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Electrodeposition of iron with co-deposition of carbon – on the nature of nanocrystalline Fe-C coatings

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Abstract

Fe-C coatings were electrodeposited from an iron-sulfate electrolyte containing citric acid as a carbon source. Differently thick coatings were deposited onto amorphous substrates, which allows substrate-unbiased nucleation and thereby enables the study of the intrinsic growth of Fe-C coatings. The internal structure of the Fe-C coating was systematically investigated applying complementary methods of materials characterization using microscopy, spectroscopy, and X-ray diffraction analysis, which was further supplemented with microhardness measurements. For the measured high carbon concentration of more than 0.8 wt pct, the experimental results indicate the formation of Fe₂C carbides. Together with the nanocrystalline carbon-free ferrite grains with strong <311> fiber texture, the carbides provide a very high microhardness of almost 800 HV, as measured for the Fe-C coatings independent of the coating thickness. The results essentially contribute to understanding of the growth characteristics and phase formation during electrodeposition of the Fe-C coatings, which is needed for their industrial applications as hard coatings.

Keywords

Iron alloys, coatings, nanocrystalline materials, electrodeposition, characterization.

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I. INTRODUCTION

Electrochemical deposition of iron from iron-sulfate baths was developed a century ago and implies the advantages of a cheap electrolyte, low operating temperature and low susceptibility to oxidation of the electrolyte [1]. Originally, electrodeposition of iron was mainly used for short-term restoration of worn or damaged surfaces of machine components [2,3], as for these applications, the ease of site-specific deposition and attractive mechanical properties of the coatings were of main interest. More recently, the intended co-deposition of other elements (e.g., tungsten, nickel, phosphorous and zinc) from advanced electrolytes inspired a revival of the original interest in iron-based coatings [4]. Of particular interest is the co-deposition of carbon and iron, and iron-carbon (Fe-C) coatings have been synthesized not only by electrochemical deposition [5-13], but also by physical vapor deposition [14-17]. Although different morphologies and structures of Fe-C coatings ranging from amorphous to crystalline and different carbon concentrations are reported for the various deposition processes, all Fe-C coatings possess very high hardness, being similar to the hardness of martensite in steels. Despite that similarity, the peculiarities of the growth of Fe-C coatings suggest essential differences to traditional hardening of steel and, hence, a different origin of microstructure and properties. Despite a general consistency in the literature regarding the good mechanical properties of Fe-C coatings, their growth characteristics and, in particular, the role of carbon in the coatings are aspects that not fully are understood yet. This, however, is essential for the promising application of Fe-C coatings as a novel type of hard and wear-resistant surfaces, which both enables straightforward repairing of worn surfaces by site-specific deposition and the large-scale deposition on components exposed to mechanical loading during operation.

Electrodeposited Fe-C coatings have a huge potential for surface engineering, including tailoring of the deposition parameters to optimize the growth characteristics and additional modifications during post-deposition treatments of the coatings. Understanding the correlation between the applied deposition conditions and the resulting microstructure is a prerequisite for the successful transfer of knowledge obtained on laboratory scale into a reliable, reproducible, large-scale

production [18,19]. In addition to the type of electrolyte and the process parameters, like current density and temperature, both nucleation and growth of electrodeposits are further affected by the nature of the substrate, which influences the size, shape, crystallographic orientation of the grains, and consequently, resulting properties of the coatings. Previous studies dedicated to electrochemical deposition of Fe-C coatings refer to an iron-sulfate bath with the addition of a small amount of carbon-containing organic acids [5-13]. The type of such organic additives has been found to determine not only the possible amount of co-deposited carbon but also the macroscopic appearance as well as the topography, morphology, and associated properties of the Fe-C coatings [7,12,13]. In addition to the electrolyte composition, also the effect of the pH value, the deposition temperature and the applied cathode current density have been investigated [5-10,12].

The present work reports on systematic studies of Fe-C coatings, which were electrodeposited from an iron-sulfate electrolyte with citric acid as additive. To investigate the intrinsic growth characteristics of the coatings, electrodeposition was carried out onto amorphous nickel-phosphorous (Ni-P) substrates under identical process parameters. Only the deposition time was varied to result in Fe-C coatings with various thicknesses up to several tenths of micrometers. Based on thorough materials characterization of the as-deposited coatings with a focus on their internal structure and the corresponding microhardness, the incorporation of carbon in the coatings is discussed, also in relation to previously reported results from the literature. The present work is dedicated to the understanding of the as-deposited Fe-C coatings, which provides the basis for further surface engineering either by tailoring the deposition process or subjecting the as-deposited coatings to post-deposition treatments.

