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Abstract. Different thermal treatments were performed for the anti-oxidation of steel surfaces, and the processes were investigated ex-situ and in-situ by surface sensitive reflection mode EXAFS experiments at the Cr and Fe K-edges. While the samples for the ex-situ studies were heat-treated in a conveyor belt furnace at temperatures between 600 and 900 °C in inert carrier gases (N_2 or Ar) using different additives such as hydrogen (H_2) and monosilane (SiH_4), the in-situ anti-oxidation treatments have been performed in a high vacuum environment (p < 10^{-6} mbar). While the ex-situ experiments suggest that SiH_4-additives are needed for the reduction of the steel to a metallic state, the in-vacuum treatments appear successful for temperatures above approx. 900 °C.

1. Introduction

The removal of oxide layers from steel surfaces is of large technological interest, for example, for fluxless brazing processes, where the presence of oxide layers prevent the wetting of the steel surface with the braze at elevated temperatures. Therefore it is required to remove these oxides while heating the base metals in a furnace together with the braze [1]. Appropriate temperatures are in the range of 900-1150 °C using Cu-Ni-alloy brazes for stainless steels, so that an additional oxidation of the steel is very likely during the required high-temperature treatments, even if the oxygen partial pressure is very low. Therefore, the investigation and the understanding of the oxide decomposition processes and their kinetics are of utmost interest in order to optimize fluxless brazing procedures. In this context, the use of additives such as hydrogen (H_2) or monosilane (SiH_4) in the furnace appears interesting in order to create reducing conditions [1-3]. Especially SiH_4 is an interesting additive, since it may quantitatively remove all oxygen and water residues in the gas phase according to the reactions $SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$ and $SiH_4 + 2H_2O \rightarrow SiO_2 + 4H_2$ [1].

The decomposition reaction was studied as a function of the conditions applied during the thermal treatments by a series of surface sensitive, reflection mode EXAFS experiments of different steel samples at the Cr and Fe K-edges in grazing incidence geometry. On one hand, the samples were heat-treated in a conveyor belt furnace, which is especially equipped for experiments with SiH_4 containing shielding gases at temperatures between 600 °C and 900 °C using well-defined temperature-time-regimes [3], and the samples were ex-situ investigated with reflection mode XAFS after their removal from the furnace. In addition, a second series of experiments were performed in-situ in order to elucidate the possibility of oxide removal from the steel surfaces under high-vacuum (p < 10^{-6} mbar).

2. Experimental details

The ex-situ reflection mode EXAFS studies were performed at the wiggler beamline 10 of the DELTA storage ring operating with 1.5 GeV electrons [4]. A Si(111) channel-cut monochromator was employed, and N_2- and Ar-filled ionization chambers were used to monitor the incident and reflected intensities, respectively. The samples were mounted on the multi-purpose diffractometer endstation to enable a precise alignment of the polished samples within the incident X-ray beam, and the measurements were performed in ambient air. A high vacuum furnace with a base pressure below approx. 4×10^{-7} mbar was used for the in-situ de-oxidation experiments at the MRH endstation of the ROBL beamline BM 20 at the ESRF. The obtained XAFS data from the steel samples were compared to those of reference compounds such as α- and γ-Fe_2O_3 (hematite and maghemite), magnetite (Fe_3O_4), FeO, goethite (α-FeOOH), $FeCr_2O_4$, Cr_2O_3, CrN as well as Fe and Cr metal foils.

The circular stainless steel samples with a nominal composition of 64% Fe, 19.5% Cr, 8.6% Ni, 2% Mn, 0.9% Cu, 0.4% Si, 0.3% Mo in wt.-% and minor traces (< 0.03%) of Ti, V, P, C and S were polished using diamond paste to a final grading of 3 μm to ensure reproducible starting conditions for the thermal treatments. A conveyor belt furnace [3] was used for the sample preparation in different high purity gases in the temperature range from 600 to 900 °C. When monosilane (SiH_4) was used for the processing, the resulting partial pressure of oxygen was adjusted to values $< 10^{-19}$ mbar. A typical thermal treatment took about 100 minutes, including the heating ramp, a hold time of 5 minutes at the desired maximum temperature, and the cooling phase. These samples were stored in dried N_2.

For the in-situ experiments at the ESRF, the samples were heated after the evacuation of the furnace, and the spectra were measured in-situ at temperatures between 600 and 900 °C. In addition to the investigation of steel samples with a native, room temperature oxide, some specimen were oxidized in air at a temperature of 300 °C to prepare a thicker oxide layer on the steel.

