Quantitative evaluation of global and local chromium contents with the EPR test on ferritic and martensitic stainless steels

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Abstract. The cause of localised corrosion phenomena in stainless steels is often related to the element chromium, which is essential for the formation and resistance of the passive layer. A lower than nominally stated content of chromium occurs when the element is highly concentrated and locally bound in chromium-rich phases or precipitates, mostly carbides, and thus locally or globally absent for passivation. The method of electrochemical potentiodynamic reactivation (EPR) is uniquely suited to demonstrate the effect of chromium depletion on the passivation. Here, the steel surface is initially active in sulfuric acid and passivation is achieved by external dynamic polarization. After passivation, the polarization direction is reversed and in chromium-depleted areas a reactivation takes place, which is detected by an increase in current. The detection limit for a reduced chromium content depends largely on the strength of the sulfuric acid used in the EPR test and the polarization speed. The relationship between the sulfuric acid concentration and the electrochemical parameters from the EPR test is shown here using the example of ferritic Fe-Cr alloys with graded Cr contents in the range of approx. 6 to 18 %. From the passivation and reactivation current densities of the EPR data, models for the detection of global and local chromium contents (detection limits) are derived. The developed models are applied to the martensitic stainless steel X20Cr13 in different heat treatment conditions and the influence on the distribution of chromium in the microstructure, which is responsible for the passivation and thus the corrosion resistance, is shown.

1 Introduction

In ferritic and martensitic stainless steels, the element chromium is the decisive alloying element for corrosion resistance, as it enables the surface to be passivated. The so-called resistance limit is a Cr content of at least 10.5 %, above which a passive layer forms under mild atmospheric conditions, which protects the iron-based material from corrosion and the formation of rust in a humid atmosphere. Ferritic stainless steels have chromium contents of more than 12 % (more frequently between 16 and 18 %) and are low in carbon (< 0.1 % C). Typical representatives of martensitic stainless steels are alloyed with 13 to 15 % (more rarely 17 %) chromium and, in contrast to the ferritic stainless steels, have increased carbon contents of more than 0.1 % so that the steel can be hardened by martensitic phase transformation. Both types of steel are almost free of nickel and therefore form a ferritic or martensitic matrix. As chromium is decisive for corrosion resistance, special attention must be paid to establish an evenly distribution and sufficient concentration in the solid solution. Phases rich in chromium (e.g. chromium carbides) can locally concentrate and bind larger amounts of chromium, so that chromium is no longer...
supporting the passivation of the matrix. Chromium is removed from the solid solution during carbide formation and the chromium content is often reduced in the immediate vicinity of chromium-rich precipitates.

For the experimental proof of chromium depletion and the resulting decrease in corrosion resistance, several corrosion tests in specific media exist, such as the various tests according to ASTM A 262, Practice A-E [1]. These tests are carried out in strong acids and at elevated temperatures and have the disadvantage that they are time-consuming, destructive and do not allow an accurate quantification of chromium depletion. In industrial practice, they are nevertheless frequently used when only simple yes/no statements on the corrosion resistance are required.

Significantly faster, more accurate and more meaningful are electrochemical methods, such as the EPR test (electrochemical potentiodynamic reactivation), which is standardized in ISO 12732 as a double-loop method [2] and is based on the work of Cihal and numerous other colleagues, which are summarized in [3]. The same procedure is described in ASTM G108-94 [4]. The parameters recommended in ISO 12732 are mainly suitable for high alloyed austenitic and duplex stainless steels. Test solutions with H$_2$SO$_4$ concentration in the range of 0.5 to 2.5 mol/L and addition of potassium thiocyanate (KSCN) between 1 and 50 mmol/L as well as a polarization rate between 2 and 15 V/h are listed. For the most frequently used austenitic stainless steel 1.4301 (AISI 304) with approx. 18 % chromium, a test electrolyte with 0.5 mol/L H$_2$SO$_4$ and 10 mmol/L KSCN and a polarization rate of 6 V/h (1.67 mV/s) is recommended. This approach has also proved successful in detecting sensitization in duplex stainless steel [5]. The electrolytes or experiment process are often further varied to study alloys with higher or lower alloy contents or to cause selective dissolution at special phases or precipitates.