II. MATERIALS AND EXPERIMENTAL METHOD

A. Electrochemical Deposition

1. Substrate

Fe-C depositions were carried out on amorphous substrates, with the aim of investigating the effect of the electrolyte and the applied process parameters without any additional influence on the coating growth. The substrates have been obtained by pretreating low-carbon steel plates by

electroless plating of a Ni-P film from the commercial electrolyte MacDermid Enthone VAND-ALLOY 4100 containing 10 to 12 wt pct P. The resulting amorphous Ni-P film with a thickness of about 20 μm ensures substrate unbiased growth during subsequent electrodeposition of Fe-C coatings. Prior to Fe-C deposition, the Ni-P substrates were subjected to cathodic degreasing at 5 V for 2 minutes followed by 2 minutes of surface activation in commercial dry acid 629 SV from EngTech Scandinavia.

2. Deposition Parameters

The electrolyte was prepared from chemicals of analytical grade with a concentration of 0.143 mol/dm³ iron(II) sulfate heptahydrate, 6.2×10^{-3} mol/dm³ citric acid monohydrate, and deionized water. The 5 L of the electrolyte were freshly mixed for each sample to avoid any possible oxidation or aging of the electrolyte as an additional influence on the microstructure and properties of the Fe-C coatings. The electrolyte temperature amounted to 50 °C and mechanical stirring was applied during deposition. The pH value of the electrolyte was maintained between 2.5 and 2.8 during deposition using a 10 vol pct sulfuric acid solution. An interstitial free steel plate was used as an anode, and the Ni-P coated plates with dimensions of 5 x 5 cm were used as cathodes. One side of these substrate plates was covered with an electrolyte-resistant tape to ensure deposition only on the side toward the anode.

Electrodeposition of Fe-C coatings was carried out at a constant current density of 3.0 A/dm², which was applied for various deposition times between 30 and 300 minutes. The applied deposition parameters and the electrolyte composition have been optimized based on previous studies on electrodeposited Fe-C coatings [5–13]. The coatings were immediately after deposition rinsed in water, followed by rinsing in ethanol and then carefully dried to avoid oxidation. The samples were protected from any contact with oxidizing environments during storage. For subsequent microstructure analysis, the samples were cut such that only the center part with homogeneous coating thickness was investigated, thus, disregarding the possibly higher current density near the sample edges.

The designation of a sample indicates the thickness of the coating, e.g., Fe-C_30 μm corresponds to a coating of 30 μm thickness deposited on the Ni-P substrate.

B. Materials Characterization

1. Chemical Analysis

The carbon content in the coatings was determined using a carbon analyzer LECO CS230, which measures the amount of CO₂ evolved by high-frequency induction heating of the sample in an O₂ atmosphere. The measurements were performed using an amount of 0.1 g of a Fe-C coating removed from the substrate.

A depth profile of the chemical composition was obtained by means of glow discharge optical emission spectroscopy (GDOES) using a Horiba equipment GD profiler 2 with Quantum XP software. The instrumental settings and procedure were established based on investigations of the crater profile using surface roughness measurements by 3D coordinate measurements with an Alicona InfiniteFocus. The GDOES measurements were calibrated with multiple low-alloy steel standards having different carbon contents up to 1.3 wt pct. The content of hydrogen and oxygen is given as measured intensity because these elements have not been calibrated.

2. Microscopic Analysis

Microscopic analysis was carried out on cross sections of the samples. Before cross section preparation, the samples were coated with a 10 µm layer of nickel to protect the surface of the Fe-C coatings. Samples were embedded in epoxy resin, which hardens at room temperature and avoids any risk of introducing artifacts to the as-deposited coatings. The cross sections were metallographically prepared and polished with OP-S for 3 minutes as a final preparation step. An Olympus GX41 light optical microscope (LOM) was used for the thickness measurements on cross sections. A FEI Quanta 200 ESEM scanning electron microscope (SEM) was used for investigations on the cross sections.

3. X-ray Diffraction Analysis

A Bruker AXS D8 Discover X-ray diffractometer equipped with an Eulerian cradle and operated with Cr-K_α radiation was used for qualitative phase analysis, line profile analysis, and quantitative crystallographic texture analysis. A Göbel mirror was used to obtain a high, intense parallel beam for phase analysis and line profile analysis, while a PolyCap optics was used to ensure a parallel beam for texture analysis along with a vanadium filter to avoid K_β-radiation.

