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In-situ analysis of the thermal evolution of electrodeposited Fe-C coatings

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Abstract

Fe-C coatings with a high amount of carbon were electrodeposited from an iron-sulfate electrolyte. Citric acid as an additive in the electrolyte, not only served as carbon source during electrodeposition, but also caused the reproducible co-deposition of oxygen and hydrogen. The various co-deposited elements (C, O, H) result in a complex nature of the as-deposited coatings and allow for deliberate alterations of the coating properties by post-deposition annealing. The thermal evolution of electrodeposited Fe-C coatings was investigated *in-situ* during isochronal annealing. *In-situ* synchrotron diffraction analysis revealed temperature dependent phase transformations, which was supplemented with *in-situ* thermal analysis for investigating the evolution of co-deposited elements and associated mass changes during annealing. Based on the determined activation energies of identified thermal events, the underlying mechanisms are discussed. The results clearly indicate the role of co-deposited elements in the coatings and suggest that they partly exist in form of organic compounds, which decompose during annealing. In addition to revealing the thermal stability of the coatings and quantifying the coating's thermal evolution, the complementary methods of *in-situ* analysis considerably improved the understanding of the as-deposited Fe-C coatings – both are essential prerequisites for the successful application of the Fe-C coatings.

Keywords

electrodeposition, annealing, phase transformations, thermal analysis, synchrotron diffraction.

1. Introduction

The electrodeposition of iron and carbon (Fe-C) coatings implies a number of advantages for improving the hardness and wear resistance of surfaces. The deposition process is commercially feasible in industry. It bases on an inexpensive and environmentally friendly electrolyte and it allows the straightforward deposition of Fe-C coatings with thicknesses up to several hundreds of micrometers. Moreover, excellent mechanical properties are consistently reported for as-deposited Fe-C coatings [1–7]. In particular the ability of producing very hard coatings with microhardness values as high as for hardened steels makes the electrodeposited Fe-C coatings very attractive for various engineering applications where high hardness and good wear resistance are important. This entails both the dedicated electrodeposition of Fe-C coatings as a final process in the fabrication of components and the repair of worn or damaged surfaces by site-specific repeated deposition. In addition to the application of Fe-C coatings in their as-deposited state, a further potential for surface engineering is provided by the chemical nature of the coatings. The co-deposited carbon and other elements, like oxygen and hydrogen originating from the applied electrolyte, play a decisive role during post-deposition heat treatments, whereby the as-deposited microstructure can be deliberately altered [4,5,7–9]. Thermal treatment of the electrodeposited Fe-C coatings, which already in their as-deposited state are fairly hard with about 800 HV [6,7] is associated with a further hardness increase of up to 1300 HV [7]. Hence, from an application point of view, the mechanical properties are very convincing and pave the way for a number of applications of Fe-C coatings. From a scientific point of view, thorough understanding of the as-deposited microstructure has hitherto not been obtained and despite good reproducibility of the electrodeposition process with consistent results in literature, the nature of as-deposited Fe-C coatings and the role of the co-deposited carbon are subject of different interpretations.

Previous studies of Fe-C coatings refer to an iron-sulfate electrolyte, which was optimized to resist the oxidation of Fe^{2+} to Fe^{3+} by the addition of a carboxylic acid that also acts as a buffer, carbon source and complexing agent [5,10]. The composition and functional groups of the carboxylic acid have been found to influence the amount of co-deposited carbon, the morphology and the associated properties of the Fe-C coatings [2,3,5,11–14]. In addition, the applied electrodeposition conditions, like the cathode current density, the pH value and the temperature

of the electrolyte [2,3,5,15], influence the current efficiency and, hence, the chemical composition, microstructure and properties of the as-deposited coatings. Typically, the electrodeposited Fe-C coatings contain high concentrations of carbon up to about 1 wt%. Such high amount of carbon considerably exceeds the solubility of carbon in iron at room temperature, which, typically for Fe-C alloys, suggests either the formation of iron carbides or the presence of carbon in supersaturated solid solution in the iron lattice. Previous investigations of electrodeposited Fe-C coatings by means of diffraction analysis consistently revealed the presence of one major phase in as-deposited coatings, which is interpreted either as ferrite (not containing carbon in thermodynamic equilibrium) [5–7,13] or as martensite (with carbon in supersaturated solid solution) [2,3,11,12,15]. The similarity of both lattices and the strong crystallographic texture of as-deposited Fe-C coatings complicate the phase analysis. The presence of a supersaturated solid solution would provide an immediate explanation for the location of carbon in the coatings, i.e. carbon would be interstitially dissolved. However, the very high measured carbon concentration would need to result in enormous changes of the iron lattice and this should cause either very broad and shifted diffraction peaks or asymmetric and even split diffraction peaks (apparently, both observations are reported). On the other hand, in case of ferrite without any carbon in its bcc lattice, the nature of the measured high amount of carbon would require the presence of a second phase in as-deposited Fe-C coatings. Indeed, diffraction analysis repeatedly revealed a second phase, but thorough phase identification is considerably hindered by the limited number of peaks; in addition to α -Fe, only one further peak is clearly evident [4–7] with only low diffracted intensities. As a consequence, phase analysis has not yet been unambiguous. As an attempt to clarify the location of the measured carbon, this second phase in the as-deposited Fe-C coatings has previously been explained as Fe₂C transition carbides [4,8,9], but alternative explanations including other co-deposited elements are possible [7]. The ambiguity of phase analysis based on the single additional peak, which consistently corresponds to a lattice spacing of $d = 0.237$ nm, is reflected in its present terminology as “nameless” peak referring to the not yet identified, “nameless”, phase in the as-deposited Fe-C coatings. A recent *ex-situ* isothermal annealing study revealed that this phase is present up to a temperature of about 300 °C [4,7,8]. Tracing the evolution of this phase by an *in-situ* annealing study and investigating the occurrence of further phase transformations is the purpose of the present work.