For ferritic stainless steels of type 1.4016 (AISI 430) with 17 % Cr, Sidhom et al. [6] have varied the test parameters very extensively to find suitable conditions for the detection of sensitization. The optimum test condition they determined was 3 mol/L H$_2$SO$_4$ without further addition of an activator and 2.5 mV/s as polarization rate. However, the distance between the experiments parameters was chosen very broadly in this study (0.1 to 6 mol/L H$_2$SO$_4$, 0.5 to 5 mV/s polarization rate) and it is therefore difficult to understand how an optimum could be determined from the results. Kim et al. used a concentration of 0.14 mol/L H$_2$SO$_4$ with 2.5 mmol/L KSCN and 1.67 mV/s as polarization rate for EPR experiments on a ferritic stainless steel X2CrTi12 (1.4512, AISI 409L), but did not specify why these parameters were chosen in this way [7]. Kumar et al. also vary the test parameters of the EPR test to investigate intergranular corrosion on heat-treated martensitic stainless steels [8]. The gradations of the H$_2$SO$_4$ concentration between 0.03 and 0.25 mol/L are quite reasonable. The optimum is a concentration of 0.03 mol/L H$_2$SO$_4$ without activator and a polarization rate of 1.67 mV/s. EPR investigations on martensitic stainless steels have been conducted and published at the Otto-von-Guericke University since 2013 [9-11]. The use of a 0.1 mol/L H$_2$SO$_4$ solution without further additives and a polarization rate of 2 mV/s for investigations at laboratory temperature (22 °C) with the use of top-mounted measuring cells has proved to be successful.

Martensitic stainless steels, with 12-15 % chromium, are closer to the resistance limit than most other stainless steels and have a significantly higher carbon content. Chromium-rich carbides can bind significant amounts of chromium. It is therefore important to know how much chromium is available in the solid solution for passive layer formation, which is essential for the corrosion protection ability. This "available" chromium content for corrosion protection cannot be determined by atomic emission spectroscopy, because chromium carbides are also ionized, and this proportion is therefore determined analytically in an integral way. Analytical EDS measurements on the other hand do only characterize the small areas of the microstructure with a broad interaction volume of several microns. It can therefore be assumed that significantly less effective chromium is present in chromium steels containing carbon, especially in the soft-annealed state with a high fraction of carbides within the microstructure. Only through austenitisation at typically 1050 °C are the carbides dissolved in the austenite due to the increased carbon solubility. The chromium of the dissolved carbides is distributed homogeneously in the solid solution by diffusion and this homogeneous element distribution is "frozen" by subsequent
quenching [12]. Subsequent tempering at excessively high temperatures and for long periods can lead to the formation of new chromium rich carbides and reduce the content of "available" chromium in the solid solution. Therefore, in the case of martensitic stainless steels, not only the effect of chromium depletion in the immediate vicinity of carbides is significant, but also the "available" content of chromium for passive layer formation and its resistance.

The aim of this study was to determine whether the EPR test could be used to quantify the "available" chromium content in the matrix and at the same time the locally reduced chromium content in the immediate vicinity of the carbides. The metrological background of the so-called "degree of sensitization" (DOS) in the standardized EPR test is based on the ratio of the reactivation and passivation current densities. It is assumed that the reactivation current results only from active metal dissolution of the sensitized portion of the surface and that the dissolution kinetic is always the same. The rest of the surface in the experiment remains passive and its share in the total current is neglected. The reactivation of the sensitized areas, however, depends on the acid concentration and the exposure time of the acid (and thus the polarization rate) and, of course, the local chromium content. Therefore, the basic idea of this work is to use the chromium and acid-dependent passivation and reactivation for the determination of the "available" chromium content as well as to develop a detection limit for the degree of local chromium depletion by a specific variation of chromium content and acid concentration in the EPR test. The model generated by the investigations was tested on the martensitic stainless steel X20Cr13 in different heat treatment states.

