Electrodeposition of FeCrNi and FeCr alloys and influence of heat treatment on microstructure and composition

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Abstract. The electroplating of iron-chromium and iron-nickel-chromium layers is an economic alternative to mild steel and hard chrome layers from chromium (VI) electrolytes. Iron-chromium and iron-nickel-chromium layers were electrodeposited using an environment friendly chromium (III) electrolyte. The layers were heat-treated at different temperatures (150 °C, 300 °C, 450 °C and 600 °C) in order to determine the temperature at which recrystallization takes place, which phases are formed and to study the influence on the element content. The phase analysis was conducted by X-ray diffraction, the chemical composition and the microstructure were characterized by the scanning electron microscopy. Both layer systems show an X-ray-amorphous structure that begins to recrystallize at a temperature of 450 °C. From a heat-treatment temperature of 600 °C, the organic additives decompose and the oxygen forms chromium oxide with the chromium.

1. Introduction
Since 2017, the use of hexavalent chromium is banned by the European Union regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) [1]. In the past, chromium layers were usually electroplated from these chromium compounds. Therefore, there is a carcinogenic and mutagenic risk during the deposition process or if chromium (VI) compounds end up in the environment and groundwater [2]. The advantage of hard chrome coatings, which are deposited from hexavalent chromium, lies in their good corrosion resistance, high hardness, wear resistance, and constant shine [3]. That is why electroplated hard-chrome layers have been used on a large scale in countless products for many years by the industry. Due to REACH, it is of great importance to find alternatives to hard chrome as quick as possible.

A potential substitute for hard-chrome coatings could be stainless steel. The advantage of these iron-nickel-chromium bulk alloys is their good corrosion resistance, especially against acids. Due to their biocompatibility, they are often used in the food industry, in systems for heat treatment and in steam generators. Because of this purpose of high-temperature applications, it is of interest to examine the iron-nickel-chromium and iron-chromium alloys with regard to their behaviour under the influence of heat [4]. However, bulk stainless steel is an expensive material. Electroplating is an economical process by which stainless-steel coatings can be applied to less expensive materials like mild steel. The excellent surface properties are retained while the material costs are reduced.

So far, only a few studies have been carried out on the galvanic deposition of stainless steel. The studies investigated the bath composition of the electrolyte and its influence on the layer composition and the microstructure of the deposited layers [5-8]. There has only been minor research activity in one study from 2019, where iron-nickel-chromium coatings are examined precisely concerning their structure and the influence of heat treatment at a temperature of 600 °C on the microstructure of the coatings. It was found that the deposited layers in the initial state have an amorphous α-Fe structure. The iron and nickel exist mainly in metallic form with small amounts of chromium oxide and the heat-treated samples have larger cracks in relation to their counterparts in the untreated state [5]. In
comparison, stainless-steel bulk alloys have a grain size of around 50 μm [9]. Furthermore, in addition to large amounts of oxygen, carbon and hydrogen, the researchers also found small amounts of nitrogen in the layers. The heat treatment reduced the carbon and hydrogen content in the layer. In addition, a crystallite size of 20–25 nm was measured. From this, it was concluded that the high carbon and hydrogen concentration is mainly responsible for the amorphous character and that the annealing outgases the only weakly bound elements. The new structure, which arose after the heat treatment, is characterized by a nanocrystalline γ-Fe phases with a few amorphous chromium oxide phases [5].

Based on the work of Bertero et al. [5], the influence of the heat treatment on the structure and the element content will be investigated further in this paper. It is now necessary to investigate if these effects already occur at lower temperatures. For example, this is the case with electrodeposited copper layers, which recrystallize at significantly lower temperatures than it is the case with bulk materials due to their high internal energy and defect density [10]. A reduction of internal stresses and the formation of new grains through heat treatment can increase the strength of the layers while at the same time increase the ductility.

2. Experimental details

2.1. Preparation of the samples

In order to study the influence of heat treatment on element composition and microstructural evolution, two chromium (III) electrolytes were used for the production of iron-nickel-chromium and iron-chromium layers. The coatings were electroplated on nickel-brass tubes with a diameter of 1 cm. At first, the tubes were cleansed in an ultrasonic bath with ethanol. After this treatment, the substrate was etched by concentrated sulphuric acid for 2 minutes and rinsed thoroughly in deionized water. A platinum-plated titanium anode was used for electrodeposition. The electrolyte solutions were magnetically stirred at 100 rpm. The temperature of the electroplating baths was stabilized by a tempered water bath.

