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Evolution of hard Fe-C electrodeposits with temperature

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ABSTRACT

The high microhardness of electrodeposited Fe-C coatings with around 800 HV after electrodeposition increased to about 1300 HV by dedicated annealing, reflecting a huge potential for surface engineering. The coatings remain nanocrystalline during annealing, but co-deposited carbon and oxygen result in temperature induced phase transformations. Energy-dispersive synchrotron diffraction revealed that carbides and oxides form during annealing of the as-deposited coating, which consisted mainly of carbon-free ferrite. The understanding of occurring precipitations was supplemented and verified by in-situ thermal analysis, which revealed the temperatures of thermal events related to decomposition reactions, the evolution of gasses and associated mass changes during annealing.

Keywords: X-ray diffraction, Coating, Nanocrystalline, Annealing, Phase transformations, Electrodeposition.

Introduction

Despite the enormous attention on iron-carbon alloys for a wide range of surface engineering applications, their synthesis by electrodeposition is still less in focus compared to, for example, thermo-chemical treatments. The addition of organic species, like carboxylic acids, to traditional iron-sulphate electrolytes provides the carbon source that enables the co-deposition of carbon together with iron, resulting in Fe-C coatings with thicknesses of up to several hundreds of micrometers. The structure and functional groups of various carboxylic additives influence the amount of co-deposited carbon and, to some extent, the morphology and associated properties of the Fe-C coatings [1–6]. High microhardness values (up to around 800 HV) [7] are consistently reported for electrodeposited Fe-C coatings and, hence, the coatings provide a favourable alternative to hardened steels. The more versatile process of electrodeposited Fe-C compared to (surface) hardening of steels allows producing hard and wear-resistant coatings on a variety of different substrates, performing site-specific deposition for repairing surfaces and tailoring the internal structure of the coatings according to the deposition process parameters, and it offers a huge potential for surface engineering by post-deposition treatment. In this respect, not only the nature of as-deposited coatings, but also their thermal stability including the evolution of the microstructure and occurring phase transformations are of interest.

In our recent work [6], we have shown that as-deposited Fe-C coatings consist of nanocrystalline grains and form strong $\langle 311 \rangle$ fibre textures independent of the coating thickness. Despite the high concentration of carbon, which amounts to 0.88 wt-% in the as-deposited coatings, the majority of grains correspond to ferrite with bcc crystal structure and the strain-free lattice spacing as measured by X-ray diffraction (XRD) does not indicate any (supersaturated) solid solution of carbon [6]. The presence of a minor second phase has been suggested by XRD, but

thorough identification of that phase is hindered by the limited number and weak intensity of corresponding peaks: only a single peak, in addition to ferrite, can be detected clearly [5,6,8,9]. This second phase may originate from the co-deposited carbon (e.g. Fe₂C carbides [6,8]), but it also may be related to further elements like oxygen and hydrogen, which indeed are detected although not quantifiable in as-deposited coatings, and/or a combination of all present elements being iron, carbon, oxygen and hydrogen. To reveal the role of these elements, which reproducibly are detected in electrodeposited Fe-C coatings [2,6–8,10,11], the present work investigates the evolution of as-deposited coatings during annealing and reveals corresponding phase transformations by means of complementary thermal analysis and diffraction analysis, further supplemented with transmission electron microscopy.

Material and methods

Electrodeposition

The same Fe-C coatings, which previously have been studied in their as-deposited state [6], have been used for the present annealing study. Deposition from an iron-sulphate electrolyte with citric acid as an additive (0.143 mol/dm³ FeSO₄·7H₂O, 6.2 x 10⁻³ mol/dm³ C₆H₈O₇·H₂O) occurred with a constant current density of 3.0 A/dm² (for details, see [6]). As cathode, thin brass strips and lead-tape were attached on a steel plate such that deposition occurred simultaneously on lead and brass, thus, under exact same conditions. The substrate material does not play a role for the present study, because the long deposition with 15 h resulted in a thick coating of 360 μm. Low adhesion of the coating on lead allowed easy detaching from the substrate to obtain stand-alone coatings for in-situ thermal analysis, while coatings on brass were used for ex-situ annealing.