2 Materials and Experimental procedures

2.1 Materials

To produce Fe-Cr alloys with chromium contents of 6 to 18 %, samples were prepared in an arc melting furnace (Compact Arc Melter MAM-1, Edmund Buehler GmbH). The different chromium contents were produced by mixing flakes of pure (Armco) iron, 1.4003 (X2CrNi12) and 1.4509 (X2CrTiNb18). This results in slightly varying contents of Ni, Mn and Si. The melting chamber was previously evacuated three times and flushed with argon to minimize oxidation during melting. Approximately 20 grams of each reference alloy were melted twice in the arc, which then solidified on a water-cooled copper plate. The chemical composition of all reference alloys was determined by atomic emission spectrometry. The main alloying and accompanying elements are listed in Table 1.

| Element | Cr | Ni | Mo | Mn | Si | N | C | P | S |
|---------|----|----|----|----|----|---|---|---|---|
| 5.8 %   | 5.26 | 0.20 | 0.01 | 0.59 | 0.20 | 0.008 | 0.016 | 0.009 | 0.004 |
| 7.3 %   | 7.32 | 0.28 | 0.01 | 0.78 | 0.28 | 0.005 | 0.019 | 0.011 | 0.003 |
| 9.3 %   | 9.34 | 0.36 | 0.01 | 0.99 | 0.37 | 0.009 | 0.025 | 0.013 | 0.002 |
| 11.2 %  | 11.19 | 0.43 | 0.01 | 1.17 | 0.44 | 0.007 | 0.029 | 0.015 | 0.002 |
| 13.6 %  | 13.56 | 0.33 | 0.02 | 0.90 | 0.46 | 0.019 | 0.025 | 0.016 | 0.002 |
| 15.8 %  | 15.80 | 0.25 | 0.03 | 0.68 | 0.49 | 0.015 | 0.029 | 0.020 | 0.002 |
| 17.4 %  | 17.36 | 0.18 | 0.03 | 0.48 | 0.49 | 0.024 | 0.022 | 0.018 | 0.002 |
| 18.0 %  | 17.96 | 0.16 | 0.03 | 0.42 | 0.51 | 0.023 | 0.025 | 0.019 | 0.002 |

The reference alloys were then homogenized at 1050 °C for 30 minutes and quenched in water. All reference alloys were then annealed at 800 °C to convert the martensitic structure into ferrite at low chromium contents (< 10 %). The samples were then cold rolled to 50 % of their initial height and...
annealed again at 800 °C for 1 hour to achieve a crystallised ferritic microstructure. The steel X20Cr13, with the chemical composition listed in Table 2, was used for further investigations.

Table 2. Chemical composition of the investigated material X20Cr13 [12].

| Element | Composition |
|---------|-------------|
| Fe      | bal. 0.23   |
| C       | 13.3        |
| Cr      | 0.02        |
| Mo      | 0.01        |
| N       | 0.02        |
| V       | 0.1         |
| Ni      | 0.29        |
| Si      | 0.33        |
| Mn      | 0.02        |
| Cu      | 0.025       |
| P       | 0.001       |

The steel X20Cr13 was examined in the soft-annealed delivery condition and two hardened and differently tempered conditions. For hardening, sheet metal samples (35 x 35 x 2 mm) were austenitized for 15 min at 1050 °C and quenched in water. One sample was tempered for 2 h at 200 °C and the other sample for 2 h at 500 °C. A clearly different corrosion behaviour is to be expected in the three conditions due to the content of free chromium in the solid solution and the effect of chromium depletion by carbides precipitation.

2.2 EPR-testing
To carry out the EPR tests, the samples were freshly ground in advance (wet grinding with abrasive paper of appropriate grain sizes), rinsed with water and ethanol, dried and then covered with a perforated (Ø 14 mm) foil so that a defined and always equally large area (1.54 cm²) of the sample is exposed to the test electrolyte. An acrylic glass tube of slightly larger diameter with a silicon sealing ring was placed on the perforated foil and clamped so that the test electrolyte cannot leak out after the measuring cell has been filled. Immediately after filling the cell with approx. 4 mL test solution, the measuring electrodes were positioned in the solution directly above the sample surface and the measurement was started. A saturated (3 M KCl) Ag/AgCl electrode was used as reference electrode (reference potential +197 mV SHE). As counter electrode an electrode of Ti/Ti mixed oxide grid with a surface that is approx. 5 times larger than the working electrode was used so that the currents can flow unhindered and without necessary compensation of a IR drop.

A series of electrochemical parameters can be obtained from an EPR test (double loop), which can be used to understand the influence of various experimental factors on the passivation and the resistance of the passive layer. Figure 1 shows schematically which electrochemical parameters were determined from an EPR test.