The iron-nickel-chromium coatings were deposited at a current density of 3.5 A/dm² under direct current. The composition of the glycine-based electrolyte for the iron-nickel-chromium coatings are chromium (III) chloride, nickel (II) chloride, iron (II) chloride, glycine, ammonium chloride, sodium chloride and boric acid. In order to give the thermodynamic equilibrium setting in the electrolyte sufficient time during the production of the electrolyte, a multi-stage process of component addition must be followed. At first, the chromium (III) chloride and the glycine has to be dissolved in deionized water. During the process of complex formation, the solution was heated to 80 °C for 30 minutes. After the solution cooled down to 25 °C, the remaining components were added. The pH value of the electrolyte was adjusted to 1 with hydrochloric acid. The deposition took place at a temperature of 35 °C.

The iron-chromium coatings were performed by using pulsed-current electroplating. A pulse-current source POWER-PULSE pe86CB-40-10-50-S/GD (platting electronic GmbH, Sexau, Germany) was used. The electrolyte consists of Cr(III) and Fe(II) chlorides, boric acid, a carboxylic acid, amide complexing agents, alcohol, a reducing agent, brighteners and wetting agents. The process of the electrolyte production was performed in two steps. In the first step, only the metal salts were completely dissolved in deionized water with boric acid and complexing agent, and in the second step the other organics were added and the pH was adjusted. The pH value of the electrolyte was set to a range between 1.5 and 1.6 with hydrochloric acid. Layers were deposited at a temperature of 30 °C. They were produced at a pulse-current density of 97 A/dm². The pulsed-current plating took place at a frequency of 109 Hz and an on–off ratio of 3:6.

From each electrolyte, a layer was deposited and cut into different samples. Each sample has a dimension of 0.5 cm x 0.5 cm. The samples were heat-treated for one hour at 150 °C, 300 °C, 450 °C or 600 °C, or 24 hours at a temperature of 450 °C. A Torvac vacuum furnace (Torvac, St. Paul, MN, USA) with a vacuum between 10⁻² mbar and 10⁻¹ mbar was used during the heat treatment. Two investigation methods (listed in chapter 2.2) were carried out to understand the microstructural changes during heat treatment of the iron-nickel-chromium and iron-chromium electroplated films and the element content, the content of impurities in particular, which is caused by the use of organic additives. For the scanning electron microscope examination, the samples were embedded conductively. The embedded samples were ground, polished and thoroughly cleaned under the influence of ultrasound.
2.2. Layer characterization

Firstly, the layer composition with regard to its average over the entire surface and its course over the layer thickness was examined. The elements of the layers were determined with an EDAX GENESIS energy-dispersive X-ray spectroscopy (EDXS) spectrometer at a LEO1455VP (Zeiss, Oberkochen, Germany) scanning electron microscope. The acceleration voltage was 25 kV. The integration time per element analysis was two minutes. The layer compositions were determined by area analysis and by point analysis as shown in figure 1 to determine the element content of the layer as a function of the depth under the surface. In addition, images were taken using scanning electron microscopy to identify microcracks.

![Figure 1](image)

**Figure 1.** Method of point analysis (red) and method of area analysis (white) for EDXS measurements.

The phases and the existence of crystallites of the deposited coatings were analysed by the X-ray diffraction (XRD, point measurements) with a D8 Discover (Bruker AXS, Billerica, MA, USA) with Co Kα radiation (tube parameters: point focus, 40 kV, 40 mA), polycap optics, a pinhole aperture with a diameter of 0.5 mm, and a 1D detector LYNXEYE XE with a step size of 0.02° and 17.8 s/step (overall measurement time per sample: 8.9 hours).