The thermal stability of Fe-C coatings with a high carbon content of 0.88 ± 0.02 wt % is followed *in-situ* during isochronal annealing from room temperature to above the austenitization temperature. The occurring phase transformations are revealed by *in-situ* diffraction analysis and discussed in relation to the evolution of co-deposited elements and associated mass changes obtained from *in-situ* thermogravimetric analysis in combination with mass spectroscopy.

2. Method

2.1 Electrodeposition of Fe-C coatings

The electrolyte was prepared from chemicals of analytical grade with a concentration of 0.143 mol/dm^3 iron (II) sulfate heptahydrate, $6.2 \times 10^{-3} \text{ mol/dm}^3$ citric acid monohydrate and deionized water. A 10 Liter electrolyte was used to minimize the change in chemical composition of the electrolyte during deposition. The electrolyte temperature was kept at 50°C and mechanical stirring was applied during deposition. The pH-value of the electrolyte was controlled during deposition and maintained between 2.5 and 2.8 using a H_2SO_4 -diluted solution. An interstitial-free steel plate was used as anode. The applied deposition parameters represent the previously optimized conditions and they result in coatings with a carbon content of 0.88 ± 0.02 wt % [6]. The cathode consisted of a $10 \times 9 \text{ cm}$ low carbon steel plate covered with a conductive lead tape, such that deposition occurred both on lead and on the steel substrate simultaneously. The backside of the cathode was covered with an isolating electrolyte-resistant tape to ensure that only the side towards the anode was deposited. Prior to electrodeposition, the cathode was pre-treated by 2 min cathodic degreasing at 5 V followed by 2 min activation in commercial dry acid 629 SV from EngTech Scandinavia. Electrodeposition was carried out at a constant current density of 3.0 A/dm^2 applied for 15 hours resulting in $360 \text{ }\mu\text{m}$ thick Fe-C coatings. The Fe-C coatings were immediately after deposition rinsed in water, then rinsed in ethanol and carefully dried to avoid oxidation. The Fe-C coatings were protected from any contact with oxidizing environments during storage. The abovementioned design of the cathode ensured that multiple identical samples were obtained from the same deposition event, in which the substrate (lead or low carbon steel) is unimportant for the finally $360 \text{ }\mu\text{m}$ thick Fe-C coatings, but allows to obtain dedicated samples for annealing.

Due to low adhesion of the Fe-C coatings on the lead tape, the coating could easily be detached from the tape, thus providing free-standing coatings. They were used for *in-situ* thermal analysis, where it was essential to quantify the chemical species that evolved in the coating material. The Fe-C coatings on low carbon steel allowed better sample handling for *in-situ* diffraction analysis during annealing. The various sample pieces used for the present study were collected at least 1 cm away from the edge of the electrodeposited plate to avoid any potential edge effect from electrodeposition.

2.2 In-situ annealing experiments

2.2.1 Synchrotron diffraction

Energy-dispersive diffraction (EDD) was performed *in-situ* at the synchrotron facility BESSY II at the EDDI beamline. In EDD, a white X-ray beam with a continuous photon energy spectrum is used at a fixed diffraction angle 2θ , and diffraction occurs for crystallographic lattice planes with spacing d_{hkl} at a photon energy E_{hkl} according to [16]

$$E_{hkl} = \frac{h c}{2 \sin \theta} \cdot \frac{1}{d_{hkl}}$$

where h is Planck's constant and c is the speed of light.

Compared to angle dispersive diffraction, the EDD mode has significant advantages, in particular for time- and/or temperature-resolved *in-situ* measurements. Complete diffraction patterns with a multitude of diffraction lines, E_{hkl} , are recorded simultaneously under fixed geometrical conditions, i.e. without scanning the 2θ angle. In addition, the very intense synchrotron radiation allows for short recording times for a complete diffraction pattern with good counting statistic. Owing to the different photon energies, the structural information contained in each diffraction line at the energy E_{hkl} has to be assigned to different average information depths [16]. For the applied symmetric diffraction geometry and a diffraction angle of $2\theta = 8^\circ$, for example, the 211 reflection of iron corresponds to an information depth of about 67 μm .