![Figure 1. Course of an EPR curve with marking of the determined electrochemical characteristic values.](image-url)
Usually the passivation and reactivation current densities ($i_{\text{pass}}$, $i_{\text{reac}}$) or the corresponding charge values ($q_{\text{pass}}$, $q_{\text{reac}}$) are used to calculate the degree of sensitization (DOS [%] = 100 * $i_{\text{reac}}$ / $i_{\text{pass}}$). Due to the ratio of the two current densities, this value is area-independent and therefore less sensitive if the area is unknown or cannot be precisely maintained. Nevertheless, important findings can be derived from the values of current densities alone, which is why a constant and precise measuring area is indispensable for experimental implementation.

2.3 Designed experiments and evaluation

In order to clarify how great a possible influence of the sample pre-treatment and the polarization speed is on the results of the EPR test, the steel X20Cr13 was examined in the soft-annealed state and the preparation was carried out with different grinding papers, which lead to differently rough surfaces. Grinding papers with grits of 180, 320 and 500 were used to ground the samples under running water.

This resulted in average $R_a$ values of 0.18 µm, 0.12 µm and 0.06 µm and $R_z$ values of 1.7 µm, 1 µm and 0.54 µm. The polarisation rate was varied with 1, 2 and 4 mV/s. The sulfuric acid concentration was kept constant at 0.1 mol/L for these experiments. The full-factorial and thus orthogonal experiment plan comprised 3 x 3 = 9 experiments and was conducted randomly with two repetitions.

To study the interaction of acid concentration and chromium content, the ferritic Fe-Cr alloys, described under 2.1, with eight graded chromium contents from 5.3 to 18 % were used. The sulphuric acid concentration was varied in gradations of 0.01, 0.0316 and 0.1 mol/L. The samples were uniformly wet ground with 500 grit paper, then dried and measured immediately. The polarization rate was 2 mV/s. The full-factorial and thus orthogonal experimental design comprised 8 x 3 = 24 experiments and was conducted randomly with two repetitions. Test points at 9.3 and 11.2 % chromium were repeated 3 to 4 times, as this is the content where reactivation changes most.

Furthermore, tests were carried out on the steel X20Cr13 in different heat treatment conditions (see 2.1). The sulphuric acid concentration was varied in gradations of 0.01, 0.0316 and 0.1 mol/L. The samples were uniformly wet ground with paper of grain size 500, then dried and measured immediately. The polarization rate was 2 mV/s. The full-factorial and thus orthogonal experimental design thus comprised 3 x 3 = 9 experiments and was conducted randomly with three repetitions.

The statistical evaluation of the influencing factors from all designed experiments was performed with simple regression models with a "standard least squares" personality.

3 Results

3.1 Influence of roughness and polarization rate

The influence of the polarization rate on the course of the EPR curves is exemplarily shown in Figure 2. The height of the passivation current density increases slightly, but especially the reactivation is different in its height and position on the potential axis.
Figure 2. Examples of cyclic polarization curves from EPR tests on the steel X20Cr13 (soft-annealed state, grit 320) in 0.1 mol/L H₂SO₄ solution, variation of polarization rate: 1, 2 and 4 mV/s.

The evaluation of the EPR curves allows conclusions about the influence of grit size and polarization rate on the characteristic values of the EPR test shown in Figure 3.

| Grit | 180 | 320 | 500 |
|------|-----|-----|-----|
| ipass [mA/cm²] | 8 | 6 | 2 |
| ireac [mA/cm²] | 4 | 2 | 1 |
| Epass [mV] | 7 | 5 | 3 |
| Ereac [mV] | 4 | 2 | 1 |
| DOS [%] | 10 | 8 | 6 |
| ip100 [mA/cm²] | 0.08 | 0.06 | 0.04 |