The calculated information depth in iron corresponds to a maximum of about 6 μm within the measured range of diffraction angles between 50 and 160 deg 2Θ .

X-ray diffraction (XRD) phase analysis was carried out applying a symmetric beam path.

Samples were measured using a step size of 0.02 deg 2Θ and a measurement time of 20 seconds per step to ensure high resolution and good counting statistics. For qualitative phase analysis, the measured diffraction angles were corrected for any offset related to the alignment of the diffractometer using a LaB_6 reference sample.

XRD line profile analysis was carried out for the 110, 200, and 211 reflections of $\alpha\text{-Fe}$. The measured diffraction patterns were fitted with a superposition of two linked pseudo-Voigt functions corresponding to the $K_{\alpha 1}$ and the $K_{\alpha 2}$ components of the applied X-rays. Only the fitting results for the $K_{\alpha 1}$ component were used for interpretation. Fitting with the pseudo-Voigt function revealed the following parameters for further analysis: (1) the 2Θ peak position, (2) the full-width-half-maximum (FWHM), (3) the shape of the peak defined by the contribution of Gaussian and Lorentzian function to the peak profile, and (4) the integrated intensity of the measured peaks. The measured peak broadening was corrected for the effect of instrumental broadening applying a LaB_6 standard powder sample. The resulting physical peak broadening was expressed as integral breadths β , calculated from the FWHM and the profile shape, and subjected to the single line method for separating the simultaneous influences of the size of coherently diffracting domains (interpreted as the crystallite size) and lattice microstrain on peak broadening [20,21].

For quantitative crystallographic texture analysis by means of XRD, 110-, 200- and 211-pole figures of $\alpha\text{-Fe}$ were measured for all samples, applying sample rotations around the surface normal (azimuth angle φ , $0 \leq \varphi \leq 360$ deg, step size 5 deg) and sample tilts (pole angle ψ , $0 \leq \psi \leq 75$ deg, step size 5 deg). Measured intensities were corrected for background intensity, and a Fe-powder standard was used to correct for defocusing associated with tilting. For texture quantification, the orientation distribution function was calculated in MTEX using the zero-range method [22]. The maxima in the inverse pole figures in normal direction to the substrate were used to determine the fiber axis $\langle uvw \rangle$, as ideal fiber textures apply for all Fe-C coatings. Inverse pole figures in directions within the plane of the coating revealed random rotations

around the fiber axis. Accordingly, the corresponding orientation densities in the normal direction are a measure of the texture strength.

4. Microhardness Measurements

The microhardness was measured using a Future Tech Inc. FM700 microhardness tester with Vickers geometry, applying a load of 10 g. Measurements were performed both on the surface and on metallographically prepared cross sections. Microhardness measurements on the surfaces of all samples represent averages over 20 measurement positions, while results from measurements on the cross sections correspond to 10 indentations in the middle of the coating.

III. RESULTS

A. Microscopic Analysis of Fe-C Coatings

Microscope investigations of the cross sections indicate uniform coatings with homogeneous coating thicknesses, as shown in Figure 1 on the example of sample Fe-C_58 μ m. While the surface roughness of the original steel substrate is still maintained in the Ni-P substrate layer (cf. Figure 1(a), steel–Ni-P and Ni-P–Fe-C interfaces), a leveling effect occurs during the growth of the Fe-C coating resulting in a smooth surface (cf. Figure 1(a), interface Fe-C–Ni). The figure indicates that the surface roughness of the Fe-C coating considerably decreased already at a thickness of 16 μ m and the surface fully leveled out for coating thicknesses of 30 μ m and above. The cross sections also revealed that the microstructure is very fine grained and cannot even be resolved with SEM (cf. Figure 1(b)).

Figure 1: Cross section of sample Fe-C_58 μ m. Ni-P corresponds to the amorphous substrate layer on top of steel, while a Ni film protects the surface of the Fe-C coating during metallographic preparation. a) LOM image, b) SEM image.

Although neither LOM nor SEM can resolve the very fine-grained microstructure of the Fe-C coatings, microscopy of the various cross sections revealed the thickness of the Fe-C coatings as a function of the applied deposition time, which allowed calculation of the deposition rate. The results shown in Table I indicate that the deposition rate is highest with 0.27 μ m/min at the beginning of the deposition, thus, for the thinnest coatings and drops to 0.19 μ m/min for the thickest coating of the present study.

