Corrosion of high alloyed steels investigated by high-temperature cyclic voltammetry and high-temperature corrosion testing

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CORROSION OF HIGH ALLOYED STEELS INVESTIGATED BY HIGH-TEMPERATURE CYCLIC VOLTAMMETRY AND HIGH-TEMPERATURE CORROSION TESTING

A. Sikora 1, H. Rojac 2, K. Adam 3, L. Krabac 2, M. Varga 2, G. Fafilek 4

1 INTRODUCTION

Atmospheric conditions and applied raw materials highly impinge on corrosion behaviour of grate bars used in sinter plants. Chlorine and sulphur come along with feed materials, which cause severe damage to oxide scales as well as bulk materials at high temperatures by forming metal chlorides and sulphates respectively [1, 2].

Both groups have relatively low melting points so that protective layers get in contact with liquid phases early during heating cycles in the sinter process, which leads to an increased corrosion rate in molten salts [3]. (K,Na)Cl and SO₃ have been identified as initial substances for reactions to (K,Na)₂S₂O₇ and (K,Na)₂SO₄ at temperatures above 400°C, whereby Cl₂ is always being formed.

Oxide scales get penetrable for chlorine in such environment, which is then able to reach the bulk material through diffusion. Depending on the partial pressure of chlorine and oxygen, chlorine interacts with the appropriate metal resulting in volatile metal chlorides. These chlorides are going to be oxidized on their way towards the surface and thus condensed to form porous oxides, which contributes additionally to increased levels of material degradation [1, 4, 5]. It has been reported in several publications that iron as well as chromium contents in the aggressed alloy are depleted by these chlorine - chloride cycles and a skeleton mainly composed of the residual alloying elements is left over [5, 6].

The material losses suffered with and without these corrosion promoting substances have been investigated on the one hand by high-temperature cyclic voltammetry and on the other hand by high-temperature corrosion testing. Finding a suitable material with a rapidly forming and adherent oxide layer for an inhospitable environment such as sinter plants is the objective of our research.

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2 EXPERIMENTAL

2.1 High-Temperature Cyclic Voltammetry (HT-CV)

This method is commonly being used for identifying oxidation and reduction processes at temperatures beyond 400°C, whereby Gibb's energy of oxide formation can be calculated thereof [7]. A cell for cyclic voltammetry at high temperatures usually consists of an yttrium stabilized zirconia as solid ion-conductive electrolyte and two or more electrodes made of platinum. A four electrode arrangement is being used for the investigations carried out at TU Vienna, thereby the electrodes are designated as reference (RE), working 1 (WE1), working 2 (WE2) and counter electrode (CE) as depicted in Figure 1 below.

The electrodes were contacted with a platinum plate for RE and CE respectively. A copper plate was applied for WE1, the sample with or without any ash substances was used as WE2 and also contacted with a platinum plate. All these components are situated in a closed quartz tube for flushing with argon gas in order to reduce the oxygen partial pressure to a minimum. The sample as well as parts of the sample holder are thus prevented from scaling during heating.

Furthermore, the cell within the closed quartz tube is placed inside a furnace allowing temperature control through thermocouples. Adjusting voltage at constant scanrate of 10 mVs\(^{-1}\) and collecting the corresponding current is done via a potentiostat as shown in Figure 2.

Reducing the oxygen level in the whole cell is the reason why calibration measurements with copper are needed. Otherwise, a 4th electrode would not be necessary. The reference potential is shifted according to the oxygen partial pressure so that a correction of the voltammograms for the potential scale has to be done. All potentials are calibrated to the reversible oxygen electrode at 10\(^5\) Pa (ROE) as a reference. Copper is an appropriate material due to its clearly identifiable oxidation and reduction peaks. Thermodynamic data of both oxidation and reduction states can be determined from the voltammogram and compared with calculated values [8]. The difference between them are typical for the respective test conditions and are therefore applied to the sample voltammogram.
2.2 High-Temperature Corrosion Testing (HT-CT)

A newly developed high temperature corrosion test (HT-CT) at the Austrian Centre of Competence for Tribology (AC²T research GmbH) is able to perform corrosion tests up to 1500°C and was selected for this study. This setup allows the mixture of gases in various predefined concentrations. Further, it is possible to test gaseous corrosion combined with salt corrosion in solid or molten state using alumina crucibles, as shown previously [9]. Hence, HT corrosion tests under close-to-reality conditions can be investigated using this setup.