Figure 3. Electrochemical characteristics of the tests carried out on X20Cr13 (soft-annealed state) in 0.1 mol/L H₂SO₄, variation of polarization rate (1, 2, 4 mV/s) and surface preparation.
The dominant influence of the polarization rate on all determined characteristic values is clearly visible. The effects on the DOS value are mainly caused by the different reactivation current densities, since the influence of time is stronger on reactivation compared to passivation. The reactivation potentials \( (E_{\text{reac}}) \) are shifted to more negative values, which can also be evaluated as a time effect. The exposure time of the sulphuric acid, which causes the freshly formed passive layer to dissolve and thus reactivate the surface, plays a decisive role. The passive current density at the reversal point at 100 mV\(_{\text{Ag/AgCl}}\) decreases using slower polarization rates as the passive layer is further strengthened by the longer time in the passive range and thus further inhibits the charge transfer of metal ions. The influence of roughness is not clearly visible in the diagram and was investigated by statistical evaluation. It is only significantly detectable during passivation \( (i_{\text{pass}}) \) and is generally low. This is understandable, since the surface is actively corroded for a short time during passivation and a levelling effect is to be expected, whereby no significant influence of the surface roughness can be recognized afterwards.

The polarization rate is therefore a decisive factor in the EPR experiment. It will also be related to the acid concentration because the strength of the acid and its exposure time influence the passive layer stability and thus the occurrence of reactivation in the EPR experiment. For the following investigations with variation of chromium content and sulfuric acid, the polarization rate was set to 2 mV/s in order not to further increase the scope of the test.

### 3.2 Variation of chromium content and sulphuric acid concentration

The effects of the chromium content of the Fe-Cr alloys and the acid concentration on the course of the EPR curves are presented in the following figures. Figure 4 shows that the passivation current density decreases with increasing chromium content while the acid concentration remains constant, i.e. the passivation process is easier, i.e. with lower charge conversion. A current density maximum due to reactivation can be seen at 9.3 and 11.2 % chromium. At 13.6 % chromium, on the other hand, the passive layer is resistant to reactivation under the selected test conditions and no increase in current density occurs during reverse polarization. The influence of the acid concentration is shown in Figure 5 using the Fe-Cr alloy with 11.2 % Cr. With a constant chromium content, the passivation current density increases with the acid concentration, i.e. a higher charge conversion is necessary for passivation. At 11.2 % Cr reactivation only appear at the highest acid concentration of 0.1 mol/L. With the two weaker acids, however, reactivation does not occur.

![Figure 4](image-url)

**Figure 4.** Examples of cyclic polarization curves from EPR tests of Fe-Cr-alloys in 0.1 mol/L H\(_2\)SO\(_4\) solution, polarization rate 2 mV/s, variation of Cr-content.
Figure 5. Examples of cyclic polarization curves from EPR tests of the Fe-Cr-alloy with 11.2 % Cr, polarization rate 2 mV/s, variation of molarity of H$_2$SO$_4$.

The passivation and reactivation current densities ($i_{\text{pass}}$, $i_{\text{reac}}$) were determined from the measurement curves and compared as a function of the eight different chromium contents in Figure 6 in relation to the applied H$_2$SO$_4$ concentrations.

Figure 6. Passivation and reactivation current densities as a function of the test parameters with variation of the chromium content of the Fe-Cr alloy and the acid concentration.

An exponentially decreasing course of the passivation current density with increasing chromium content can be seen. At the lowest chromium content of 5.3 %, the curve flattens out somewhat, which probably indicates a problem with an IR drop due to the relatively high currents. A stronger scatter of the individual values occurs for the medium and lowest acid concentration at high chromium contents of 16 to 18 %. This can be explained by the fact that the steel strives to passivate themselves during the
test in the weaker acids and are therefore less active during passivation. This is particularly noticeable with 0.01 mol/L H\textsubscript{2}SO\textsubscript{4}.

Up to a certain chromium content, the reactivation current densities also show an exponential decrease in current density with increasing chromium content. However, there is a transition range where the current density is abruptly very low. No reactivation occurs and the value reflects the passive current density (note: in the absence of reactivation, the average passive current density was used as a value to avoid the value "0").

The influence of the acid concentration can be seen in the level of the current density values. The average values of the passivation current densities over all chromium contents are 4.86 mA/cm\textsuperscript{2} for 0.1 mol/L, 2.64 mA/cm\textsuperscript{2} for 0.0316 mol/L and 1.13 mA/cm\textsuperscript{2} for 0.01 mol/L and are statistically significantly different. The reactivation current densities have a similar gradation with respect to the acid concentration. However, they are no longer comparable with the passivation current densities due to the abrupt drop from a certain chromium content. With the low chromium contents, they are still at a comparable level, which shows that there is an almost uniform surface reactivation with approximately the same dissolution kinetics. This is understandable, since chromium is evenly distributed in a defined quantity, which also explains the sudden transition between reactivated and non-reactivated.

