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Monitoring of the Oxide Formation on Steel Surfaces by Using Optical Reflectivity Combined with Mass Spectrometry

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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. ^[1, 2, 3] Whereas the MS-Probe allows the determination of the oxide coverage only after the thermal treatment, the optical reflection measurement can reveal the building up or reducing of the oxides in-situ. The experiments reported in this paper show that the formation of reducible as well as non-reducible oxides can be monitored using the reflectometer. With the reflectivity measurement the surface conditioning of the steel surface for the hot dip galvanization can be characterized.

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 variable 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 or oxygen 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. ^[1] Typical oxide layer depths range between 50 and several 100 nm, where 100 nm corresponds to a surface coverage of $520 \text{ mg} \cdot \text{m}^{-2}$, assuming the density of Fe_2O_3 .

For the study of the processes going on in continuous hot dip steel galvanization lines Hot Dip Process Simulators (HDPS) are used. ^[2, 3] The composition of the gas phase near to the steel surface can be monitored by the introduction of a mass spectrometer probe into the HDPS. ^[4–6] A further step for the controlling of the oxide coverage at the steel surface is the in-situ measurement of the thickness of the oxide layer in the HDPS which is the intention of this paper. Such an oxide thickness measurement is also of interest for the application in a continuous hot dip steel galvanization production line.

2. Description of the Oxide Sensor

The determination of thin films on metals by the measurement of optical reflectivity is a known technique. ^[7] As a subgroup of it, the ellipsometric thickness measurement cannot be applied for the determination of oxide layers on a surface from rolled steel, since the roughness of such a material is too high. For steel qualities as used in hot dip galvanization lines the measurement of the diffuse reflectance appears to be adequate for the determination of the oxide coverage. A schematic of a diffuse reflectance setup is shown in **Figure 1**.

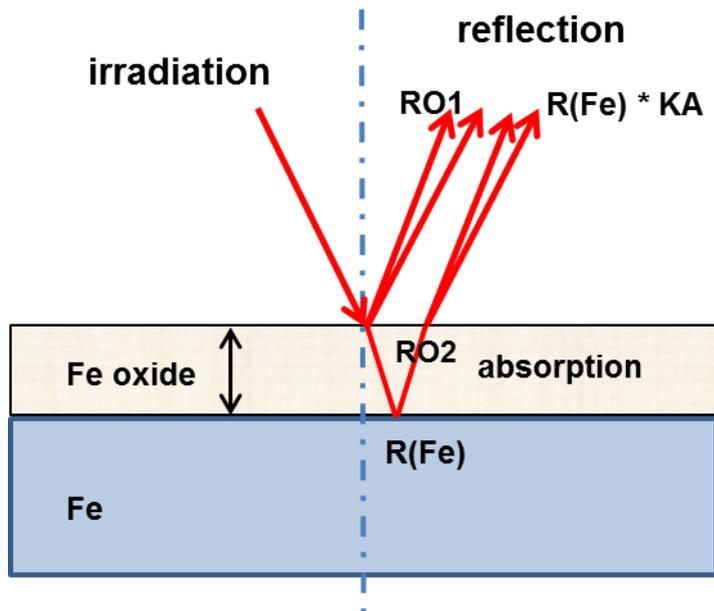


Figure 1. Concept of the diffuse reflection at the oxide covered steel surface.

The incident radiation is reflected at the oxide surface ($RO1$) as well as at the metal ($RO2$), where the latter penetrated the oxide layer twice. $RO2$ is determined by the reflectivity of the metal $R(Fe)$ and the optical absorption KA of the oxide. Depending on the degree of the surface roughness, the emerging radiation is distributed around the specular reflected ray. The reflectivity, defined as the ratio of the reflected to the incident irradiance, is independent of the polarization of the incident radiation if the latter propagates perpendicular to the sample surface which is the preferred arrangement in this paper. The thickness of the oxide layer can be calculated using the Fresnel formulae, if the optical constants of the metal and the oxide are known. Since this is not the case for the materials under consideration, the thickness measurement device has to be calibrated with reference samples of known oxide thicknesses.