B. Chemical Analysis

Chemical analysis applying the LECO system determined the carbon concentration to be 0.88 ± 0.02 wt pct, which represents an average value over the whole thickness of a coating. The presence of such a high carbon concentration is confirmed by GDOES, which further supplements with the depth distribution of relevant elements like carbon, oxygen, and hydrogen. In the depth profiles shown on the example of sample Fe-C_16 μ m in Figure 2, the first few micrometers should be disregarded as they relate to the running-in period during sputtering from the surface. The interface between the Fe-C coating and the substrate, seen as a drop in carbon, oxygen, and hydrogen concentrations, is obtained after a total time of about 160 seconds, which corresponds to a sputter depth of 22 μ m. A homogenous distribution of carbon is measured across the coating thickness. In addition, significant intensities are measured for hydrogen and oxygen, which reveal that these elements are present in the coatings, although they cannot be quantified. The slightly decreasing content of hydrogen could be an artifact from the sputtering process and local heating of the measured region, which would result in a higher concentration in the beginning of the measurement when hydrogen may diffuse toward the surface.

Figure 2: GDOES depth profile measured for the sample Fe-C_16 μ m. The concentration of carbon refers to the left y-axis, while measured intensities for hydrogen and oxygen refer to the right y-axis.

C. X-ray Diffraction Analysis

The XRD patterns of the Fe-C coatings are shown in Figure 3 and clearly reveal the presence of α -iron (JCPDS card 6-696). Depending on the coating thickness, the various reflections show different intensity ratios indicating slight changes of the preferred grain orientation with coating thickness. Also, independent of the thickness, further peaks in addition to the ones from the α -iron phase are observed for the measured samples at about 58.05 deg 2Θ , 137.59 deg 2Θ and 150.73 deg 2Θ (an additional peak at 126.5 deg 2Θ should be disregarded because it refers to the K_{β} radiation, which has not been filtered out). While the peak around 58.05 deg 2Θ is of highest intensity and free-standing, the other peaks are less distinct and hardly visible with only small intensity in the wide tails of the α -iron peaks (cf. inserts in Figure 3). Such weak and overlapping peaks considerably complicate straightforward phase analysis for the present Fe-C coatings. Thorough peak fitting was carried out, also for the overlapping and weak peaks, and the resulting d-spacings of all fitted peaks are shown in Table II. The table reveals that all peaks shift slightly

toward larger d-values when the thickness of the coating increases from 8 μm to 30 μm , without remarkable further changes at 58 μm . Such changes of d-values suggest changes of residual stresses and/or chemical changes in the coatings. As that observed shift toward larger d-values with increasing thickness is most pronounced for the first two peaks (cf. Table II), another observation seems particularly interesting in this respect. Table II indicates a correlation between these two peaks, thus, the 110 reflection of α -iron and the peak of the yet unidentified phase having a d-spacing of about 0.236 nm: irrespective of the coating thickness, the ratio of the lattice spacing between both peaks remains constant with 1.163 ± 0.001 .

Similar challenges with phase identification, as encountered in the present work, have been reported in literature, but inconsistent conclusions on the crystalline phases in the Fe-C coatings indicate that the nature of growth and phase formation in such electrodeposits is still under discussion. While there is general agreement in the literature (and the present work) that the peaks of highest intensity in the measured diffraction patterns refer to an iron-rich phase, different explanations for the presence of carbon and the corresponding formation of carbon-containing phases have been reported [5-9,14,15,23]. The various hypotheses for the presence of carbon in the Fe-C coatings are discussed and verified for the present samples below (see Section IV).

Figure 3: X-ray diffraction pattern of Fe-C coatings. (The maximum value of 160 °2 Θ corresponds to the upper limit of the measurement range and, therefore, the broad α -211 cannot be recorded completely.)

