In the present paper the results of a four-year investigation of the wear mechanisms affecting anode furnace linings are described. At the time when this study was initiated, the entire lining (apart from the tuyere blocks) consisted of a traditional direct-bonded magnesia-chromite brick. The latter suffered from acute wear due to the stringent chemical, thermal and mechanical conditions imposed. As a result of a microstructural study of samples prepared from industrially worn bricks, the major degradation mechanisms influencing the refractory lining were unravelled. On the basis of the identification of different wear zones in the lining, an optimised refractory configuration was proposed and installed in order to prolong the furnace campaigns. Distinct magnesia-chromite qualities were selected for the different wear zones. During the two following relinings worn bricks from various locations in the lining were collected and investigated. It was confirmed that refractory degradation in anode furnaces comes as a consequence of the combined action of chemical, thermal and mechanical drivers, which interact synergistically with one another. Depending on the region in the lining the relative importance of the drivers varies. Specific attention was given to the chemical wear mechanisms, namely: copper and slag components infiltration, forsterite formation and spinelisation. As a result of the installation of the new, zoned lining configuration a significant improvement of the overall lining lifetime was achieved.

Keywords:
Copper anode furnace – Refractory lining – Magnesia-chromite bricks – Degradation mechanisms

Optimierung einer feuerfesten Anoden-Ausmauerung durch Verwendung verschiedener Magnesia-Chromit-Feuerfest-Typen


Schlüsselwörter:
Kupfer-Anodenofen – Feuerfest-Ausmauerung – Magnesia-Chromit-Steine – Abnutzungsmechanismen

Optimización de un revestimiento refractario de un horno ánodo usando distintos tipos de refractario de magnesia-cromita
1 Introduction

Crites et al. have indicated that within the field of copper making the most notable feature of refractory selection is the almost universal use of magnesia-chromite bricks [1]. With respect to the refractory wear mechanisms considerable research has been carried out applied in Flash Smelters and Peirce-Smith converters [2-8]. For anode furnaces, however, this is not the case. In anode furnace linings, copper manufacturers usually apply the same type of bricks as in converters. Nevertheless, the operating conditions and melts encountered in these reactors are not identical. For example, the generation of sulphur dioxide, which is a source of significant refractory stress in converters [8], is not a problem in refining furnaces; neither is corrosion by molten matte. On the other hand, refining (anode) slags have higher basicities and copper oxide levels than smelting or converting slags [5]. This implies that the wear mechanisms affecting anode furnace linings can be substantially different from those reported in Flash Smelters and converters.

The present paper, therefore, targets a systematic study of the wear mechanisms in anode furnace linings by investigating refractories collected from several industrial anode furnace linings. The goal of this work is twofold: to unravel the chemical, thermal and mechanical (physical) refractory degradation mechanisms and subsequently optimise the refractory lining configuration. At the time when this study was initiated the entire anode furnace lining (apart from the tuyere blocks) consisted of just one refractory type. This was a medium-quality magnesia-chromite brick belonging to the first generation of direct-bonded refractories. The overall lining lifetime was only eleven months as a result of a non-uniform wear rate, with some areas completely worn and others almost intact. Therefore, an optimisation of the lining configuration was desirable. Ideally, magnesia-chromite bricks would be entirely replaced by cheaper and environmental-friendly chrome-free alternatives. However, concurrent work by the present authors [9] – using laboratory finger tests – revealed that all investigated chrome-free materials (mainly based on the magnesia-spinel system) were highly prone to penetration and chemical corrosion by copper and anode slag components. As slag corrosion is a crucial component of the overall wear mechanism in an industrial set-up it was decided not to use chrome-free alternatives in the anode furnace linings. Developing a zoned magnesia-chromite lining was thus the only realistic possibility.

The research strategy used in this work is as follows. Through a combination of the first post-mortem results and the knowledge developed through the laboratory finger testing, it became possible to deduce a (simple) zoned lining configuration, which was subsequently installed and industrially tested. This procedure was then repeated. In total, three consecutive lining configurations were thus monitored and investigated, rendering samples (including distinct magnesia-chromite types) from various locations in the anode furnace linings. This procedure intends to obtain representative wear mechanisms for the different locations in the furnace and to work out a general scheme of the refractory degradation phenomena affecting the anode furnace linings. A concurrent goal is to obtain a fully optimised anode furnace lining configuration.

2 Experimental

2.1 Furnace and process description

The present study was carried out at Cumerio’s copper smelter in Bulgaria (Cumerio Med). In this plant, the fire-refining of blister copper is done in two 250-t rotary anode furnaces (Figure 1). The furnaces have a cylindrical shape and are able to rotate along their longitudinal axes. Their walls consist of a working lining, insulation lining and a steel shell on the outside. The furnaces dimensions are approximately 9 m in length and 3 m in diameter. Blister copper is poured into the anode furnace having a temperature of 1170 to 1200 °C. During the oxidation step, the bath temperature increases up to 1250 °C. In the de-oxidation step it subsequently rises up to 1280 to 1300 °C. Temperatures in excess of 1300 °C are seldom experienced under normal operational practice.