![Figure 3: Schematic of the HT corrosion test routine: a) Overview, b) Setup of samples and corrosives within crucibles used in this routine](image)

A schematic overview of the test rig is given in Figure 3. As seen in Figure 3a, the test rig mainly consists of an alumina tube furnace. The gas feeding and mixing are realized by flow rate controllers and mixing unit, both controlled by computer. The gases are led from gas cylinders through a mixing flute and then fed into the tube furnace.

Samples were cut to a dimension of 7x10x10 mm and subsequently grinded with a SiC grinding paper with a grain size of 6 µm. The samples were weighed and measured in order to calculate their sample surface and determine the corrosion rate after the test. Six samples of each material, as seen in Table 1, were tested for statistical purpose. As seen in Figure 3b, the bottom part of alumina crucibles was first filled with sinter mixture, subsequently, three samples of the same material were placed over it and finally, the samples were completely covered with the sinter mixture. As a last step, a defined amount of corrosive salts extracted from sinter mixture was put on top of the sinter-mixture-covered samples in order to make testing conditions harsher and to increase the corrosion rate.

After crucible preparation, a gas mixture according to the proportions of field measurements was set and the temperature control was activated. The crucibles (max. of 3 crucibles per test routine) were placed into the furnace, the thermal insulation was mounted and the furnace was nitrogen-purged, so that no corrosion took place during the heating. When the temperature reached 1000°C, the test controller opened the gas valves and a reality-near simulation of the HT corrosion process started. After 24 h, a feeding of corrosive gases was interrupted and...
nitrogen was introduced into the tube furnace in order to stop the corrosive attack. Subsequently, the furnace was cooled down to room temperature. After the test the sinter adhered to the sample was removed and total mass loss was determined in order to calculate the corrosion rate (see section 3.2).

2.3 Tested materials
To cover a broad spectrum of ferrous materials, four different alloys were chosen for investigation. Two model alloys, namely Fe10Cr10Ni and Fe15Cr were examined alongside two commercially available HT steels, 1.4777 and 1.4841. All steels vary in their chemical composition, as seen in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>Cr [wt.%]</th>
<th>Ni [wt.%]</th>
<th>Si [wt.%]</th>
<th>C [wt.%]</th>
<th>Mn [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe10Ni10Cr</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe15Cr</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.4841</td>
<td>24.8</td>
<td>19.8</td>
<td>1.7</td>
<td>0.08</td>
<td>1.2</td>
</tr>
<tr>
<td>1.4777</td>
<td>28</td>
<td>0.6</td>
<td>1.7</td>
<td>1.3</td>
<td>0.7</td>
</tr>
</tbody>
</table>

3 RESULTS AND DISCUSSION

3.1 High-Temperature Cyclic Voltammetry (HT-CV)
Current densities at specific potentials are equitable with corrosion rates of tested materials at prevailing oxygen partial pressures considering the scanrate. An oxygen partial pressure of $10^5$ Pa is linked to a potential of 0.0 V in calibrated voltammograms, where current densities are being taken from, as given in Figure 4. Passive state current densities ($i_{pass}$) are gathered in doing so for comparison of different alloys at temperatures between 500 and 700°C.

![Figure 4: Voltammogram of Fe10Ni10Cr without ash at 600°C and 10 mVs⁻¹](image-url)
3.2 Quantitative analysis of corrosion and corrosion rates

Mass losses due to HT-CT were determined by samples weighing before and after the test. To remove the adherent corrosions scales etching was performed according to ASTM G1-03 [10] standard to determine the real mass loss due to corrosion. The corrosion rates $r_{\text{corr}} \text{[g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}]$ were calculated via total mass loss, the surface area and the exposure time.

HT cast steel 1.4777 points out a low corrosion rate of $29.8\pm7.4 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, HT steel 1.4841 shows $9.9\pm3.5 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, the model alloy Fe15Cr entails a higher $r_{\text{corr}}$ of $395.4\pm19.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and the other model alloy Fe10Cr10Ni $240.3\pm38.6 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$.

A strong dependence of the $r_{\text{corr}}$ on different alloying elements can be pointed out at this point.

3.3 Correlation of both techniques

A correlation analysis done at AC$^2$T has been carried out in order to see how their data obtained from HT-CT match with HT-CV data as depicted in Table 2 below. HT-CT measurements at AC$^2$T are always done with sinter ash and salt in a corrosive atmosphere (synthetic air, CO$_2$, SO$_2$, HCl) at 1000°C and 1 atm for 24h, while HT-CV tests are carried out with or without sinter ash at 500, 600 and 700°C.