All Fe-C coatings have in common that the 211 reflection of α -iron is of highest intensity in the Θ -2 Θ scans, the 110 of α -iron is clearly visible, and the 200 reflection of α -iron is of very low intensity or fully absent. Comparing the measured intensity ratios with the JCPDS card of randomly oriented α -iron, the presence of a pronounced preferred orientation of grains in the Fe-C coating is obvious. For its quantification, crystallographic texture analysis by means of pole figure measurements has been carried out. For all Fe-C coatings, the pole figures revealed the presence of fiber textures with rotational symmetry of the measured intensity distributions as shown in Figure 4 on the example of sample Fe-C_16 μ m. For fiber textures, inverse pole figures in normal direction straightforwardly allow quantification of the fiber axis, which describes the preferred orientation in the growth direction of the coatings. All Fe-C coatings consist of a {311}

fiber texture, as shown in Figure 5. The fiber axis $\langle uvw \rangle$ and the corresponding orientation densities in multiples of random distribution are summarized for all samples in Table III. Although the $\langle 311 \rangle$ fiber axis is rather strong for all coatings, slight changes of the texture strength are observed as a function of coating thickness: The strength of the $\langle 311 \rangle$ increases slightly with coating thickness.

Figure 4: Pole figures of α -iron as measured by XRD for the sample Fe-C_16 μ m.

Figure 5: Inverse pole figures in growth direction obtained by XRD measurements.

It would be of interest to further analyze the $\langle 311 \rangle$ oriented grains as they represent the majority of grains in the Fe-C coatings, but as the 311 is a forbidden reflection for the bcc α -iron, it is not accessible from a Θ - 2Θ scan. Instead, the 211 reflection (corresponding to grains deviating by about 10 deg from the real $\langle 311 \rangle$ preferred orientation) shows the highest intensity in the diffraction pattern, but it does not allow for accurate peak profile analysis. Due to substantial peak broadening, the 211 exceeds the available measurement range (only up to 160 deg 2Θ can be measured by conventional XRD); thus, it cannot be recorded completely, and weak peaks of a second phase overlap with the left tail at lower 2Θ of the 211 peak. Both hinders thorough peak

profile analysis of the 211 peak, and therefore, only the 110 peak of α -iron has been used for quantification of both crystallite size and microstrain from the measured peak profiles. Accordingly, the corresponding results in Table IV do not represent the average over all grains of the Fe-C coatings, but instead they reflect data for $\langle 110 \rangle$ -oriented grains only, which constitute a minority of all grains. The crystallite size of $\langle 110 \rangle$ grains is in the order of about 10 nm and does not change with coating thickness. The microstrain evolves with coating thickness, and shows a sudden change in the thickness range between 16 and 30 μm .

D. Microhardness

High microhardness values of almost 800 HV0.01 have been measured for all Fe-C coatings, almost independent of the coating thickness, as shown in Table V. Microhardness measurements on the cross sections verified the high microhardness of Fe-C coatings.

IV. DISCUSSION

The chemical analysis revealed co-deposition of carbon with an average concentration of 0.88 ± 0.02 wt pct C and indicates that oxygen and hydrogen are present in the Fe-C coatings (cf. Figure 2). These elements certainly originate from the citric acid in the electrolyte, although hydrogen also might be caused by hydrogen evolution, which is a typical phenomenon occurring during electrodeposition. Despite intensive attempts applying various methods of dedicated high-resolution microscopy and element analysis, it remains challenging to quantify and locate the co-deposited hydrogen and oxygen in the coating, and this work will continue. The reducing nature of the interface between cathode and electrolyte is likely either to decompose citric acid into smaller fragments of a carboxylic form or to result in the incorporation of species in their elemental form in the microstructure of the Fe-C coatings. Then, they would likely react with iron, producing hydroxides, oxides, or carbides. In thermodynamic equilibrium, none of these elements (carbon, oxygen, hydrogen) is expected to be in solid solution in α -iron, which is unambiguously identified by XRD.

XRD also revealed that the microstructure of α -iron is nanocrystalline with crystallite sizes just below 10 nm for the $\langle 110 \rangle$ -oriented grains. Neither coarsening of the nanocrystalline grains as a

function of coating thickness nor any growth selection from the interface toward the surface has been observed by XRD or SEM. Although the nanocrystalline nature of the coatings would allow segregation of elemental carbon (and oxygen and hydrogen) in the numerous grain boundaries, the present study does not allow for such a conclusion, and dedicated high-resolution microscopy with chemical analysis at grain boundaries is in progress. The present study, however, clearly indicates a second phase, in addition to α -iron, as revealed by the additional peaks shown in Figure 3 and quantified in Table II. Also, being of low intensity and partly overlapping with peaks of α -iron, which considerably complicates straightforward phase analysis, the origin of these additional peaks, having d-spacings of 0.2360 nm, 0.1228 nm, and 0.1183 nm, has to be discussed.