Characterization methods

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 piece of substrate-free coating material, detached from the lead-tape and weighing 250-260 mg, was placed in an alumina crucible. Isothermal annealing experiments were carried out at temperatures of 200, 250 and 300 °C, respectively, with a holding time of 24 h at each temperature. Each of the isothermally treated samples, was subsequently further subjected to two cycles of isochronal annealing from 40 °C to 800 °C, using a heating rate of 2 K min⁻¹ and a cooling rate of 40 K min⁻¹, whereby the second isochronal annealing was used to correct for the instrumental background of the first isochronal annealing. As a reference, an as-deposited coating was subjected to the two isochronal heating cycles. Annealing was carried out in an inert atmosphere of argon gas (99.999 mol-% purity).

Identical counterparts of the coating on brass substrates were used for furnace annealing in a lower temperature range up to a maximum of 300 °C. Such furnace annealing was carried out for 24 h at isothermal temperatures of 200, 250 and 300 °C, respectively, in an inert argon (99.999 mol-% purity). Qualitative phase analysis was carried out for each sample at the synchrotron diffraction facility BESSY II using energy-dispersive diffraction (EDD) at the EDDI beamline [12]. EDD spectra were recorded for 600 s applying a symmetric diffraction geometry with a constant scattering angle $2\theta = 14^\circ$, corresponding to a maximum information depth of about 100 µm. For phase analysis, the diffraction lines were fitted with pseudo-Voigt functions. A gold reference standard was used for calibration of the energy offset.

Fe-C coatings in both the as-deposited state and after annealing at 300 °C for 24 h have been prepared for transmission electron microscopy (TEM) analysis. Applying the focused-ion beam lift-out technique in a dual beam FEI Helios EBS3 microscope, samples were prepared in plan view at about half of the total thickness of the 360 μm thick Fe-C coatings. TEM investigation applying bright field imaging (BF) and selected area electron diffraction (SAED) was carried out with an accelerating voltage of 300 kV using a Joel 3000F microscope.

Microhardness measurements were performed on metallographically prepared cross sections of the exact same Fe-C coatings of the present diffraction analysis. A Future Tech Inc. FM700 microhardness tester with Vickers geometry was applied with a load of 25 g and represented data average over five measurements per sample.

Results and discussion

The EDD spectra of the as-deposited and ex-situ annealed Fe-C coatings are shown in Figure 1. Consistent with results from conventional laboratory XRD [6], the as-deposited coating mainly consists of α -iron and a second phase is indicated by one additional peak at 21.51 keV (Figure 1(a)) corresponding to a d-spacing of 0.2365 nm, which confirms our previous measurements. Although this single peak of an additional phase is reproducibly measured and also reported in literature [5,6,8], the corresponding phase analysis has not yet been unambiguously, as mentioned above (therefore, here, it is referred to ‘nameless peak’), and it is of interest to follow the evolution of this peak/phase by annealing. Figure 1(b) shows that the nameless peak remains unchanged even after annealing of 24 h at 250 °C, and its position, intensity and width are identical to the ones for the as-deposited coating. In the same temperature range, where the nameless peak still is unaffected, Fe_3O_4 (magnetite) develops (cf. Figure 1(b)). As the applied inert gas excludes oxidation from the furnace and no oxide layer has been found on the surface,

the formation of magnetite has occurred throughout the coating. This confirms that oxygen has been present already in the as-deposited coating, which agrees with the detection of oxygen by chemical analysis with glow discharge optical emission spectroscopy and electron energy loss spectroscopy, although quantification of the as-deposited oxygen concentration has not been possible yet [6]. While the oxide is detected already at 200 °C, still there is no clear indication for a carbon-containing phase (except from the vague relation to the nameless peak) and first at 250 °C, carbides of Fe₃C (cementite) are clearly detected (cf. Figure 1(b)). With further increasing temperature to 300 °C, both magnetite and cementite further evolve towards higher intensities, while the nameless peak simultaneously reduces in intensity. Although of low intensity, the nameless peak is still present after annealing at 300 °C, as indicated by the observed asymmetry of the higher intense peak of Fe₃C at about the same position (cf. Figure 1(b)). The decrease in intensity of the nameless peak, simultaneously with a significant increase in the intensities of all peaks related to both Fe₃C and Fe₃O₄ suggest that the phase related to the nameless peak contains carbon and oxygen.