The optical layout of the Oxide Sensor (OS) as used in this paper is shown in **Figure 2**. The normal incidence of a narrow band laser beam is realized by using a central mirror which area is small compared to the cross section of the reflected radiation cone. The parameters of the laser: central wavelength: 690 nm; single mode; maximum optical output: 30 mW;

laser spot diameter at the sample: ca. 5 mm; integrated reference diode for the output power control. Typically, the laser was operated at 15 mW and the output was kept constant within $< 0.2\%$. The laser output was modulated with typically 10 Hz to allow the subtraction of the thermal background radiation.

The optical layout as shown in Figure 2 was also applied at the running steel sheet in a hot dip galvanization plant which will be described in a separate paper.

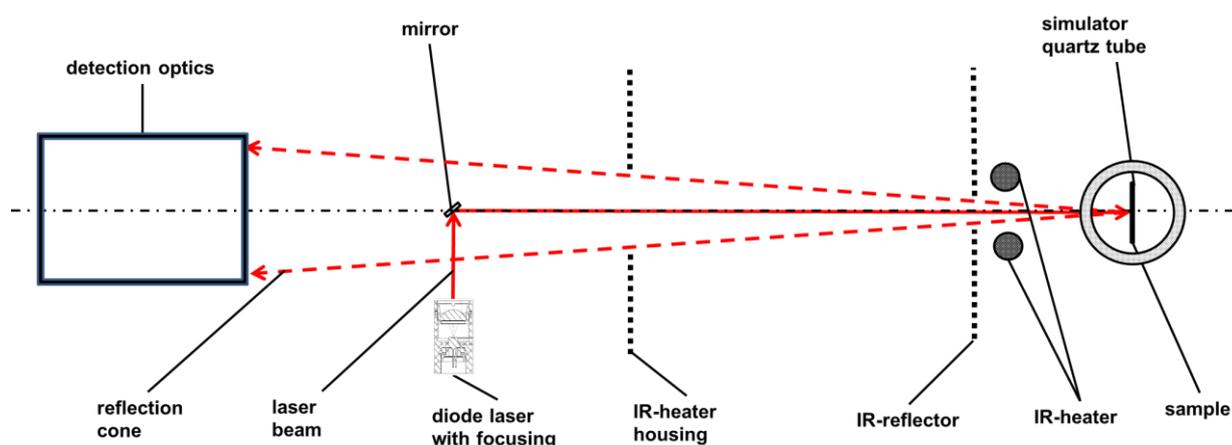


Figure 2. Optical layout of the Oxide Sensor (OS) integrated into the HDPS.

3. Measurement Concept

The presuppositions for the zinc wetting during the hot dip galvanization process are the existence of a reactive iron layer at the steel surface and a low concentration of non-reducible oxides of alloying elements. Particularly high strength steels with high contents of Al, Si or Mn tend to form such oxides which cannot be reduced at the temperatures applied in hot dip galvanization furnaces. [2, 3, 8, 9, 10] The active iron layer at the steel sample is characterized by a high reflectivity. Consequently, the reduction and oxidation at the steel surface can be monitored with the OS during the thermal treatment within the HDPS. In this way the proof of the existence of the iron coverage is the oxidation and subsequent reduction which means that the reflectivity varies between the levels characteristic for the oxidized and

the reduced surface, respectively. If the reflectivity of an oxidized surface will not increase while applying reducing conditions in the HDPS, this means that non-reducible oxides exist at the surface. The following experiments in this paper are based on the correlation between reflectivity and oxide coverage with the intention to evaluate the process conditions for the HDPS which are suitable for the formation of the active iron coverage with a minimum concentration of non-reducible oxides at the surface. Since the thermal reactor used for this study is also equipped with a mass spectrometer probe, taking gas samples near the sample surface, the reaction products formed at the sample surface can be monitored too.^[4] E.g., the determination of the water vapor concentration formed during the reduction step allows the quantification of the iron amount produced during this process.^[6] Following this procedure, one is able to study the oxidation and reduction processes without interrupting the heat treatment of the sample. Also, the oxide thickness measurement can be carried out without exposing the sample to the ambient air which would be necessary for GDOES (Glow Discharge Optical Emission Spectrometry)^[6].