The co-deposited oxygen cannot solely explain these peaks, which do not match with Fe_2O_3 (hematite) or Fe_3O_4 (magnetite), and the presence of hydrogen does not refer to any phase related to these peaks without speculations. However, the location of carbon, which has been measured with a high concentration of more than 0.8 wt pct C in the as-deposited coatings, has not been explained yet. It also is not consistently reported in the literature, although similar experimental results have been obtained. The following possibilities can be discussed and will be related to the present results.

In early studies of Fe-C coatings [6-9], observations of peak asymmetries have been related to a supersaturation of the bcc α -Fe (ferrite) phase resulting in a tetragonal distortion of the iron lattice corresponding to the bct α' -Fe (martensite) phase. For the well-known formation of martensite in steel, the tetragonal distortion of the lattice originates from the preferred incorporation of carbon on octahedral interstitial lattice sites in the z-axes compared to the x- and y-axes, which for steels is a consequence of the diffusionless transformation from the fcc iron lattice (austenite) [24]. This explanation for tetragonal martensite and the corresponding peak asymmetry due to the presence of double reflections of 101 and 110 for α' -Fe, however, does not apply for the present electrodeposited samples, where there is no obvious reason for a preferred occupancy of interstitial sites with carbon along one particular direction only. Furthermore, the high concentration of carbon in the present samples would cause a remarkable peak splitting due to the high tetragonal distortion of the lattice. Such splitting of the iron peaks into two distinct peaks, which are apart from each other according to the lattice expansion/contraction in z- or x-

and y-direction, has not been observed by XRD (cf. Figure 3). If, instead, carbon would be incorporated with equal probability on all interstitial sites, the strong supersaturation of the lattice would cause a remarkable peak shift in XRD. Large supersaturation of bcc α -Fe with carbon has been reported for vapor-deposited films (up to 5 wt pct) [14,15] and in steels after severe deformation [25], thus, for nonequilibrium states. Although electrodeposition often does not provide thermodynamic equilibrium and, thus, favors the formation of nonequilibrium phases, there is no experimental evidence for the present Fe-C coatings that carbon is in a supersaturated solid solution in the α -Fe phase. For determining the undisturbed lattice spacing even in the potential presence of stresses, XRD has been performed in the strain-free direction of the Fe-C coating (by tilting the sample around the azimuth angle of $\psi_0 = 41.43$ deg) and has revealed the lattice spacing of the (110) crystallographic planes with $d_0 = 0.2026$ nm, which agrees exactly with data for carbon-free α -Fe (JCPDS card 6-696) and rejects the possibility of any carbon-supersaturation of the α -Fe lattice. The high concentration of carbon is therefore likely to have caused precipitations, as discussed below.

Consistent with recent studies on Fe-C coatings [5,13,23] is the present observation of an additional peak corresponding to a lattice spacing of $d = 0.2360$ nm (cf. Figure 3 and Table II). Phase analysis has mainly to be based on that peak because it is the only one (in addition to the peaks of α -Fe) that is of high intensity and not overlapping with others. Further peaks corresponding to d-spacings of 0.1228 and 0.1183 nm indicating a second phase can support various hypotheses for phase identification. In the following, the presence of carbides is discussed.

For carbon-steels, Fe_2C carbides can exist as either hexagonal $\epsilon\text{-Fe}_2\text{C}$ (JCPDS card 36-1249) or orthorhombic $\eta\text{-Fe}_2\text{C}$ (JCPDS card 37-999), both being transition carbides toward the formation of Fe_3C at higher temperatures [26-29]. Both $\epsilon\text{-Fe}_2\text{C}$ and $\eta\text{-Fe}_2\text{C}$ are very similar to each other, and earlier in the literature [5], $\epsilon\text{-Fe}_2\text{C}$ was reported for Fe-C coatings. The actual lattice parameters of the transition carbides have been reported to be alloy specific [30] and can therefore vary slightly. The $\epsilon\text{-Fe}_2\text{C}$ carbide having lattice parameters of $a = 0.2735$ nm and $c = 0.4339$ nm [30] can explain the measured peaks corresponding to $d_{\epsilon-100} = 0.2369$ nm, $d_{\epsilon-103} = 0.1234$ nm, and $d_{\epsilon-200} = 0.1184$ nm. The $\eta\text{-Fe}_2\text{C}$ carbide having lattice parameters of $a = 0.4704$ nm, $b = 0.4318$ nm, and $c = 0.2830$ nm can also explain the measured peaks according to $d_{\eta-011}$

= 0.2367 nm, $d_{\eta-230} = 0.1228$ nm, and $d_{\eta-022} = 0.1183$ nm. Even the slight peak asymmetry (see magnified insert in Figure 3) can be assigned to η -Fe₂C. Other carbides, like Fe₃C, Fe₅C₂, Fe₇C₃, cannot explain the observed results and certainly are not present in the as-deposited Fe-C coatings.