In-situ annealing experiments during EDD analysis were performed in an Anton Paar DHS 1100 Domed Hot Stage under continuous flow of inert argon gas (99.999 mol % purity) at a constant

pressure of 1.4 bar. As-deposited Fe-C coatings on the low carbon steel substrate, were placed on the heating element (alumina plate) onto which they were mounted by mild clamping. The temperature was measured with a Pt-Pt10Rh thermocouple fixed to the stage. Isochronal annealing was performed from 30 °C to 800 °C using a heating rate of 2 K/min and an acquisition time of 30 seconds per EDD spectrum, resulting in a high resolution of one diffraction pattern per Kelvin. For qualitative phase analysis, the diffraction lines were fitted with pseudo-Voigt profile functions. A gold reference standard was used for calibration of the energy offset. The peak position was corrected for thermal expansion using the linear thermal expansion coefficient for ferrite of $\alpha = 15.1 \text{ (} 10^{-6} \text{ K}^{-1}\text{)}$, which was obtained for the present samples from their EDD spectra measured during cooling from 800 °C to room temperature after isochronal annealing.

2.2.2 Thermal analysis

Simultaneous thermogravimetry (TGA) and differential thermal analysis (DTA) were performed in a Netzsch STA 449F3 coupled with a Netzsch QMS 403 Aëolos quadrupole mass spectrometer (MS). The setup enables the detection and identification of evolved gases in time correlation with enthalpy and mass changes. For each measurement, a substrate-free coating weighing about 250 mg was placed in an alumina crucible. The sample chamber was pumped to vacuum and flushed with argon three times prior to each measurement. Heating was carried out in an inert atmosphere created by flowing argon gas (99.999 mol % purity) through the chamber with a rate of 30 mL/min.

A sample was subjected to three cycles of isochronal heating from 40 °C to 1000 °C using a heating rate of 2 K/min. Before the thermogravimetric analysis and in between the sequential heating cycles, the sample was hold for 2 hours at 40 °C to ensure a stable and consistent environment. The cooling rate was set to 40 K/min. The first and second isochronal annealing were adjusted for instrumental background by using the second and third isochronal annealing, respectively.

From isochronal annealing experiments applying different heating rates, the activation energies for thermal events measured by DTA were evaluated by means of a Kissinger analysis applying

different heating rates [17]. For each thermal event, the activation energy was determined from the slope of the straight line obtained by plotting $\ln(T_F^2/\Phi)$ versus $1/T_F$, where Φ corresponds to the applied constant heating rates of 2 K/min, 10 K/min, 20 K/min and 40 K/min, respectively. T_F corresponds to a fixed stage of transformation f' measured for the various heating rates. The values for T_F refer to the maxima of exothermic peaks, which were determined by fitting a Gaussian function to the background subtracted peaks.

3. Results

3.1 Diffraction analysis

In-situ diffraction analysis during isochronal annealing of an as-deposited Fe-C coating using a heating rate of 2 K/min revealed the as-deposited phases, along with the temperature induced phase transformations from room temperature to above the austenitization temperature. Figure 1 shows the acquired EDD spectra with high temperature resolution (one diffraction spectrum per Kelvin) as a contour plot.

The as-deposited coating mainly consists of α -Fe (JCPDS 6-696). According to the strong $\langle 311 \rangle$ fiber texture of the as-deposited Fe-C coating [6], only the 110 and 211 reflections of α -iron are detected, while the 200 reflection is absent. The strain-free lattice spacings d_0 for the 110 and 211 reflections of α -Fe were determined for the as-deposited coating by tilting the sample around the strain-free direction ($\psi_0 = 41.16^\circ$), providing $d_{0_{110}} = 0.20273$ nm and $d_{0_{211}} = 0.11706$ nm, respectively. Both d-spacings match the corresponding values for carbon-free α -Fe (JCPDS 6-696 with $d_{110} = 0.20269$ nm and $d_{211} = 0.11702$ nm), which indicates that carbon-free bcc ferrite is present in the as-deposited coating. The measured peaks are broadened corresponding to the nanocrystalline nature of the coating, which previously has been quantified with an average crystallite size of 15-40 nm [7]. Apart from ferrite, only one additional peak is detected in the as-deposited coating, namely at 37.5 keV (cf. Figure 1). This peak corresponds to a d-spacing of 0.237 nm. It has been previously reported from conventional laboratory X-ray diffraction phase analysis [4–6,8], but, as mentioned above, no clear phase identification is

possible based on that single peak only and, therefore, in the following, it is referred to as the “nameless phase”.