4. Experimental

For the experiments described below a laboratory thermal reactor as reported in [4] was used. Essentially, it consists of an IR-heated quartz tube in a controlled reducing or oxidizing gas flow with a defined dew point. The sample temperature was measured with a thermocouple soldered to the sample. The composition of the gas near to the sample surface was continuously measured using a mass spectrometer probe (MS-probe) as well as the reflectivity in the center of the sample with the OS described above. The major elements of

the steel samples with the dimensions: 90x20x1 mm³ used in this study are compiled in Table 1.

sample	C	Si	Mn	Al	Cr
Dual Phase steel 500	0,07	0,10	1,40	0,05	0,50
TRIPAI (TRansformation Induced Plasticity steel)	0,19	0,12	1,60	1,51	0,023
St1 = TRIPSi (TRansformation Induced Plasticity steel)	0,30	0,23	1,21	0,040	0,12

Table 1. Composition of the steel samples used in this study. Concentrations in %.

4.1 Influence of the oxidation temperature

An example of the reflectivity measurement during the thermal treatment of a low alloyed sample is displayed in **Figure 3**. The falling edge of the reflectivity is slightly shifted towards shorter time, because of the mean value over 20 s was formed. Whereas the reflectivity R is recovered after oxidation at 500°C and subsequent reduction, this is only partly the case at 600°C and completely impossible at 700°C, indicating the formation of non-reducible oxides.

Figure 4 shows the same low alloyed sample as used in Figure 3, but here the same sample was reduced at 800°C, then oxidized at 400°C, again reduced at 800°C and the last two steps repeated with prolonged oxidation duration. The same cycles were started again at increasing oxidation temperatures. One finds, that the high reflectivity, as characteristic for a reduced steel surface, is reproduced after oxidation and subsequent reduction for the oxidation temperatures 400°C and 450°C. This applies for the two degrees of oxidation realized by increasing the duration of the oxidation cycle. For the oxidation temperature of 500°C the reflectivity before oxidation cannot be reproduced completely but the reflectivity decreases slightly after each oxidation. From Figure 4 follows that the thickness of the oxide

coverage reached a limit where the reflectivity stays at its lowest value, determined by the optical background of the reflectometer.