### Table 2: Correlation of test results obtained by HT-CV and HT-CT

<table>
<thead>
<tr>
<th>Materials with ash (wa) [CEST] and materials with ash (1000wa) [AC2T]</th>
<th>Materials without ash [CEST] and materials with ash (1000wa) [AC2T]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{Pearson}}$</td>
<td>$R_{\text{Pearson}}$</td>
</tr>
<tr>
<td>500wa vs 1000wa</td>
<td>0.9276</td>
</tr>
<tr>
<td>600wa vs 1000wa</td>
<td>0.9563</td>
</tr>
<tr>
<td>700wa vs 1000wa</td>
<td>0.7730</td>
</tr>
</tbody>
</table>

Additionally, correlation coefficients are graphically processed in Figure 5, while current densities ($i_{\text{pass}}$) and corrosion rates ($r_{\text{corr}}$) have been put in relation to the reference material 1.4777 ($i_{0\text{pass}}$ and $r_{0\text{corr}}$), shown in Figure 6.

HT-CV and HT-CT results correlate very well in both cases, i.e. materials with and without ash. However, a bit lower correlation is given between HT-CV data with ash at 700°C and HT-CT at 1000°C. This inconsistency at 700°C is being discussed in the following section. A strong dependence of both measured parameters $i_{\text{pass}}$ and $r_{\text{corr}}$ can be pointed out, which are affected by present corrosives, temperature and the materials chemical composition.
3.4 Discussion on ongoing Corrosion Processes and Phenomena

Figure 7 presents a cross sectional SEM analysis of the steel 1.4777. On the right the scale formation is presented in greater detail, on the left an EDX element mapping is presented pointing out differences throughout the scale.

As seen in this figure, oxidation and uniform corrosion due to corrosive salts in molten state are the prevalent corrosion mechanisms. A comparatively dense corrosion scale is formed, enabling the migration of salts and oxygen on a relatively low level. The scale is dominated by oxides: a thick iron oxide rich scale with small amounts of Mn is formed on the outside. At the inside of the scale a more Cr dominated, Fe-Cr mixed oxide layer is formed. The corrosive anions like S and Cl
are enriched at the boundary zone between oxide scale and base material enabling high temperature corrosion due to the permanent contact between corrosive and base metal. Similar behaviour can be pointed out at all materials investigated. High $r_{\text{corr}}$ indicate a more porous layer formation, which improves the migration of corrosive anions directly to the base metal. If Ni is present in the bulk, the outer layer is a spinel type Fe-Ni-Mn mixed oxide.

The presented scale formation origins from the composition of the ash, which has been analysed by AC$^2$T using XRD and ICP-OES. Main ingredient is potassium chloride (KCl), followed by potassium calcium chloride (KCaCl$_3$), sodium chloride (NaCl) and sulphur. Corrosion promoting products of the ash in the sinter atmosphere might therefore be mainly potassium pyrosulphate (K$_2$S$_2$O$_5$) as well as chlorine. Materials alloyed with Ni do have less protection against corrosion due to the fact of reacting to NiSO$_4$ at temperatures between 650 and 750°C, which prevents the formation of a closed Cr$_2$O$_3$ scale [11]. A difference between alloys with and without Ni could not be found in our research so that other reactions must be active.

Lower correlation between 700°C and 1000°C stem from accelerated reactions between sinter ash and the oxide scale at temperatures around 700°C, which are not investigated in their entirety. Once liquid phases are formed on surfaces, material reactions take place according to the type of oxides formed as well as partial pressures of O$_2$, Cl$_2$ and SO$_3$. Not so, if comparing tests with sinter ash at 700°C as depicted in Figure 6. Scale types might be easy penetrable considering the activity of potassium pyrosulphate and other molten salts as well as the chlorine – chloride cycle at this temperature. Corrosion rates are therefore equally high, irrelevant which alloy is exposed to such environment.

### 4 CONCLUSION AND OUTLOOK

Based on the presented results, following concluding remarks can be presented:

- The corrosion promoting atmosphere in the sintering plant largely consists of potassium chloride (KCl), potassium calcium chloride (KCaCl$_3$), sodium chloride (NaCl), sulphur and oxygen.

- Scale formation is mainly oxide based, although molten salt corrosion is predominating at 700°C, indicating a highly corrosive environment with active oxide scale dissolution and chlorine based degradation.

- Both applied test methods can simulate the corrosive attack in sintering plants at lab scale. Combining both methods enables the assessment of material-selection maps of various alloys according to their ability of forming protective and adherent oxide layers on the bulk material.

Combined effects of wear and corrosion at elevated temperature needs to be analysed in future studies. The assessment of a HT tribocorrosion test is therefore crucial.
ACKNOWLEDGEMENT

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LITERATURE