During annealing, a sudden drop of the intensity of all peaks was observed at around 100 °C. After careful consideration and exclusion of any experimental reason for this intensity drop, the only explanation is a sudden change of the sample height (related to the occurring evolution of the coating with temperature, as discussed later in this manuscript) and accordingly, the sample was repositioned by adjusting the stage height. This is reflected in slight fluctuations of the diffracted intensities in Figure 1 until they stabilized at around 144°C. At that temperature, still only α -Fe and the “nameless phase” are present.

With continued heating, the formation of magnetite Fe_3O_4 (JCPDS 76-0957) is detected at about 259 °C and cementite Fe_3C (JCPDS 77-0255) forms at about 310 °C (cf. Figure 1). The formation of both phases confirms the presence of oxygen and carbon in the as-deposited coating, which are known to be co-deposited during electrochemical deposition [6], although the nature and location of these light elements in the as-deposited coatings could not be clarified yet. The formation of magnetite and cementite, as revealed during *in-situ* annealing in the present study, is consistent with previous *ex-situ* observations after isothermal furnace annealing of Fe-C coatings [7].

With increasing temperature, the precipitation of magnetite and cementite proceeds as indicated by continuously increasing intensities of their corresponding diffraction peaks (cf. Figure 1). A remarkable change is observed at a temperature of 328 °C, which seems to be related to the transformation of the “nameless” phase. The intensity of its corresponding peak at 37.5 keV drops suddenly and the peak finally disappears, while at the same time a new peak develops near the original one. The partly overlapping intensities of the “nameless” peak and the new one cause some asymmetry of the measured peak profile. This hinders accurate peak fitting at this temperature and, therefore, the intensity decrease of the “nameless” peak and the corresponding transformation temperature of the “nameless phase” cannot be quantified precisely. In accordance with a further evolution of cementite Fe_3C , the newly arising peak originates from Fe_3C . At about the same temperature of the disappearance of the single peak related to the “nameless phase”, another observation from the diffraction results is of interest. Again, similarly

as observed at about 100 °C, as mentioned above, changes of the sample height and associated intensity changes of all peaks were recorded and required repositioning of the sample by readjusting the stage height (also this observation is related to the evolution of the coating and will be discussed together with results from the thermal analysis later in this manuscript).

At a temperature of about 571 °C, the transformation of Fe₃O₄ to wüstite FeO (JCPDS 77-2355) occurs (cf. Figure 1). Finally, at about 727 °C, the phase transformation from α -Fe ferrite to γ -Fe austenite (JCPDS 31-0619) occurred and, simultaneously, the peaks corresponding to Fe₃C drop in intensity, because carbides dissolve and carbon goes into solid solution in austenite. Peaks corresponding to FeO are still present above the austenitization temperature.

Figure 1: Synchrotron energy-dispersive diffraction spectra of in-situ annealing of an as-deposited Fe-C coating using a heating rate of 2 K/min from 30 to 800 °C.

3.2 Thermal analysis

3.2.1 Thermogravimetry, differential thermal analysis and mass spectrometry

The *in-situ* isochronal annealing by simultaneous DTA and TGA coupled with MS, using a heating rate of 2 K/min (i.e. the same as applied during *in-situ* diffraction analysis), revealed further information on the thermal stability of the as-deposited Fe-C coating. The results in Figure 2a and 2b correspond to the first annealing to 1000 °C and the subsequent annealing of the same sample to 1000 °C, respectively. The signals recorded by MS have been correlated to the individual elements using their ion mass. The measured species involved H_2^+ , O_2^+ and CO_2^+ having a mass/charge ratio of 2 amu, 32 amu and 44 amu, respectively. Although the measurement was carried out in an inert Ar atmosphere, a low concentration of impurities in the gas such as O_2 and H_2 is seen as background in the beginning of the experiment. An increase in the DTA signal in Figure 2 relates to an exothermic reaction and a decrease indicates an endothermic reaction.

The first annealing cycle to 1000 °C (cf. Figure 2a) shows a mass loss just prior to an exothermic reaction at about 114 °C. The relatively low temperature and the increase in intensities of H_2 suggest that the reaction is related to dehydrogenation of absorbed hydrogen trapped in the as-deposited coating, which is a typical phenomenon during electrodeposition. This hydrogen originates from electrolysis at the cathode surface and results in a current efficiency of the deposition process below 100% (in fact, a current efficiency of only 60 % applies for the present deposition [7]). The simultaneous decrease in O_2 is likely related to its reaction with the desorbed H_2 from the sample and the corresponding formation of H_2O before reaching the MS detector. Energy is removed from the system in the temperature range following the exothermic reaction at 114 °C, which is interpreted as hydrogen desorption.

At around 250 °C, an increase in CO_2 is detected, but at this temperature neither the DTA signal nor the mass loss gradient change.