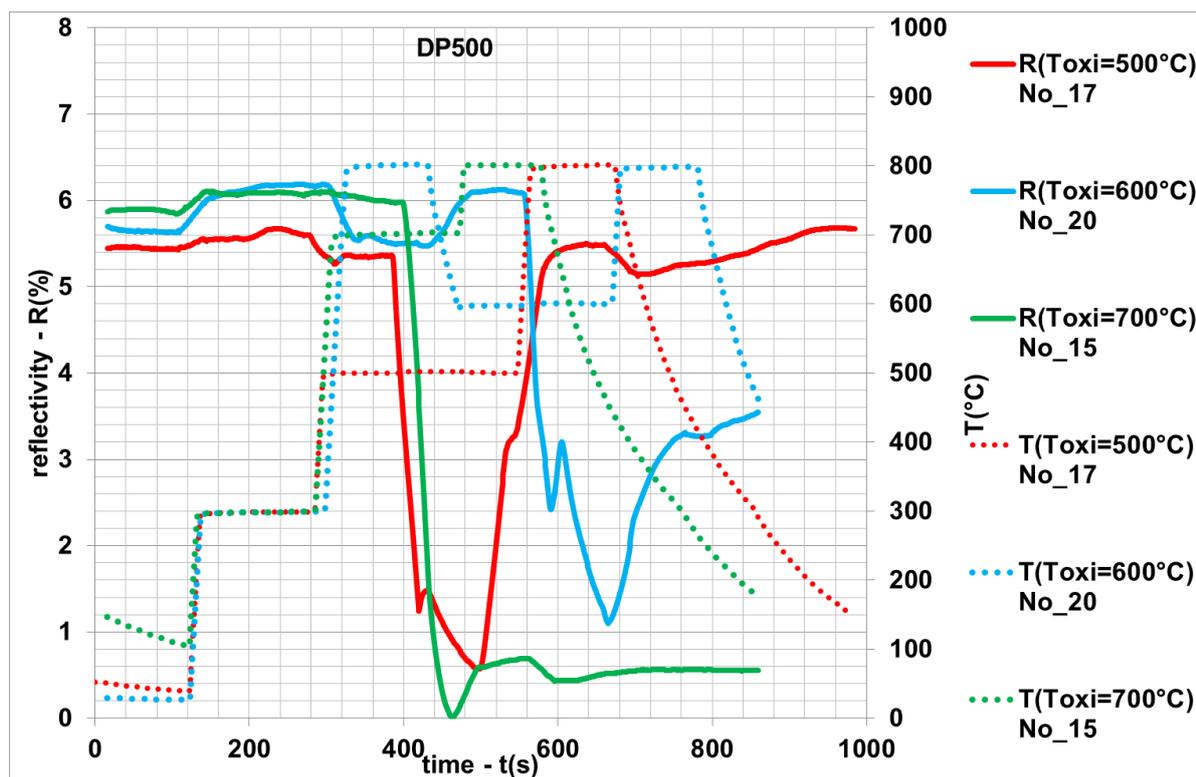


Figure 3. Reflectivity of three low alloyed steel samples during the reduction – oxidation – reduction cycle using various oxidation temperatures. $N_2 + 5\% H_2; 0.5\% O_2$ for 100 s at 500 and 600°C (starting at 400 s and 560 s, resp.), resp.; $0.1\% O_2$ for 50s at 700°C (starting at 400 s).

