100 nm depth corresponds to a surface coverage of 520 $\text{mg} * \text{cm}^{-2}$.

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 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].

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

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☆ This article is dedicated to Jim Holcombe, in recognition of his academic, mentoring and scientific achievements, and his service to the spectroscopic community.

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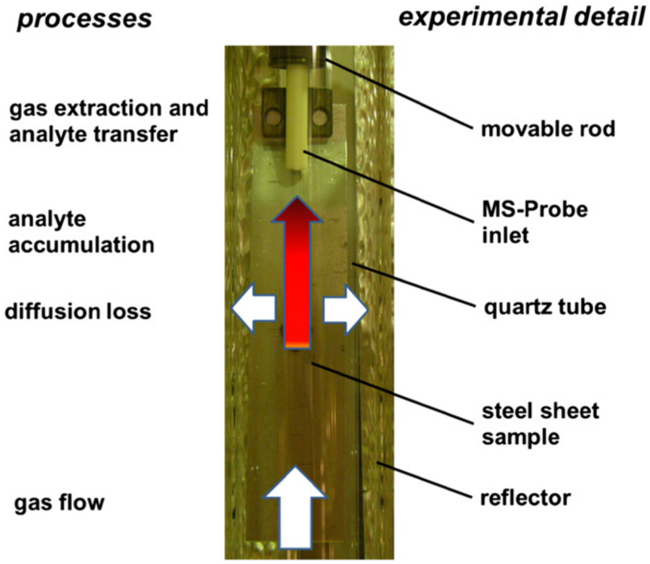

Fig. 1. Schematic of the main transport processes near the sample surface within a thermal reactor with MS-Probe [5].

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:

$$C + H_2O \rightarrow CO + H_2 \tag{1}$$

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:

$$3H_2 + Fe_2O_3 \leftrightarrow 3H_2O + 2Fe \tag{2}$$

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.

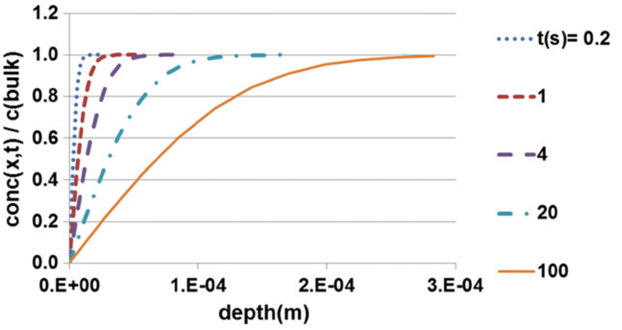

Fig. 2. Normalized carbon concentration at a high reaction rate at the surface (cs = 0) with the parameter duration, as calculated according to Eq. (4). Diffusion constant D = 5E−11 $m^2 * s^{-1}$.

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:

$$\partial c/\partial t = D*\partial^2 c/\partial x^2 \tag{3}$$

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

The solution of Eq. (3) can be written as:

$$c(x, t) = cs + (co - cs)*\mathrm{erf}(x/xd) \tag{4}$$

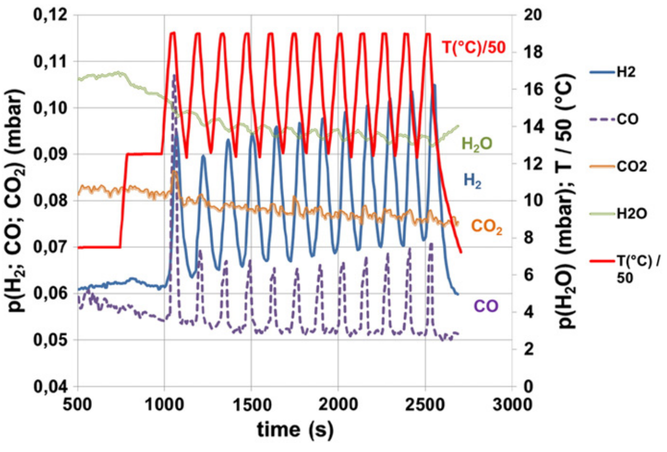

Fig. 3. Partial pressures measured using the MS-Probe while repeated heating of the steel sample (TRIPAL; 1400 ppm C; sample 222_2) from 500 to 760 °C. Heating rate: 5 K/s; hold time at 760 °C: 20 s; Ar flow rate: 3 l/min; dew point: 10 °C. The H_2 peaks are wider compared to the CO peaks because of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