[Figure 1a&1b]

To verify the phase transformations as revealed by diffraction analysis and to understand the nature and evolution of the nameless peak/phase of the as-deposited coatings, thermal analysis during isochronal annealing of both an as-deposited coating and previously isothermally annealed coatings for 24 h at 200, 250 and 300 °C has been carried out by simultaneous DTA, TGA and MS analysis. Figure 2 shows, on the example of occurring weight changes, the thermal desorption of H₂O (related to desorption of hydrogen), and the enthalpy changes, that the as-

deposited Fe-C coating undergoes four thermal events at distinct temperatures during isochronal annealing.

The first event at around 115 °C is defined by an exothermic peak (cf. Figure 2), a desorption of hydrogen and corresponding mass loss, which is related to dehydrogenation of adsorbed hydrogen originating from the electrolysis of water during the deposition process. The entrapment of hydrogen into the growing coating is typical for electrodeposition and manifests in reduced current efficiency, which indeed for the present samples amounted to 60.5 %. This atomic or molecular hydrogen can easily evaporate and, accordingly, this reaction only is measured for the as-deposited coating and not for the already annealed samples. The second event at around 275 °C (cf. Figure 2) is visible for the as-deposited sample and for samples annealed at 200 °C and 250 °C, and relates to a thermal decomposition, which is characterized by a further release of hydrogen and a mass loss. The observation that the hydrogen release in the second event is lower for the 250 °C annealed sample compared to 200 °C and not occurring after higher annealing temperature of 300 °C, indicates that the corresponding phase still is intact after isothermal annealing at 200 °C, partly decomposed after 250 °C annealing and fully decomposed at 300 °C. The precipitation of Fe₃C for samples annealed at 250 °C and 300 °C, respectively, as measured by EDD (cf. Figure 1(b)), further reveals that carbon originally is bound to the phase decomposing at the second event. As the nameless peak/phase still is recorded by EDD after isothermal annealing at 250 °C without any changes compared to its as-deposited state, the occurring thermal decomposition in the second thermal event does not seem to relate to that phase. The third event at around 360 °C (cf. Figure 2) is identified as a thermal decomposition by an exothermic reaction, a further release of hydrogen and a mass loss. This thermal decomposition at 360 °C is measured for all samples, but is much less prominent for the 300 °C

annealed sample, where only the mass loss and a release of hydrogen indicate the reaction. This could be associated with the nameless peak/phase measured by EDD, since the intensity of the peak has decreased significantly after isothermal annealing at 300 °C (cf. Figure 1b). Such a correlation would reject the hypothesis that the nameless peak originates from Fe₂C (either ϵ - or η -phase, as previously suggested [6,8]), since its transformation into Fe₃C cannot be associated with a mass loss or release of hydrogen [13]. The temperature of 360 °C is also higher than the reported transformation temperature of ϵ/η -Fe₂C to Fe₃C [13], but is in good agreement with a former study of the decomposition of ferrihydrite [14]. The suggestion of the nameless phase being a hydroxide would be supported by the observed release of hydrogen during annealing and the measured d-spacing of the nameless peak with $d = 0.2365$ nm ($E = 21.51$ keV, Figure 1) would correspond to $d_{004} = 0.234$ nm of FeOOH (ferrihydrite), although this is the only observable peak of that phase, as mentioned above. However, ferrihydrite, as the possible second phase in the as-deposited Fe-C coating, only consists of iron, oxygen and hydrogen, but not carbon. Accordingly, its decomposition would not account for the release of carbon required for the growth of Fe₃C. Instead, the carbon required for the growth of Fe₃C may originate from the phase decomposing in the second event. Accordingly, the 300 °C annealed sample has already underwent that decomposition fully, which has supplied carbon for the growth of Fe₃C, and, simultaneously, ferrihydrite related to the third event has partly decomposed and released oxygen for the growth of Fe₃O₄. The fourth event at around 505 °C (cf. Figure 2) is revealed as a small exothermic reaction for the as-deposited sample only. This event is not associated with any mass loss or release of hydrogen. The observed temperature of that event does not relate to any expected transformation of α -Fe, Fe₃C or Fe₃O₄ [15–17], but a second exothermic reaction has

been reported for ferrihydrite [14], which explains that only the as-deposited coating further evolves at that temperature.