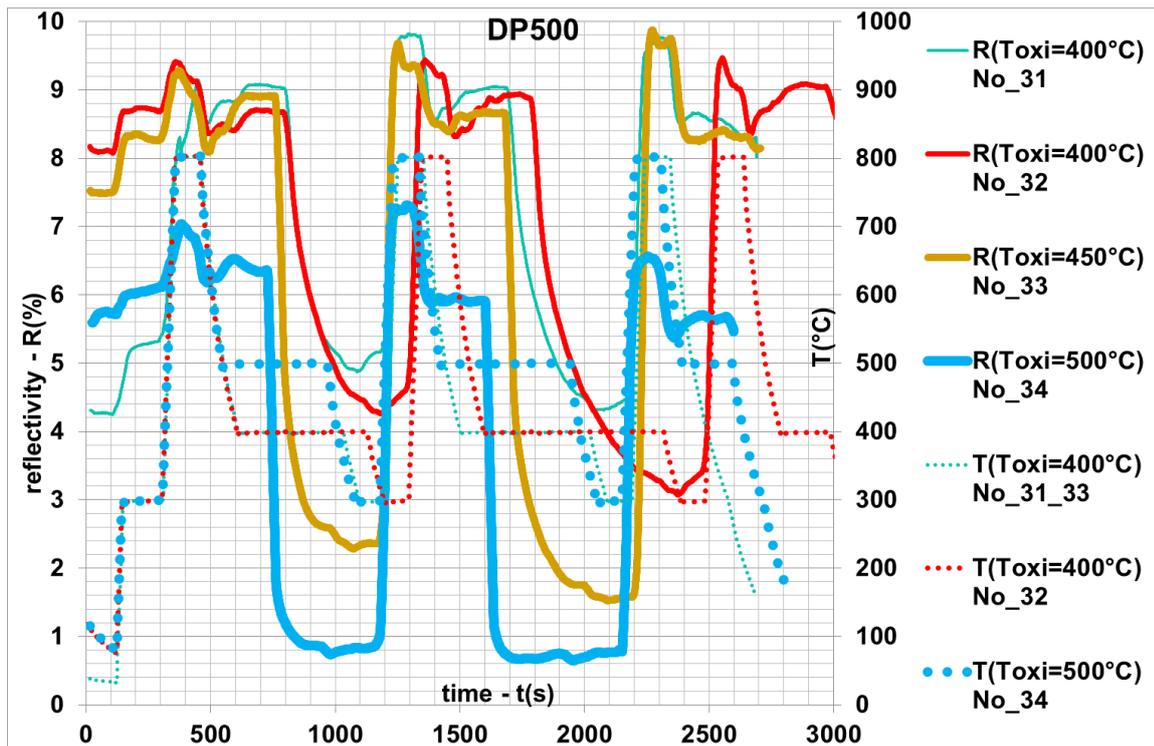


Figure 4. Reflectivity of the same low alloyed steel sample (DP500) during the repeated reduction – oxidation – reduction cycles using various oxidation temperatures. Reduction: $N_2 + 7.7\% H_2$, oxidation: $N_2 + 0.46\% O_2$: No_31 for 100 s and 200 s; No_32: for 200 and 400 s; No_33 and No_34: for 100 s and 200 s. The oxidation started 200 s after the beginning of the respective soaking step. Total pressure: 1300 mbar.

The pressure readings of hydrogen and oxygen using the MS-probe in addition to the reflectivity from the experiment No_34 displayed in Figure 4 are shown in Figure 5. One may notice a delay of the rising edge of the pressure reading of ca. 20 s behind the falling edge of the reflectivity, which is due to the travel time of the gas through a capillary into the mass spectrometer. Besides the real gas concentrations near to the sample surface the synchronization between the increase of the oxygen concentration and the respective decrease of the reflectivity can be noticed. The decrease of the reflectivity stands for a corresponding formation of the oxide layer at the surface of the steel sample while adding oxygen. The subsequent addition of hydrogen and increasing the temperature leads to a removal of the oxide layer as indicated by the respective increase of the reflectivity. But it can

be noticed in Figure 5 that the reflectivity was not restored completely after the reduction.

This implicates the formation of a non-reducible oxide layer such as SiO_2 or MnO .