### 3.3 Modelling for the determination of the chromium content from EPR tests

The passivation current densities shown in Figure 6 correlate very well with the chromium content and acid concentration. Applying the ordinary least squares method to the test series showed the significance of both effects, but also a significant interaction between chromium content and acid concentration. From the model created, the graphical representation is shown in Figure 7 and formulas for predicting the total chromium content "available" for passivation from the passivation current density were derived. Since the formulas were derived from experimental results, they are only valid for the investigated ranges and selected metrological settings.

![Figure 7](image)

**Figure 7.** Graphical representation of the model from the test series with variation of Cr content and acid concentration with formulas for predicting the Cr content from passivation current densities.

The reactivation current densities shown in Figure 6, on the other hand, show an unsteady course and cannot be satisfactorily adjusted by the ordinary least squares method. Therefore, a logistic adjustment was used, i.e. it was modelled according to the probability of exceeding (or not exceeding) a defined limit value. The limit value used was 0.06 mA/cm\textsuperscript{2}. Figure 8 shows a graphical representation of the logistic model derived from this.
Figure 8. Graphical representation of the model from the test series with variation of chromium content and acid concentration for predicting the chromium content from reactivation current densities.

From the model for the reactivation current density it can be seen at what chromium content and at what acid concentration reactivation is likely. The model can be used, for example, to set a specific acid concentration to detect any chromium depletion and thus achieve a specific detection limit. It is also possible to determine the degree of depletion of a sample with unknown chromium depletion more precisely by experiments with graded acid concentration.

3.4 Application of the models on the X20Cr13 in different heat treatment conditions
In order to apply the models, investigations were carried out on the steel X20Cr13 in the soft-annealed state and in two hardened and tempered conditions. The corresponding microstructures and Vickers hardness values are presented in Figure 9.

Figure 9. SEM images of the different microstructures of the studied stainless steel X20Cr13: a) soft annealed, b) hardened and tempered for 2 h at 200 °C, c) hardened and tempered for 2 h at 500 °C.

The soft annealed condition has many large carbides rich in chromium in a ferritic matrix which has a lower chromium content than the nominal chemical composition of the steel. This soft annealed condition was austenitized at 1050 °C for 15 min and then quenched in water. During this process, all carbides are dissolved in the austenite, chromium is homogeneously distributed in the matrix and a
homogeneous chromium content is assured in the martensitic matrix formed by quenching. Tempering at 200 °C for 2 h merely relaxes the distorted martensite and does not cause significant carbide formation and sensitization. Tempering at 500 °C, on the other hand, produces numerous microcarbides throughout the matrix, which lead to strong sensitization.

Figure 10 shows the corresponding values for the passivation and reactivation current densities of the stainless steel X20Cr13 in dependence on tested microstructure and applied H₂SO₄ concentration.

The dependence of the current densities on the acid concentration is clearly visible in three states. The passivation current densities of the soft-annealed condition are significantly higher than those of the other two hardened states, which differ only slightly from each other, but are nevertheless statistically significant. In contrast, the reactivation current densities are quite different. The soft-annealed state shows reactivation at 0.1 mol/L and 0.0316 mol/L, but not at 0.01 mol/L. In contrast, the hardened and at 200 °C tempered state shows no reactivation at all three acid concentrations since chromium is homogeneously distributed in the martensitic matrix. The pronounced carbide formation during tempering at 500 °C causes a noticeably clear reactivation at all three acid concentrations. If the relationships and generated formulas of Figure 8 are applied to the measured passivation current densities, the calculated contents of "available" chromium involved in the passivation reactions can be estimated and is presented in Table 3.
Using the reactivation current densities, the limit value of 0.06 mA/cm² can be used to decide whether reactivation has occurred or not. The soft-annealed sample shows reactivation at 0.0316 mol/L, but no more at 0.01 mol/L. In conjunction with Figure 8 it can be deduced from this (probability = 1, second curve from the left) that reactivated areas have a high probability of a chromium content of about 10 %. In comparison with the mean value for the "available" chromium content in Table 3, which is also approx. 10 %, it can be concluded that there is no local chromium depletion, but that the ferritic matrix of the soft annealed condition is uniformly depleted in chromium and the derived chromium content is clearly below the chromium content of the chemical analysis in Table 2. The missing chromium is thus obviously bound in carbides and the solid solution is uniformly depleted.