To test the suggestion of either ε -Fe₂C or η -Fe₂C carbides, XRD has been carried out under various sample tilts and rotations, but no additional reflections or higher intensities could be revealed. However, when tilting the sample about the angle ψ , the intensity of the 110 α -Fe lowers until the peak fully disappears at $\psi = 12$ deg and the intensity of the peak, corresponding to the d-spacing of 0.2360 nm, does the same, thus, the intensity changes of both peaks are correlated. This suggests a crystallographic orientation relation between α -Fe and ε -Fe₂C or η -Fe₂C, respectively. This is further supported by the observation of a correlated peak shift between 110 α -Fe and the supposed 100 ε -Fe₂C or 011 η -Fe₂C, which occurs independent of the coating thickness as mentioned above (cf. Table 2). The low intensities of measured XRD peaks for carbides of ε -Fe₂C or η -Fe₂C suggest a low volume of carbides in the coating, and the rather broad peak(s) further indicate that the corresponding carbide phase is nanocrystalline and might be fine dispersed. In an attempt to locate these carbides, the embedded samples were re-polished and etched with Murakami etchant for a dedicated SEM investigation, but no carbon-rich phase could be resolved. In conclusion, despite the clear experimental evidence of a second phase and the strong suggestion that it is associated with the formation of Fe₂C carbides in the Fe-C coatings, its final identification requires further investigations.

Independent of the nature of the not-yet clearly identified carbide, which is present in the as-deposited Fe-C coatings in addition to α -Fe, the carbide phase is expected to contribute essentially to the high hardness of the coatings being in the order of that of martensitic steels. Both ε -Fe₂C and η -Fe₂C carbides are associated with excellent mechanical properties [31-34], but also the nanocrystallinity of ferrite grains and the detected additional elements of H and O, comprising the peculiar nature of electrodeposited coatings, contribute to the high hardness. Being metastable carbides, the thermal stability of ε -Fe₂C and η -Fe₂C is expected to be limited, which provides an additional possibility for further surface engineering by post-deposition treatments.

Already at fairly low coating thicknesses, the coating growth is fully dictated by the deposition process and reproducible coatings can be deposited reliably. Final applications of the Fe-C coatings utilizing their high hardness and related wear resistance, certainly aim at thick coatings and the observed changes of the deposition rate might become relevant. The observed lowering of the deposition rate after 120 minutes might be affected by several influences: changes of the chemical concentrations in the electrolyte during the longer deposition times, a passivation of the steel anode by a magnetite layer developed on its surface during deposition or an increase of the hydrogen evolution at the cathode surface. The lowered deposition rate and the substantial change in microstrain, which may be related to each other, had no apparent effect on the macroscopic appearance of the Fe-C coatings having a dark shiny color, as well as neither on their microstructure nor the resulting microhardness.

V. CONCLUSION

Fe-C coatings were electrochemically deposited from an iron-sulfate electrolyte with citric acid as an additive. The very high microhardness of the as-deposited coatings and their chemical composition containing 0.88 wt pct C suggest a similarity to martensitic steel, but such rushed terminology is not appropriate for the present Fe-C coatings. No tetragonal martensite has been detected; instead, the Fe-C coatings consist of carbon-free ferrite and a second phase of ϵ -Fe₂C or η -Fe₂C carbides. While these carbides are known to form during low-temperature tempering of as-quenched martensite, for the present Fe-C coatings, it cannot be concluded whether the carbides form directly during deposition or whether they result from an initial as-deposited phase with a high driving force for carbide precipitation during continued deposition. The Fe-C coatings are nanocrystalline and exhibit a strong fiber texture with a $\langle 311 \rangle$ fiber axis in growth direction. The chemical composition of the coatings, their microstructure, and the high microhardness of almost 800 HV have been observed to be independent of the coating thickness. This indicates the strong impact of the deposition conditions on the coating growth and offers the possibility for tailoring the microstructure and properties by further optimization of the electrodeposition process.