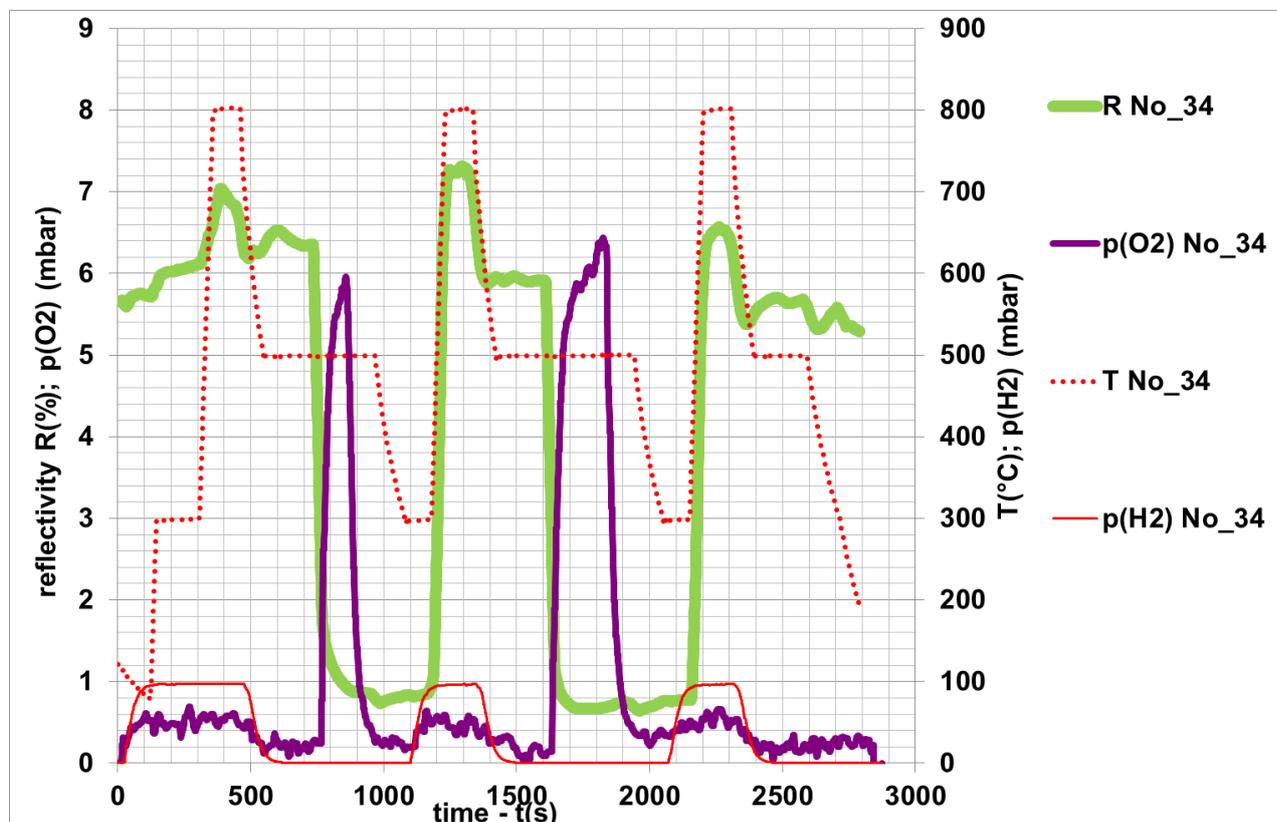


Figure 5. Records of the reflectivity, oxygen pressure $p(\text{O}_2)$ and hydrogen pressure $p(\text{H}_2)$.

The same sample (DP500) was exposed to 0.46 % O_2 for 100 and 200 s, resp., sample temperature: 500 °C; total pressure: 1300 mbar.

As the second example the TRIPAl sample with 1.5 % Al was studied. The reflectivity measurements applying various oxidation temperatures are shown in **Figure 6**. After a reduction step, during a soak step at 300, 350 and 400°C, resp., a small amount of oxygen was introduced in steps while the dew point was held below -40°C. It is visible that the oxidation takes place at 300°C already and becomes faster with the increasing temperature. For all the oxidation temperatures the initial reflectivity is not recovered after the reduction step, indicating the presence of non-reducible oxides. The differences of the initial

reflectivities in Figure 6 are due to the variations of the samples by the manufacturing process. In contrast to the findings for the DP500 sample, for the TRIPAI sample the oxidation step leads to non-reducible oxides even at low temperatures. Consequently, a bad wettability of such a TRIPAI sample has to be expected. Figure 6 illustrates the stepwise growth of the oxide layer thickness exposing the surface to small oxygen concentrations for a short time. It is also interesting to notice that the oxidation takes place at the temperature of 300°C already.