[Figure2]

Supplementing the results from diffraction analysis and thermal analysis regarding the presence and thermal evolution of phases in the Fe-C coating, TEM reveals that the as-deposited coating is nanocrystalline. The applied plan-view investigations show average grain sizes of 15-40 nm for the as-deposited coating, as shown in Figure 3(a). These grains result in fine rings in the SAED pattern shown in Figure 3(b), which correspond to the ferrite phase, in agreement to the results from synchrotron diffraction for the as-deposited coating (cf. Figure 1). In addition to ferrite, also a uniformly occupied diffraction ring indicating magnetite Fe_3O_4 is detected, which has not been revealed by synchrotron diffraction. Based on the knowledge of co-deposited oxygen [6], the oxide may have formed during electrodeposition but with too low volume fraction for being detected by synchrotron diffraction covering a larger sample volume, but it also may indicate the challenges of preventing oxidation of ferrite during preparation, handling or storage of the thin TEM lamella. Interestingly, there are no diffraction spots matching the d-spacing of the nameless peak or other spots related to the nameless phase, which is known to be present in the as-deposited coating based on EDD (cf. Figure 1); however, both diffraction methods relate to a different measurement direction in the coating.

[Figure3]

After ex-situ annealing at 300 °C for 24 h (same sample as used for EDD), the ferrite grains are still nanocrystalline and Figure 4(a) in plane-view reveals an average size of the grains in the order of 30-50 nm. The corresponding SAED pattern (Figure 4(b)) for this annealed Fe-C

coating clearly reveals that cementite Fe_3C and magnetite Fe_3O_4 have formed during annealing. This is consistent with synchrotron diffraction results of the annealed coatings, which reveal magnetite formation already after annealing at 200 °C with nanocrystalline dimensions as indicated by the fairly broad peaks (cf. Figure 1).

[Figure4]

Microhardness measurements on cross sections of the nanocrystalline Fe-C coatings revealed high microhardness of $784 \pm 12 \text{ HV0.025}$ for the as-deposited coating. The occurring phase transformations during annealing suggest a further hardness increase. Indeed, isothermal annealing at 200, 250 and 300 °C increased the microhardness of the Fe-C coatings to $883 \pm 28 \text{ HV0.025}$ (200 °C), $957 \pm 17 \text{ HV0.025}$ (250 °C) and $1286 \pm 27 \text{ HV0.025}$ (300 °C). The absence of significant grain growth of ferrite and the evolving oxide and carbide phases being of small dimensions and distributed within the whole coating according to the origin of carbon and oxygen from the electrodeposition process, essentially contribute to the observed increase of the hardness by annealing.

Conclusion

The applied complementary methods of microscopy, diffraction analysis and thermal analysis strongly support the understanding of both the as-deposited Fe-C coatings as well as their evolution during annealing. The results reveal the important role of carbon, oxygen and hydrogen, which previously have been detected in as-deposited coatings, but are challenging to be quantified by chemical analysis. The origin of carbon, oxygen and hydrogen strongly relates to the deposition process with citric acid as an additive and complexing agent in the iron sulphate electrolyte. Although mainly the co-deposition of carbon has been intended for the electrodeposited Fe-C coatings, the formation of phases during deposition and the occurring phase transformations during annealing are clearly governed by more than just carbon and iron.

The synergetic effect of all these elements together with the nanocrystalline nature of the coatings explain the excellent mechanical properties of the electrodeposited Fe-C coatings and make them a favourable candidate for wear resistant surfaces.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Figures

Figure 1: Energy-dispersive diffraction spectra of Fe-C coatings: as-deposited (black) and after isothermal annealing for 24 hours at 200 °C (red), 250 °C (blue) and 300 °C (green). (a) Overview. Note: The peak at 33.61 keV corresponds to an escape peak from α -211. b) Magnified region to indicate phase transformations, see details in the text.

Figure 2: Thermal analysis by DTA, MS and TGA for Fe-C coatings: as-deposited (black) and after isothermal annealing for 24 hours at 200 °C (red), 250 °C (blue) and 300 °C (green). The signal from H_2O^+ is used as a marker for the desorption of hydrogen, since hydrogen released from the sample will react with the oxygen impurity in the argon ($2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$) and produces an increased signal of H_2O . The numbers 1 to 4 corresponds to the thermal events described in the text.

Figure 3: TEM micrograph (a) and corresponding selected area electron diffraction pattern (b) of the as-deposited Fe-C coating in plan-view.

Figure 4: TEM micrograph in plan view (a) and corresponding selected area electron diffraction pattern (b) of the Fe-C coating ex-situ annealed at 300 °C for 24 hours.