3. Results and Discussion

3.1. Element composition

By using EDXS, the composition of the iron-nickel-chromium and iron-chromium layers was determined (mass fractions w). The elemental compositions for all samples were measured by area analysis, including the metallic species iron, chromium and nickel and the contamination by oxygen, carbon and phosphorus, and are listed in table 1. The representative individual measured mass values represent the element content over the entire layer thickness. It is noticeable that the carbon as well as the oxygen content are in a similar range for both layer systems.

| Sample  | wCr (%) | wFe (%) | wNi (%) | wC (%) | wO (%) | wP (%) | s (µm) |
|---------|---------|---------|---------|--------|--------|--------|--------|
| FeCrNi  | 15      | 50      | 19      | 6      | 10     | <0,1   | 19     |
| FeCr    | 21      | 58      | <0,1    | 4      | 9      | 8      | 29     |
Figure 2. EDXS measurements of the impurities over the entire layer surface of the iron-nickel-chromium (left) and iron-chromium coatings (right).

As seen in the profiles of the impurity contents over the entire layer cross-section in figure 2, there is no proof for diffusion of the organic elements during the heat treatment, as it was observed by Bertero et al. as well [5]. The reason for this may be small differences in the compositions of the initial states of the individual samples. Therefore, a diffusion of carbon, oxygen and phosphorus through heat treatment cannot be excluded. It is interesting to note that based on the course of the curves of the iron-nickel-chromium samples for all heat treatments, the oxygen and carbon contents possess an almost constant ratio. This indicates that the two elements are largely present in chemical compounds in the layers. Furthermore, one can assume that this compound originates from the used additives, which are incorporated into the layer. Compared to the studies by Bertero et al., the oxygen content of the as-deposited iron-nickel-chromium layers measured in this study is around \( w_0 = 4 \% \) higher. The carbon content of around \( w_c = 6.4 \% \) is in the same range. After the heat treatment of 600 °C of the iron-nickel-chromium layers a oxygen content of \( w_0 = 8.2 \% \) and a carbon content of \( w_c = 2.4 \% \) were measured [5].

In this investigation such a decrease in the carbon content as a result of heat treatment could not be proven. The curves of the iron-chromium layers show a different ratio. The oxygen and phosphorus contents possess an almost constant ratio. Up to a heat-treatment of 300 °C the carbon content is nearly constant. However, the carbon content of the sample heat-treated at 450 °C is \( w_c = 2 \% \) higher. The value of the heat-treatment at 450°C, 5 µm can be seen as a measurement deviation.

Figure 3. EDXS measurements of the carbon content (left) and the oxygen content (right) of the iron-nickel-chromium layers. The measuring points show the distance to the substrate.

In the figure 3, \( s \) means the layer thickness starting from the substrate. The illustrated data are representative individual measured values. This also applies to figures 4 and 5. Figure 3 shows that the oxygen contents over the layer thickness are approximately the same for all heat-treatment stages. It is noticeable that the carbon content near the substrate and the surface of the heat-treated layers is higher.
than in the middle of the layer (area between 5 µm and 14 µm). The samples at room temperature are an exception. A possible cause is that the carbon diffuses during the heat-treatment to the rim of the layers. As with the area analysis, there is no significant influence of the heat treatment on the total carbon and oxygen contents in the layers.

![Figure 4](image1.png)

**Figure 4.** EDXS measurements of the carbon content (left) and the oxygen content (right) of the iron-chromium layers. The measuring points show the distance to the substrate.

The curves in figure 4 show that the carbon content of the iron-chromium layers seems to increase due to the heat treatment. The reason for this trend could be the inhomogeneous composition along the entire sample because of a poor electrolyte throwing power and uneven incorporation of electrolyte additives. A comparison of the two layers highlights that the iron-chromium layers show a trend towards fewer impurities with increasing distance from the substrate, while the iron-nickel-chromium-layers show an indifferently incorporation of carbon and oxygen. Consequent one can deduce a strong influence of the used individual electrolyte additives on the degree and distribution of the impurities. However, all of the layers have in common that the carbon is significantly higher near the substrate than near the surface. From this, one can conclude that in the beginning, more carbon is co-deposited. Above a distance from the substrate of approximately 8 µm, it can be observe that the amount of carbon is significantly less but remains constant. Similarly, the amount of oxygen in the layers, which is around \( w_O = 10\% \) near the substrate and nearly constant above a layer thickness of 8 µm (between \( w_O = 7.5\% \) and \( w_O = 9\% \)). This indicates also a diffusion of oxygen during the heat-treatment.