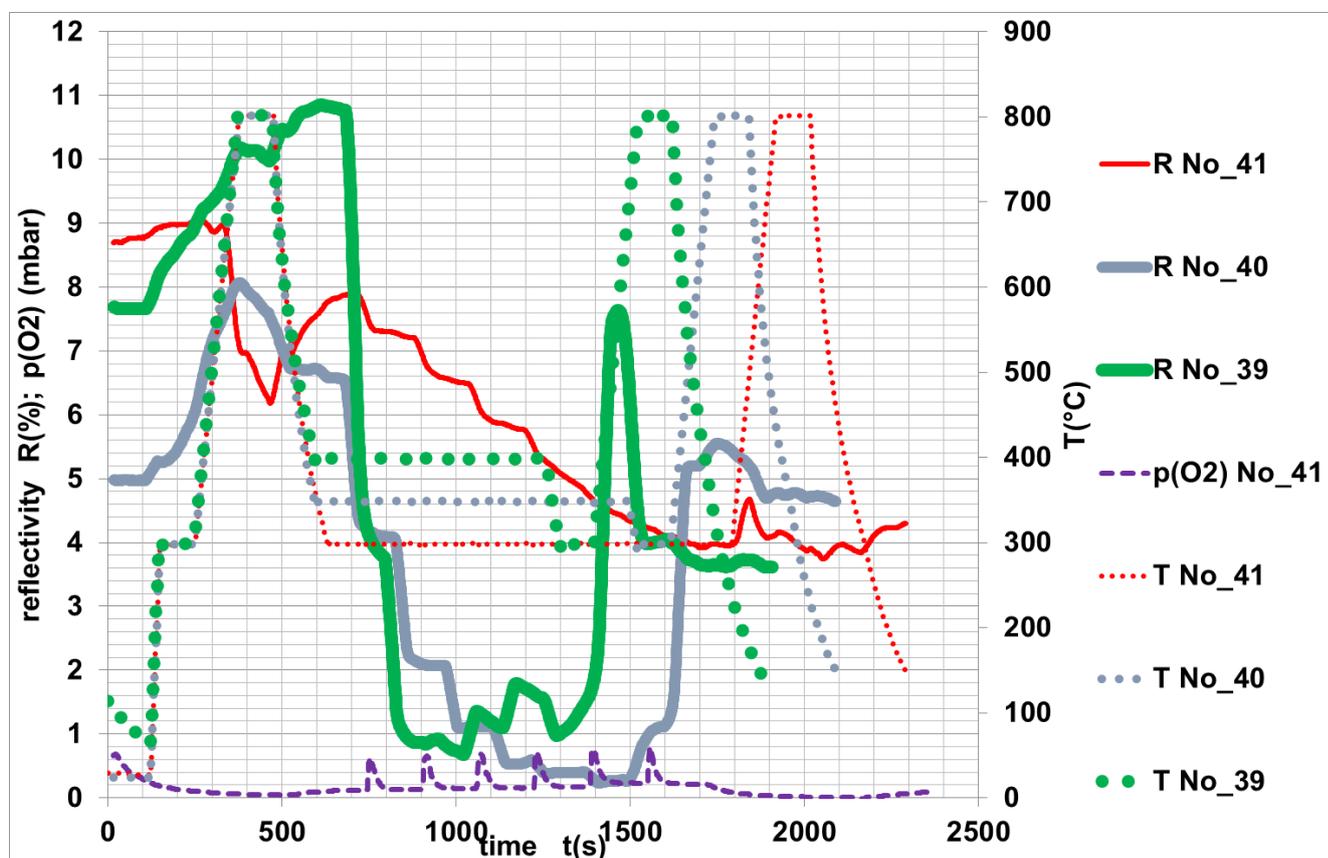


Figure 6. Reduction – oxidation – reduction cycles with the untreated TRIPAI samples at oxidation temperatures of 300 (No_41); 350 (No_40); and 400°C (No_39), resp. Oxygen was introduced 6 times for 10 s at 0.33 % for No_39 and 0.11 % for No_40 and No_41, resp. The dew point was below -40°C during the oxidation step.

4.2 Influence of the humidity

If water vapor is present during the oxidation, the reflectivity of the sample before the oxidation step can be reproduced after the reduction step. An example for this behavior can be seen in **Figure 7** for measurement No_67, where the oxidation took place at a dew point of 10°C and the sample temperature of 500°C. After the reduction step at 700°C, the reflectivity was slightly higher than before the oxidation. If the same sample undergoes the same procedure several times, the final reflectivity stays at a high level. It is remarkable, that after the initial oxidation at a high dew point that sample can be oxidized at a low dew point of -20°C, resulting in the same high reflectivity after the reduction step. This observation is in contrast to the oxidation of untreated samples as shown in Figure 5.

The steel grade ST1 (see Table 1), was oxidized at various temperatures in a dry atmosphere and could be completely reduced at 800°C. The oxidation – reduction process was repeatable, similarly to the findings with the DP500 sample.