At 310 °C, a relatively small exothermic peak is measured and directly followed by a more pronounced exothermic peak of much higher intensity with a maximum at 360 °C. These exothermic reactions are accompanied by a small increase in O_2 and CO_2 at around 340 °C along

with a change in the mass loss gradient. Simultaneously, the intensity of H_2 increases significantly and reveals a maximum at 375 °C. The associated desorption of hydrogen continues until a temperature of around 436 °C is reached. Energy is removed from the system in the temperature range following the exothermic reaction at 360 °C, which is interpreted as hydrogen desorption.

A relatively small exothermic peak is measured at 505 °C, without a notable change in the TGA or MS signals. An endothermic peak at 570 °C indicates the phase transformation of Fe_3O_4 to FeO , in accordance with diffraction analysis (cf. Figure 1). At the same temperature, a change in intensity for CO_2 is measured, along with an increased mass loss, which is related to decarburization. At 705 °C a small peak in the CO_2 intensity is measured, which is followed by a pronounced endothermic peak at 725 °C corresponding to the austenitization temperature, thus, the transformation of α -Fe ferrite to γ -Fe austenite.

The second heating cycle to 1000 °C (cf. Figure 2b) reveals an exothermic peak at 295 °C and endothermic peaks at 585 °C and 725 °C corresponding to the phase transformation of FeO (which is still present after the first heating cycle) to Fe_3O_4 , the phase transformation of Fe_3O_4 to FeO and the formation of austenite, respectively. There is no apparent mass change, before decarburization is measured by an increased intensity for CO_2 at around 590 °C.

a)

b)

Figure 2: Simultaneous thermogravimetry, differential thermal analysis and mass spectrometry to detect and identify thermal events, in correlation to the evaporated gases. The black left axis corresponds to the DTA signal and the red left axis corresponds to the measured mass loss. The right axis corresponds to the various desorbed gasses measured by MS. Figure 2a refers to the first annealing cycle and Figure 2b reflects the second annealing cycle of the same coating. The applied heating rate corresponds to 2 K/min.

3.2.2 Determination of activation energies

Applying different heating rates for isochronal annealing of as-deposited Fe-C coatings (similar to the example shown for 2 K/min in Figure 2a), three separate thermal events are recorded as exothermic peaks by DTA in the temperature range up to 500 °C, which is shown in Figure 3a. The heating rate affects both the temperatures of the occurring thermal events and their corresponding intensities in the DTA curves: with increasing heating rate, the peak temperature and the recorded intensities increase. The corresponding Kissinger plot in Figure 3b provides the activation energies of the three thermal events. The relatively small exothermic peak measured at 310 °C for 2 K/min (and correspondingly higher temperatures for increased heating rates, cf. Figure 3a) is not included in the Kissinger analysis as it overlaps with the exothermic peak of much higher intensity, which hinders an accurate peak fit. The thermal events relate to the desorbed gasses measured by MS, as explained below.

The first thermal event (at around 114 °C for $\Phi = 2$ K/min) corresponds to dehydrogenation, where the co-deposited hydrogen originating from electrolysis at the cathode surface (see above) is released from the sample. The calculated activation energy of this first thermal event amounts to 40 kJ/mol.

The second thermal event is indicated by an exothermic peak (at around 284 °C for $\Phi = 10$ K/min) and corresponds to an activation energy of 98 kJ/mol. For the low heating rate of 2 K/min the second thermal event cannot be verified experimentally due to too low peak intensity (cf. Figure 3a) and therefore it cannot be related to the desorbed elements according to Figure 2a.

The third thermal event (at 360 °C for $\Phi = 2$ K/min) was clearly detected by its exothermic peak for all heating rates and corresponds to an activation energy of 151 kJ/mol. This event is characterized as a thermal decomposition, which relates to a mass loss, an enthalpy change and the release of H₂ (cf. Figure 2a). Furthermore, the increased intensities of O₂ and CO₂ measured at 340 °C (cf. Figure 2a) suggest that also carbon and oxygen are released during this third thermal event.

Figure 3: Isochronal Kissinger analysis (a) differential thermal analysis during isochronal annealing of an as-deposited sample applying heating rates of 2, 10, 20 and 40 K/min (b) Kissinger plot for different thermal events measured for isochronal annealing with heating rates of 2, 10, 20 and 40 K/min.