3. Results and discussion

3.1. Ex-situ EXAFS experiments

A comparison of ex-situ reflection mode Fe K-edge EXAFS data obtained from a sample reduced in an atmosphere containing silane at 900 °C with a sample treated in pure N_2 is shown in figure 1. As can already be deduced from these raw data, the sample treated without SiH_4 suffers from substantial oxidation as indicated by the intense white line feature directly above the Fe edge, while the heat treatment in silane-containing media efficiently avoids surface oxidations, as indicated by the presence of strong metallic features in the related spectrum.
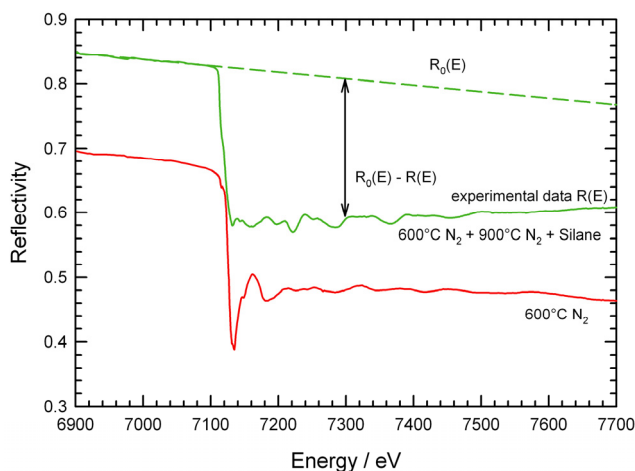

Figure 1. Ex-situ reflection mode EXAFS spectra (incidence angle $\phi = 0.1°$) of two steel samples with different heat treatments at the Fe K-edge: Annealing in pure N_2 at 600 °C for 25 min. and an additional heating in a mixture of N_2 and addition of 20 ppm SiH_4 at 900 °C for 5 min. (——), and for comparison, solely annealing in pure N_2 at 600 °C for 5 min. (——). The latter spectrum is vertically shifted by -0.1 for a better comparison of the measured reflection mode fine structures of the two samples.

For a more detailed interpretation of the measured data, a linear pre-edge background $R_0(E)$ was fitted to the experimental data as shown in figure 1, interpolated to the post edge region and the normalized difference $R_0(E) - R(E)$ was calculated in order to obtain a measure of the absorption. For grazing

angles smaller than the critical angle of total reflection, the absorption coefficient is approximately proportional to $R_0(E)$ - $R(E)$ as shown in refs. [5, 6], and thus, such an approach is sufficient to allow for a qualitative XANES analysis using the extracted data, i.e. a comparison to reference compounds.

The XANES spectra determined this way are compared to spectra of suited model compounds in figure 2. As can be seen in figure 2(a), the heat treatments in pure noble gas or nitrogen atmospheres generally lead to strong iron oxide contributions, even if H_2 is added, as indicated by the white line features, the edge position and the post-edge absorption features. Obviously, traces of oxygen in the process gas lead to oxidation at elevated temperatures. While the native, untreated steel sample shows features near the edge that can be related to metallic iron, the spectra of the heat treated samples are governed by strong oxide features. Since the penetration depth of the X-rays is about 3 nm for the chosen incidence angle of $\phi = 0.1°$, it can be concluded that the thickness of the iron oxide layer is at least of the order of about 5 nm in the absence of SiH_4 during the heat treatments. By contrast, for the sample treated in silane containing atmosphere, the measured spectrum at the Fe K-edge closely resembles that of metallic, body centered iron, and no distinct iron-oxide features were found. Compared to the XANES of the Fe metal reference, the amplitude of the EXAFS oscillations are slightly damped due to the grazing incidence geometry and the simple data analysis applied. It should also be noted, that no evidence e.g. for Fe-Si-compounds such as $FeSi_2$ or mixed Fe-Cr-oxides were found in the present experiments. As can be deduced from the spectra obtained at the Cr K-edge (figure 2(b)), there are strong contributions from chromium oxide in all of the treated steel samples. However, only in the Cr K-edge spectrum of the steel sample treated in an atmosphere with SiH_4 additions, indications for metallic Cr can be found (see the arrow in figure 2(b)).
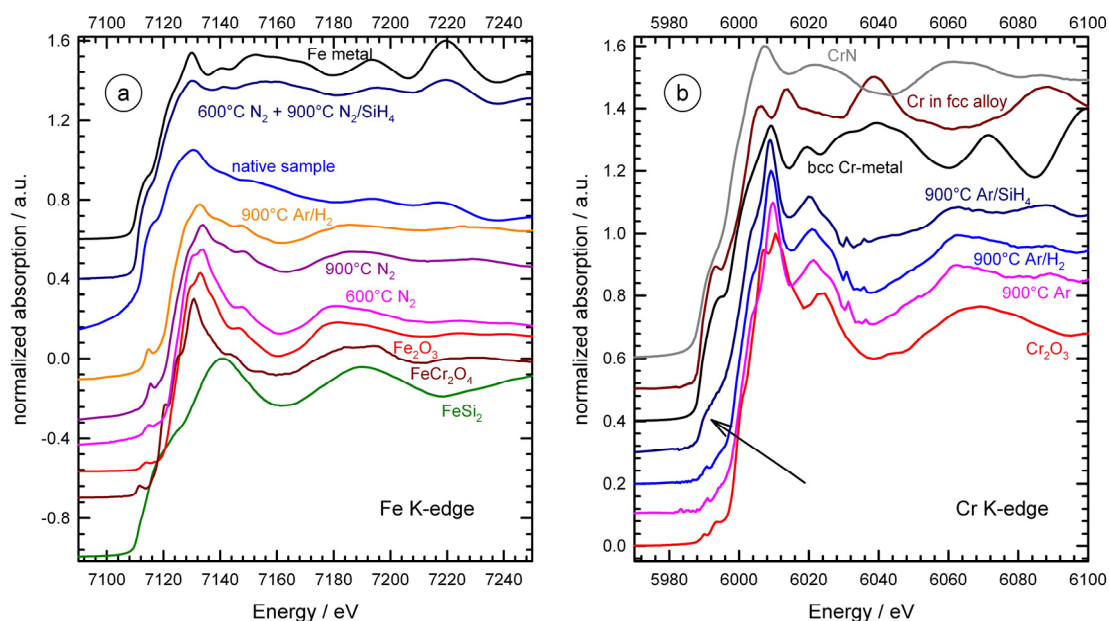