![Figure 5](image2.png)

**Figure 5.** EDXS measurements of the phosphorus content of the iron-chromium layers. The measuring points show the distance to the substrate.
Considering figure 5, the phosphorus content shows the opposite trend to the carbon and oxygen contents. Looking at the figures, the phosphorus content is lowest at the beginning of the deposition and that more phosphorus is incorporated during the further the layer grows. The largest amount of phosphorus is found near the surface.

3.2. Phase analysis

Figure 6 shows that an X-ray amorphous or nanocrystalline structure for RT, 150 °C and 300 °C exists for the iron-chromium layers. An iron-chromium austenite phase only forms after a heat treatment at 450 °C for one hour. Iron phosphide and cubic chromium-iron phases (austenitic) are forming by heat treating samples for 24 hours at a temperature of 450 °C. At a temperature of 600 °C, chromium oxide phases are added. The large peak at $2\theta = 30^\circ$ can most likely be assigned to carbon that is incorporated into the lattice. This hypothesis is supported by an increase of the peak intensity due to the heat treatment and the longer holding time. Based on the previously discussed course of the oxygen content over the layer thickness, chromium oxides form at 600 °C. A chromium-oxide formation due to oxygen from the atmosphere can be ruled out based on these curves. The small peaks marked with the number 1 derive from the substrate.

![Figure 6. XRD measurements of electrodeposited iron-chromium layers in dependence of the heat-treated condition.](image)

For the iron-nickel-chromium layers shown in figure 7, an X-ray amorphous or nanocrystalline structure for RT, 150 °C and 300 °C can be observed. The individual visible small peaks originate from the substrate. A monoclinic iron-nickel-chromium phase and an austenitic lattice can only be detected above a heat-treatment temperature of 450 °C. It is noticeable that the heat-treatment processes at 450 °C for one hour and for 24 hours are difficult to distinguish from each other. It can be concluded that the duration of the treatment has no influence on the type of phases, but the slightly reduced peak width indicates a further-progressed recrystallization of these phases. At a heat-treatment temperature of 600 °C, pronounced peaks appear which probably indicate grain growth. Bertero et al. also found that the annealing caused recrystallization. The mean crystallite size is projected at 20 - 25 nm [5]. The heat treatment probably leads to recrystallization of the iron-nickel-chromium austenite and the chromium oxide. Furthermore, chromium-oxide peaks are present at a heat-treatment temperature of 600 °C. Presumably, these compounds of carbon and oxygen only decompose above a temperature of 600 °C.
and the oxygen forms chromium oxide with the chromium. The large peak at \(2\theta = 30^\circ\) is also seen for the iron-nickel-chromium layers. Most likely, this can be assigned to carbon that is incorporated into the lattice. The peaks with the number one correspond to the substrate.

![XRD measurements of electrodeposited iron-nickel-chromium layers in dependence of the heat-treated condition.](image)

**Figure 7.** XRD measurements of electrodeposited iron-nickel-chromium layers in dependence of the heat-treated condition.