4. Discussion

For the present samples, carbon-free ferrite is clearly detected as the major phase in as-deposited coatings, but XRD also indicates an additional crystalline phase, which cannot be identified from the measured single peak and therefore, so far, is called the “nameless phase”. As an approach to discover the nature of this phase, synchrotron diffraction has been carried out also in transmission and under various sample tilts and rotations (not shown here), but no additional reflections could be revealed. The applied *in-situ* analysis during isochronal annealing by means of energy-dispersive synchrotron diffraction allows tracing the occurring phase transformations with an excellent temperature resolution. Although such *in-situ* diffraction analysis provides the thermal stability of the electrodeposited Fe-C coatings and supports an interpretation of the as-deposited nature of the coatings, in fact, it only can detect crystalline phases. The combination of *in-situ* diffraction analysis with *in-situ* thermal analysis for the same as-deposited Fe-C coatings, as in the present work, supports the interpretation by cross-linking with the temperature-dependent evolution of co-deposited elements (carbon, oxygen, hydrogen) during annealing. The complementary results obtained from both methods of *in-situ* analysis provide the following interpretation of the thermal stability of Fe-C coatings and, based on the coating’s thermal evolution, conclusions regarding the as-deposited Fe-C coatings can be drawn, as discussed in the following. The specific temperatures stated in the discussion refer to the data obtained for *in-situ* isochronal annealing experiments using a heating rate of 2 K/min unless otherwise noted.

4.1 Low temperature range – below 200 °C

Already at a relatively low temperature of about 114 °C, co-deposited hydrogen desorbs from the coating (cf. Figure 2a). This confirms that hydrogen indeed is present in as-deposited coatings, which previously has been suggested from chemical analysis (although hydrogen could not be quantified [6,7]) and is reflected in a low current efficiency of only 60.5 % for the applied deposition process. The determined activation energy of 40 kJ/mol for this first thermal event indicates that this hydrogen, which originates from electrolysis at the cathode during deposition, has been trapped in either microvoids or grain boundaries, for which trap activation energies for hydrogen evolution of 35.15 kJ/mol or 17.2 kJ/mol [18], respectively, are reported for pure iron. The nanocrystalline microstructure of the as-deposited Fe-C coating [6,7] provides a high

number of grain boundaries for trapping and the reported temperature of hydrogen evolution from grain boundaries (105 °C for a heating rate of 3.06 K/min [18]) agrees well with the present observation of dehydrogenation.

Diffraction analysis did not immediately indicate this first thermal event of dehydrogenation, because no phase transformations are detected and still only ferrite and the nameless phase are present (cf. Figure 1) at these low temperatures. However, the observation of a sudden change in the sample height, reflected by sudden intensity changes and the need of readjusting the sample as described above, clearly relates to the release of hydrogen. Despite the reproducible and consistent observations of the simultaneous occurrence of the dehydrogenation and the sample height changes at all applied heating rates, thorough understanding of that phenomenon is not yet obtained.

In earlier studies of Fe-C coatings [4,9], the exothermic reaction, which clearly relates to dehydrogenation as described above, was also observed, but it was interpreted as the first stage of tempering martensite, where carbon atoms are redistributed resulting in carbon segregation and clustering in an apparent martensite matrix. Although the temperature is similar to the first step of tempering martensite, the release of hydrogen at that temperature as observed in the present work and the missing indication of martensite in the as-deposited coating exclude that the exothermic peak is caused by a redistribution or clustering of carbon. Furthermore, the activation energy for carbon clustering is reported to be significantly higher with about 80 kJ/mol [19].

4.2 Medium temperature range – between 200 °C and 380 °C

After co-deposited hydrogen from electrolysis during deposition is released (first thermal event), subsequent chemical changes imply the desorption of CO₂ at a temperature of about 250 °C (cf. Figure 2a), which indicates the second thermal event. At the same temperature of 250 °C, a previous study on the same as-deposited Fe-C coatings, which however were investigated by *in-situ* isochronal annealing after preceding *ex-situ* isothermal furnace annealing [7], revealed a characteristic desorption of hydrogen. This desorption of hydrogen at 250 °C is clearly not related to the hydrogen from electrolysis, which was already released during the *ex-situ* isothermal annealing. The present *in-situ* analysis could not detect the characteristic desorption

of hydrogen at 250 °C as part of the second thermal event, due to the ongoing desorption from the first thermal event and a corresponding broad peak of hydrogen evolution in a wide temperature range (cf. Figure 2a). Although the temperature of the second thermal event could not be experimentally determined for a heating rate of 2 K/min (cf. Figure 3a), linear regression from the three measured values at higher heating rates (cf. Figure 3b) allowed to calculate the corresponding temperature to amount 250 °C and the recorded signals for H₂ and CO₂ support that (cf. Figure 2a). The detected desorption of both CO₂ and H₂ associated with the second thermal event suggest a relation between hydrogen, oxygen and carbon in the as-deposited coating. The observation that hydrogen still evolves at this temperature indicates that the element is not just present as trapped atoms or molecules in microvoids or grain boundaries (as described above for hydrogen from electrolysis, released in the first thermal event), but additionally constitutes a phase in the as-deposited coating, which is stable up to higher temperature.