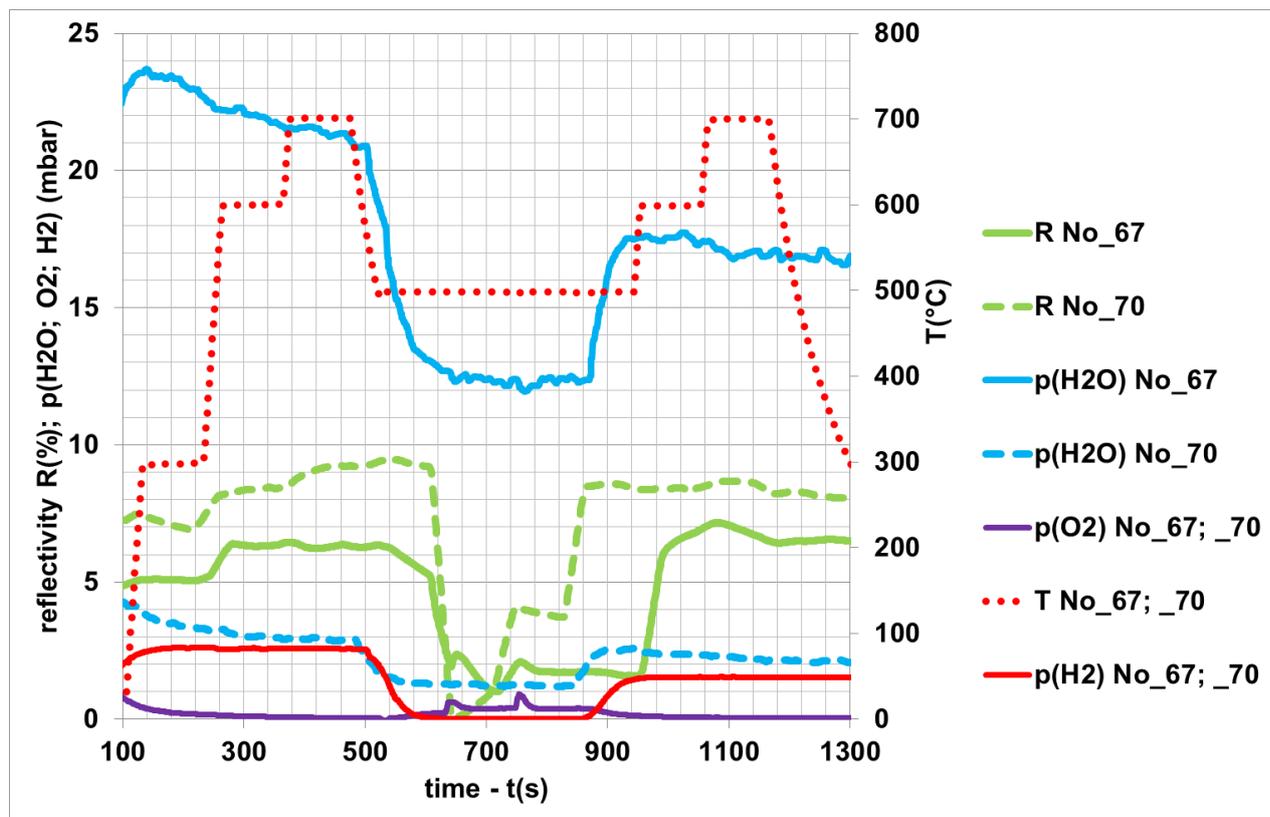


Figure 7. Reduction – oxidation – reduction cycles with the untreated TRIPAl sample at oxidation temperatures of 500 °C. Oxygen was introduced 2 times for 10 s at 0.33 %. The untreated sample was oxidized at the dew point of 10°C (No_67). The procedure was repeated two times and followed by the oxidation step at the dew point of -20°C (No_70).

5. Conclusion

The concept of the in-situ measurement of both, the composition of the gas phase around a sample and the reflectivity of the surface of the sample during the thermal treatment within a HDPS helps to reveal the underlying processes. In particular, the conditions for the formation of non-reducible oxides of the alloying elements at the surface can be efficiently followed up. The build-up and the decomposition of oxides at the surface can be quantified as a function of the temperature and the concentration of reactive gases. Repeated cycles of oxidation and reduction allow the identification of non-reducible oxides, but also, how to avoid its formation.

The expectation, that the presence of water vapor supports the formation of internal oxides could be confirmed by the reflectivity measurements reported in this paper (see Figure 7). [11,

^{12]} This will help finding the adequate temperature and gas composition within the hot dip galvanization furnace for the surface conditioning, particularly of HSS steels. Since the same sample can be treated repeatedly within the HDPS, the experiments with the TRIPAI samples in Figure 7 suggest, that the internal oxidation inhibits the further diffusion of alloying elements to the surface. This conclusion could be drawn without undergoing the sample an additional surface analysis such as GDOES. It is a further benefit, that the oxide coverage of the sample is measured without air exposition, which would happen when applying the GDOES.

The combination of the optical reflection measurement with mass spectrometry within a HDPS helps to find optimized parameters for the galvanization process and delivers the data for calibrating the optical reflectometers which are incorporated in a hot dip galvanization plant for the direct process control.

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