A completely different picture emerges with the hardened sample, which was tempered at 200 °C. Even at an acid concentration of 0.1 mol/L, no reactivation is observed. This means that, considering the relationships shown in Figure 8 (probability = 0.5, first curve from the right), the chromium content is higher than 12 % everywhere in the martensitic matrix, which also corresponds to the average "available" chromium content of 12.29 % in Table 3.

The hardened and tempered at 500 °C condition shows a clear reactivation even at 0.01 mol/L. If the correlations in Figure 8 are applied (probability = 1, first curve from the left), the result is a chromium value of 9.8 % or even less, which is clearly below the value of the determined "available" chromium content of 12.11 %. This means that there is a strong and localised chromium depletion at this heat treatment condition.

4 Conclusions

The EPR test has several advantages in comparison to exposure tests in specific test media. In addition to a significantly faster test procedure, which can also be used in mobile applications, a further advantage is that the degree of sensitization (DOS) can be quantified. However, due to the integral measuring method (current related to the entire measuring surface), it is not yet possible to distinguish whether the reactivation is due to a larger reactivated area or a more strongly reduced chromium content. Both effects are mixed in the DOS characteristic value and complicate the scientific clarification of the mechanisms of chromium depletion and their effects on corrosion behaviour.

With the investigation strategy shown in this study for ferritic Fe-Cr alloys, the first step was to determine the chromium content that is effectively available for passivation. A mathematical model was derived from the results obtained and tested on a martensitic stainless steel. The passivation current density correlates with the acid concentration and the chromium content which is effectively available for passivation. On the steel X20Cr13 it was shown that this does not necessarily correspond to the nominal Cr content of the spectrometric analysis. In the soft annealed condition, more than 3 % chromium are bound in carbides and therefore are not available for passivation. With an "available" chromium content of only about 10 %, the corrosion resistance is severely diminished, as this value is even below the resistance limit. After heat treatment, significant amounts of chromium diffuse back into the matrix and more than 12 % chromium are available for passivation.

Table 3. Predicted chromium content from the formulae in Figure 7.

| sample                | H₂SO₄ [mol/L] | i_pass [mA/cm²] | predicted Cr [%] | Cr [%] (average) |
|-----------------------|--------------|-----------------|-----------------|------------------|
| Soft annealed         | 0.1          | 6.84            | 9.87            |                  |
|                       | 0.0316       | 2.59            | 10.46           | 10.03            |
|                       | 0.01         | 1.17            | 9.85            |                  |
| Hardened +            | 0.1          | 3.39            | 11.66           |                  |
| tempered at 200 °C    | 0.0316       | 1.16            | 13.10           | 12.29            |
|                       | 0.01         | 0.456           | 12.11           |                  |
|                       | 0.1          | 3.95            | 12.17           |                  |
| Hardened +            | 0.0316       | 1.39            | 12.51           | 12.11            |
| tempered at 500 °C    | 0.01         | 0.551           | 11.66           |                  |
In the case of unfavourable tempering treatment, renewed chromium depletion is possible, but in this case, it is mainly localised in the vicinity of microscopic carbides. The primary aim of the EPR test is to detect chromium depletion as a result of this local chromium depletion. The selected test conditions are decisive for the success of this detection, which is why there are always only recommendations for certain groups of stainless steels. Local chromium depletion is indicated when the chromium content in the depletion zone is sufficiently reduced to cause reactivation, or the acid is strong enough to trigger reactivation. This was investigated and modelled in the investigations with the Fe-Cr alloys under variation of the sulphuric acid concentration. With the help of the established logistic model, a detection limit for the desired detection of chromium can now be set and suitable test conditions selected. In addition, it is possible to estimate by how much the chromium content in these depletion zones has been reduced on unknown samples by varying the acid concentration. In conjunction with the "available" chromium content determined from the passivation current density, a much better explanation of the underlying mechanisms is possible.

Acknowledgements
The funding of parts of this work by the German Research Foundation (DFG) under grant no. 330472124 is gratefully acknowledged!
Thanks go to Mrs. B.Sc. Marie Becker for conducting a series of electrochemical experiments.

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