All the elements involved in the second thermal event are provided by the citric acid in the electrolyte, which seems to promote the incorporation of an additional phase, which is supposed to be an organic compound consisting of carbon, oxygen and hydrogen during electrodeposition and which decomposes at 250 °C. A previous study on as-deposited Fe-C coatings revealed by photoelectron spectroscopy that carbon is bound to both hydrogen and oxygen and found that an organic compound is incorporated in the coating in the form of (COOH) [2]. With EDD, this organic phase is not revealed, indicating that it either is not crystalline or of too low volume fraction for measureable diffracted intensities and therefore the present study does not allow an interpretation of the chemical structure of the organic compound. However, the precipitation of magnetite and cementite is a consequence of the decomposition of the organic compound and identified by the *in-situ* diffraction analysis in the corresponding temperature range. The first presence of an oxide phase, namely magnetite Fe₃O₄, is revealed by diffraction analysis at a temperature of 259 °C, hereafter it evolves with increasing temperature. The slow growth rate of magnetite during heating with 2 K/min, as indicated in Figure 1 by the slowly evolving diffraction intensities for the Fe₃O₄ reflection around 34.8 keV at temperatures below 320 °C, could explain the absence of an exothermic peak in DTA for this low heating rate. Together with oxygen used for the formation of oxides, also carbon is provided by the decomposition of the organic compound in the second thermal event and results in the formation of carbides as Fe₃C at

310 °C (cf. Figure 1). A relatively small exothermic peak is measured around 310 °C in the first heating cycle to 1000 °C by DTA as a shoulder of the exothermic peak related to the third thermal event at 360 °C (cf. Figure 2a) and suggests a relation the Fe₃C formation.

It is noted that the “nameless phase”, which previously was considered an explanation for the location of the measured high concentration of carbon in the as-deposited coatings [4,8,9], still is present at 250 °C (cf. Figure 1). A previous study further revealed that the as-deposited “nameless phase” is still present even after *ex-situ* isothermal annealing for 24 h at 250 °C, thus, it does not decompose with the second thermal event [7] and is not responsible for the formation of magnetite and cementite at this temperature. From the present *in-situ* study, it is known that the “nameless phase” remains stable up to a temperature of 328 °C.

Although missing a clear experimental verification, it has been suggested previously that ϵ/η -Fe₂C transition carbides could be present as minor phase in the otherwise ferritic as-deposited Fe-C coatings [4,8,9], because they would explain the “nameless phase”, although the similarity of the two possible carbides, ϵ -Fe₂C and η -Fe₂C [20,21], does not allow their distinction from the present data. Assuming meta-stable ϵ/η -Fe₂C in the as-deposited coating, a transformation to Fe₃C would be expected during annealing. The reported enthalpy change and the temperature range of 260 °C to 350 °C for that transformation would be associated with an activation energy of 200 kJ/mol [19]. For the present Fe-C coatings, such transformation is not indicated by the second thermal event having a much lower activation energy of 98 kJ/mol. The third thermal event, which occurs at a temperature of 360 °C with an activation energy of 151 kJ/mol is associated with a mass loss and desorption of at least hydrogen (cf. Figure 2a). This rejects that it is related to the transformation of Fe₂C to Fe₃C and, thus, questions the presence of Fe₂C at all.

The complementary results from *in-situ* diffraction analysis and thermal analysis indicate that the disappearance of the “nameless phase” at about 328 °C (cf. Figure 1) is related to the third thermal event, which is recorded by a strong exothermic peak with a temperature maximum at 360 °C. The pronounced release of hydrogen strongly suggests that hydrogen is included in the “nameless phase”. This evolution of hydrogen marks the decomposition of the “nameless phase” and, at the same time, explains the abovementioned observation of the sudden change in the sample height during *in-situ* diffraction analysis in that temperature range (similar to the sample

height changes at low temperature in relation to dehydrogenation during the first thermal event, see above). In addition to hydrogen, to a lesser extent also O₂ and CO₂ evolve during the third thermal event (cf. Figure 2a), which suggests also oxygen and/or carbon as elements in the “nameless phase”. The simultaneous desorption of hydrogen and oxygen indicates that it originates from the family of hydroxides, e.g. ferrihydrite as previously suggested [7]. Ferrihydrite is reported as being nanocrystalline with an average domain size of around 2.7 nm and poor crystallinity [22–24]. The formation of ferrihydrite is known to be favored [25], compared to the more commonly known iron oxides as hematite Fe₂O₃ or goethite α -FeOOH, in an environment of organic molecules and a high supply of iron. Both of these factors are valid at the coating/electrolyte interface during deposition of the present Fe-C coating and the formation of metal hydroxides during electrodeposition of different coatings is well known [26]. Although the majority of the electrolyte consists of Fe-ions in their oxidation state Fe²⁺, the presence of Fe³⁺ being required for the formation of ferrihydrite is likely due to the thermodynamically favored oxidation reaction of Fe²⁺ to Fe³⁺ in air. The hexagonal crystal structure of ferrihydrite would even explain some low intensity peaks causing an asymmetry for the 211 α -Fe peak, as previously reported from conventional laboratory XRD [6]. Ferrihydrite has strong adsorptive capacity and a large surface area that acts as a sink for organic matter [24]. This makes the sorption of also carbon-containing species at the surface of ferrihydrite likely and explains that the evolution of all the co-deposited elements (hydrogen oxygen, carbon) is recorded during the third thermal event, thus, with the decomposition of the “nameless phase”. The transformation of ferrihydrite into either magnetite or hematite, depends on the environment and access to oxygen [27]. A distinct exothermic peak maximum was reported [27] at about 360 °C as the thermal transformation of ferrihydrite into magnetite, and an additional transformation can occur at 505 °C [27], both fit well with the present data. The transformation of ferrihydrite is expected to be non-reversible and it is indeed not observed in the second heating cycle of the Fe-C coating. The corresponding introduction of a name for the yet “nameless phase” certainly is premature and its experimental verification as carbon-associated ferrihydrite is ongoing.