### 3.3. Microstructure

The deposited iron-chromium-nickel layers and iron-chromium layers show a uniform and bright surface. To investigate the tightness of the layers, the results of the investigations of the detection of microcracks are presented in figure 8. Clearly, it shows that heat treatment increases the number and the size of the microcracks in the iron-chromium layer as well as in the iron-nickel-chromium layers. The cracks run through from the surface to the substrate. This indicates an increase in the internal stresses of the layers due to heat treatment. When comparing the as-deposited iron-nickel-chromium samples with the ones that were heat-treated at 300 °C or 450 °C, it can be seen that the cracks are getting more pronounced with rising heat-treatment temperature. This observation can not be made for the iron-chromium samples. Previous similar work reports that cracks are only observed in layers thicker than 5 mm. However, the crack formations occurred a short time later or in the next few days after exposure to the atmosphere after the deposition [8]. It is assumed that the galvanic deposition of chromium (III) alloys creates high overpotentials, which lead to a rise in the pH value at the cathode and the incorporation of chromium hydrides. These chromium hydrides are hexagonal close packed (hcp) and unstable. Over time, they decompose into metallic chromium, which is body-centered cubic (bcc). During this phase transition, the volume of the chromium shrinks by approximately 15 %, which results in a cracking of the layer [5]. This process was accelerated and reinforced by a heat treatment, which resulted in increased crack growth and widening of the cracks. The results of this investigation support this theory because recrystallization only starts at a temperature of 450 °C. Therefore, the recrystallization does not contribute to crack growth at lower heat-treatment temperatures.
4. Conclusions
Galvanic depositions of iron-nickel-chromium and iron-chromium were examined. Heat treatments were carried out on these deposits in order to investigate their influence on the microstructure and the layer composition as well as the crystallinity of the layers. The appearance of the electrodeposited layers shows a uniform and bright surface with a silver-gray color which is suitable for decorative applications. The heat treatments had a negative effect on crack growth. Therefore, one can assume that this does not relieve any internal stresses in the layers, but rather intensify them. However, these internal stresses could have positive effects on wear behaviour and result in an increase in hardness. When considering the element analyses in combination with the results of the crystallinity, we assume that the additives used in the iron-nickel-chromium and the iron-chromium layers are incorporated into the layer and decompose at a temperature of about 600 °C. The released oxygen along with the chromium form chromium oxide. Moreover, there is no evidence that the heat treatment leads to a reduction of the co-deposited organic compounds. High proportions of carbon and oxygen were measured in both layers, the origin of which can be traced back to the additives used and the formation of passive layers due to the influence of the atmosphere can be largely excluded. X-ray amorphous layers were obtained for the layers at room temperature and the heat treatment at 150 °C and 300 °C. It has been observed that recrystallization already starts at a temperature of 450 °C. An increase in the holding time probably leads to a progressive recrystallization and thus improves ductility despite massive internal stresses. On the basis of future wearing and hardness tests it is possible to examine the influence of heat treatment on the tribological properties of the layers. Further investigations can prove if an increase in the holding time also enables a reduction in the amount of the co-deposited organic compounds.

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Figure 8. Scanning electron microscopy micrographs of cross-sections of electrodeposited a) Iron-chromium coatings and b) Iron-nickel-chromium coatings.
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References
[1] Alfort H J 2016 Wann kommt das Verbot für Chrom(VI)? Journal für Oberflächentechnik 56 68-71
[2] Pellerin C and Booker S M 2000 Reflections on hexavalent chromium: health hazards of an industrial heavyweight Environmental Health Perspectives 108 A402-A407
[3] Schade C and Käszmann H 2013 Galvanisch abgeschiedenes Chrom - Ein Blick auf die mechanischen Eigenschaften WOMag 1-7
[4] Kalweit A, Paul C, Peters S and Wallbaum R 2006 Handbuch für Technisches Produkt design (Berlin Heidelberg: Springer Verlag)
[5] Bertero E, Manzano C V, Pellicer E, Sort J, Ullig R M, Mischler S, Michler J and Philippe L 2019 Green Cr(III)-glycine electrolyte for the production of FeCrNi coatings: electrodeposition mechanisms and role of by-products in terms of coating composition and microstructure RSC Advances 9 25762-25775
[6] Bertero E, Manzanoa C V, Bürki G and Philippe L 2020 Stainless steel-like FeCrNi nanostructures via electrodeposition into AAO templates using a mixed-solvent Cr(III)-based electrolyte Materials and Design 190 1-7
[7] Hasegawa M, Yoon S, Guillonneau G and Zhang Y 2014 The electrodeposition of FeCrNi stainless steel: microstructural changes induced by anode reactions Physical Chemistry Chemical Physics 16 26375-26384
[8] Philippe L, Heiss C and Michler J 2008 Electroplating of Stainless Steel Chem. Mater. 20 3377-3384
[9] Baldenebro-Lopez R J, Gomez-Esparza C D, Corral-Higuera R, Arredondo-Rea S P, Pellegrini-Cervantes M J, Ledezma-Sillas J E, Martinez-Sanchez R and Herrera-Ramirez J M 2015 Influence of Size on the Microstructure and Mechanical Properties of an AISI 304L Stainless Steel - A Comparison between Bulk and Fibers Materials 8 451-461
[10] Brongersma S H, Richard E, Vervoort I, Bender H, Vandervorst W, Lagrange S, Beyer G and Maex K 1999 Two-step room temperature grain growth in electroplated copper,” Journal of Applied Physics 86 3642-3645