The homogeneous and reproducible deposition process, resulting in reliable Fe-C coatings independent of the applied coating thickness, allows for both the comparison of different coatings and the adaption of the thickness to a given purpose or application, which is important

for industry. Furthermore, the obtained understanding of the incorporation of co-deposited carbon as fine carbides provide the essential prerequisite for a wide range of applications, where the ability to deposit thick coatings with high hardness is very attractive. Further properties, like adhesion, wear resistance, and corrosion resistance, as well as the coating's thermal stability, are currently being investigated. One of the most critical properties is the oxidation resistance of iron-based materials, but oxidation would only restrict the potential applications to lubricated surfaces and not be a general hindrance for technical applications.

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498 **Tables**

499 Table 1: Thickness measurements and calculated average deposition rate.

Deposition time [min]	Thickness [μm]	Average deposition rate [$\mu\text{m}/\text{min}$]
30	8	0.27
60	16	0.27
120	30	0.25
300	58	0.19

500

501

502 Table 2: d-spacing [nm] obtained from peak profile fitting of XRD patterns with diffraction
503 angles $^{\circ}2\Theta$, as measured for Fe-C coatings (cf. Figure 3).

$^{\circ}2\Theta$	Phase	hkl	Fe-C_8 μm	Fe-C_16 μm	Fe-C_30 μm	Fe-C_58 μm
58.1			0.2360 nm	0.2361 nm	0.2366 nm	0.2364 nm
68.6	α -iron	110	0.2027 nm	0.2031 nm	0.2033 nm	0.2032 nm
106.2	α -iron	200	0.1430 nm	0.1431 nm		
137.6			0.1228 nm	0.1228 nm	0.1229 nm	0.1228 nm
150.7			0.1183 nm	0.1183 nm	0.1184 nm	0.1184 nm
156.7	α -iron	211	0.1168 nm	0.1169 nm	0.1169 nm	0.1169 nm

504

505 Table 3: Crystallographic texture of Fe-C coatings with varying thickness.

Sample	Fiber axis $\langle uvw \rangle$	Strength [m.r.d.]
Fe-C_8 μ m	$\langle 311 \rangle$	9.3
Fe-C_16 μ m	$\langle 311 \rangle$	9.3
Fe-C_30 μ m	$\langle 311 \rangle$	10.4
Fe-C_58 μ m	$\langle 311 \rangle$	11.2

506

507 Table 4: Integral breadth β [$^{\circ}2\Theta$], corrected for any instrumental effects, and corresponding
508 crystallite size D [nm] and microstrain ε [rms], as obtained from XRD profile analysis.

Sample	β [$^{\circ}2\Theta$]	D [nm]	$\varepsilon \cdot 10^{-3}$ [rms]
Fe-C_8 μ m	1.6195	9.8	0.37
Fe-C_16 μ m	1.9473	8.2	0.44
Fe-C_30 μ m	2.0360	8.7	3.50
Fe-C_58 μ m	2.0969	8.1	2.70

509

510 Table 5: Microhardness of Fe-C coatings measured from the surface and cross section of the
511 coatings. *Cross sections with low coating thickness cannot be measured reliably.

Sample	Surface - HV0.01	Cross section - HV0.01
Fe-C_8 μ m	775 $\pm$ 24	*
Fe-C_16 μ m	780 $\pm$ 25	*
Fe-C_30 μ m	780 $\pm$ 20	792 $\pm$ 16
Fe-C_58 μ m	775 $\pm$ 16	789 $\pm$ 14

512

513 **List of figures**

514 Figure 2: Cross section of sample Fe-C_58 μ m. Ni-P corresponds to the amorphous substrate layer
515 on top of steel, while a Ni film protects the surface of the Fe-C coating during metallographic
516 preparation. a) LOM image, b) SEM image.

517

518 Figure 2: GDOES depth profile measured for the sample Fe-C_16 μ m. The concentration of
519 carbon refers to the left y-axis, while measured intensities for hydrogen and oxygen refer to the
520 right y-axis.

521

522 Figure 3: X-ray diffraction pattern of Fe-C coatings. (The maximum value of 160 $^{\circ}2\theta$
523 corresponds to the upper limit of the measurement range and, therefore, the broad α -211 cannot
524 be recorded completely.)

525

526 Figure 4: Pole figures of α -iron as measured by XRD for the sample Fe-C_16 μ m.

527

528 Figure 5: Inverse pole figures in growth direction obtained by XRD measurements.

529