4.3 High temperature range – above 380 °C

After dehydrogenation of hydrogen from electrolysis (first thermal event) and the release of co-deposited carbon, oxygen and hydrogen by decomposition of both an organic phase (second

thermal event) and the “nameless phase” (third thermal event), the ferrite phase is still present, while magnetite and cementite have formed additionally.

A transformation of Fe_3O_4 to FeO was consistently revealed by both diffraction and thermal analysis at a temperature of 570 °C, which fully agrees with thermodynamics. Diffraction analysis at room temperature of a previously annealed sample (not shown here) revealed that FeO still is present after cooling, which is promoted by a rapid cooling rate [28]. This explains the exothermic peak at 295 °C in the second heating cycle shown in Figure 2b as a transformation of still present FeO into Fe_3O_4 , which then again transforms to FeO at higher temperature (interestingly, the second heating cycle, Figure 2b, indicates a temperature of 585 °C, compared to 570 °C in the first heating cycle, Figure 2a).

The austenitization temperature measured by DTA and EDD is in good agreement with the theoretical value of 727 °C for iron-carbon alloys in thermodynamic equilibrium. The diffraction analysis revealed an immediate transformation from $\alpha\text{-Fe}$ to $\gamma\text{-Fe}$ without a measurable co-existence of both phases, which verifies that the actual carbon content of 0.88 wt% in the Fe-C coatings is close to the eutectoid concentration of 0.76 wt% for Fe-C alloys. The transformation of $\alpha\text{-Fe}$ into $\gamma\text{-Fe}$ occurs at the same temperature in the second heating cycle to 1000 °C as measured by DTA (cf. Figure 2b).

5. Conclusion

The thermal evolution of electrodeposited Fe-C coatings was investigated systematically during isochronal annealing up to 800 °C by means of complementary methods of *in-situ* analysis. With *in-situ* energy-dispersive synchrotron diffraction, the crystalline phases in the as-deposited coating and the temperature-induced phase transformations were revealed with unique temperature resolution. With *in-situ* thermal analysis under the same isochronal annealing conditions, the evolution of co-deposited elements and associated mass changes were followed, and this supported the interpretation of the diffraction data and further allowed conclusions on non-crystalline phases. Thus, some method-specific limitations can be disregarded by their complementary use, assuming that the *in-situ* experiments based on diffraction, thermogravimetric and spectroscopic analysis are carefully carried out with appropriate and

consistent annealing conditions. In the present work, the complementary information from the applied *in-situ* methods essentially enhanced the understanding of both the as-deposited nature of the Fe-C coatings and their thermal stability.

As-deposited Fe-C coatings consist of i) ferrite, ii) a crystalline phase, possibly containing hydrogen, oxygen and iron (previously called the “nameless phase”), iii) a phase containing carbon and most likely also hydrogen and oxygen either being amorphous or constituting a low amount of a crystalline phase and iv) free hydrogen in atomic or molecular form. During annealing, already at low temperature (about 114 °C), the free hydrogen is released from the sample (first thermal event). At about 250 °C (second thermal event), again dehydrogenation occurs, but at the same time also oxygen and carbon redistribute and/or leave the sample, which indicates the decomposition of a phase containing all co-deposited light elements originating from the citric acid used as additive in the electrolyte. At this temperature, the crystalline “nameless” phase still remains unchanged, but decomposes at about 328 °C (third thermal event) with an associated release of hydrogen and carbon and oxygen from that phase, which subsequently form oxides and carbides at higher annealing temperatures.

The results highlight the essential role of the light elements carbon, oxygen and hydrogen, which are co-deposited together with iron. All these elements, thus, not only the intendedly co-deposited carbon, define the as-deposited state of the Fe-C coatings and rule their overall thermal evolution as well as the associated mechanical properties. The observed temperature-dependent changes provide a useful guide for dedicated post-deposition annealing treatments towards deliberate alterations of the internal structure and associated properties of electrodeposited Fe-C coatings.

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