Figure 2. Comparison of the XANES spectra determined from ex-situ reflection mode EXAFS spectra (incidence angle $\phi = 0.1°$) of several steel samples with different heat treatments as indicated, with spectra of suited reference compounds: (a) Fe K-edge, (b) Cr K-edge. The arrow in (b) indicates the position of the Cr K-edge of the metal in the sample treated in silane containing atmosphere.

From the present experiments it remains however unclear, at which stage of the heat treatment the Cr-oxides are formed: Due to the ex-situ processing, it cannot be excluded that the oxides have been entirely removed in the hot zone of the conveyor belt furnace. The underlying thermodynamics indicate that even Cr_2O_3 should decompose for the applied temperatures and gas compositions [1]. However, as also suggested by the heat treatments conducted at lower temperatures around 600 °C,

Cr_2O_3 and also the less stable iron oxides were still present on the surface of the steel after the heat treatments. This suggests that the oxides found after the removal of the samples from the furnace were formed during the cooling phase from the hot central temperature back to room temperature.

3.2. In-situ EXAFS studies

According to the ex-situ measurements presented in the previous section, a de-oxidation was performed under vacuum conditions in order to study the thermal stability of iron and chromium oxides at elevated temperatures. An example of a grazing incidence EXAFS measurement at 900 °C is presented in figure 3. As can be seen, structures of metallic iron can at least be partly recovered in comparison to the air-oxidized surface. However, it is important to keep in mind the iron phase diagram with substantial contributions of cubic face centered Fe (austenite) for T > 700 °C, so that a more detailed temperature dependent investigation of the base steel is required here. At the Cr K-edge, no substantial changes of the XANES could be found during the first de-oxidation experiments in vacuum, suggesting that the oxygen partial pressure might still be to large for a Cr-oxide removal.
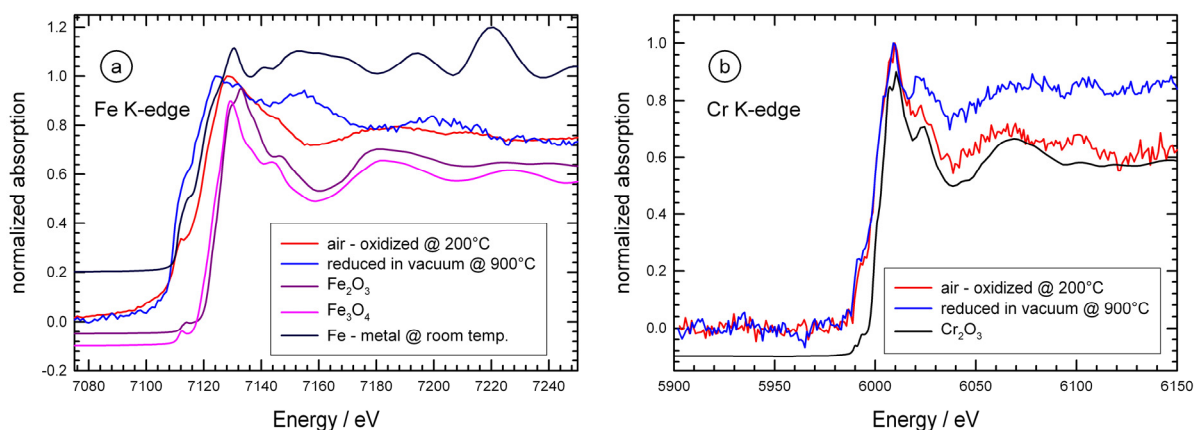

Figure 3. Comparison of the XANES from a steel sample measured in-situ in reflection at elevated temperature in vacuum with the XAFS of reference compounds: (a) Fe K-edge and (b) Cr K-edge.

4. Conclusions

Ex-situ and in-situ XAFS experiments have been conducted to study the thermal de-oxidation of steel surfaces. The results have shown that the iron oxides can be completely removed by a treatment in SiH_4-containing gas atmospheres as well as in vacuum for T ≈ 900 °C. By contrast, contributions of Cr-oxides are always detectable after the thermal treatments. The decomposition of those oxides as well as in-situ experiments during SiH_4-treatments will be subject of future experiments.

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