In the oxidation operational stage, impurities are removed by injecting air (4 to 5 bar) through two tuyeres into the melt. The main impurities in blister copper are: sulphur, iron, arsenic, antimony, lead, zinc, bismuth, cobalt and nickel. As long as copper is abundant it is oxidised first. The impurities are being oxidised through direct interaction with oxygen. The resulting oxides rise to the surface to form a slag layer. The principal reactions are:

\[
2[Cu] + 0.5(O_2) = [Cu_2O] \quad (1)
\]

\[
[Me_{Ca}] + 0.5(O_2) = [MeO]_{slag}, Me = \text{metal impurity} \quad (2)
\]

\[
[Si]_{Ca} + (O_2) = (SO_2) \quad (3)
\]

At the same time oxygen dissolves in copper:

\[
(O_2) = 2[O]_{Cu} \quad (4)
\]

The symbols are used as follows: liquid phase: [ ], solid phase: [ ], gas phase: ( ), [X]L: component X dissolved in a liquid (L).

Some of the copper oxide becomes a constituent of the slag layer. The amount of slag is rather small: 5 to 10 wt.-% of the copper amount. The slag contains copper, copper

![Fig. 1: Rotary copper anode furnace](image-url)
oxides and iron oxides as main components plus the oxides of the impurities and some silica in minor amounts. The results of chemical analyses are presented in Table 1. The skimmed slag is recycled to the converters.

Table 1: Average chemical composition of anode slag (wt.-%)

<table>
<thead>
<tr>
<th>Slag components</th>
<th>Cu</th>
<th>Fe</th>
<th>SiO₂</th>
<th>Pb</th>
<th>Zn</th>
<th>As</th>
<th>Sb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>44.5</td>
<td>26.6</td>
<td>5.5</td>
<td>0.9</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The oxygen concentration in the desulphurised copper is in the order of 0.6 wt.-%. Due to the extremely low solubility of oxygen in solid copper (0.002 % at 800 °C) [10], almost all of this oxygen would precipitate as Cu₂O during copper solidification, which would cause up to 6 wt.-% of oxide inclusions in the solid copper. Copper oxide precipitation is minimised by removing most of the oxygen from the molten copper with hydrocarbons. For this purpose propane is introduced through the tuyeres:

\[(C_3H_8) + 10{O} = 3(CO_2) + 4(H_2O) \quad (5)\]

The final oxygen content is normally below 0.1 wt.-%. At the end of the process the copper surface is covered with a coke layer to prevent reoxidation. Finally, the metal is tapped through a tapping hole in the backside of the barrel and cast into anodes by means of an anode-casting wheel. No flux is added during the fire-refining process in the anode furnaces since the quality of the produced anode copper is high enough (i.e. > 99.5 % Cu).

2.2 Industrial trials

With the exception of the tuyere blocks, where a special magnesia-chromite-zirconia brick (based on fused magnesia-chromite grains) was employed, medium-quality magnesia-chromite refractories were the only material used in the old lining. During the general relining of the furnaces, bricks from different locations of the worn lining were collected. A plan of an anode furnace with the collection areas (zones) is presented in Figure 2.

As a result of a detailed post-mortem assessment (described later in the paper) of this first set of industrially-worn samples, it was found that different wear patterns exist in the lining. The results acquired from the microstructural study together with the results from our laboratory experiments [9] showed that the tested chrome-free materials are not suitable for application in anode furnace linings. Therefore, a zoned magnesia-chromite lining was proposed in which three brick qualities compatible with the specific requirements per zone were used. The goal of this installation was to extend the overall refractory service lifetime. Table 2 shows the chemical compositions and the physical properties of the used brick types. MC1 belongs to the first generation of direct-bonded bricks fired at temperatures of 1650 to 1700 °C. Figure 3a shows a BSE image of its as-delivered microstructure. The examination revealed that this

<table>
<thead>
<tr>
<th>Components &amp; properties</th>
<th>MgO [wt.-%]</th>
<th>Cr₂O₃ [wt.-%]</th>
<th>FeO [wt.-%]</th>
<th>Al₂O₃ [wt.-%]</th>
<th>CaO [wt.-%]</th>
<th>SiO₂ [wt.-%]</th>
<th>BD [g/cm³]</th>
<th>CCS [MPA]</th>
<th>AP [vol.-%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractory type</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MC1</td>
<td>58</td>
<td>19</td>
<td>15</td>
<td>6.0</td>
<td>1.5</td>
<td>0.5</td>
<td>3.15</td>
<td>33</td>
<td>17.5</td>
</tr>
<tr>
<td>MC2</td>
<td>60</td>
<td>19</td>
<td>13.5</td>
<td>6.0</td>
<td>1.3</td>
<td>0.2</td>
<td>3.22</td>
<td>70</td>
<td>17.0</td>
</tr>
</tbody>
</table>

* Data provided by refractory supplier

Fig. 2: Anode furnace plan with collection areas; 1 – Barrel wall, opposite tuyere 1; 2 – Barrel wall, opposite tuyere 2; 3 – Bottom, opposite the mouth; 4 – Side wall, below the gas outlet; 5 – Side wall, below the burner inlet; 6 – Roof, near the charging mouth; T1 – Close to tuyere 1 block; T2 – Close to tuyere 2 block; MID – Middle part of barrel wall; TAP – Barrel wall, near the tap hole

Fig. 3: BSE overview images of the as-delivered microstructure of MC1 (a) and MC2 (b); Per – periclase, Chr – primary chromite spinel, CMS – calcia-magnesia silicate, Presin – presintered grain

Table 2: Chemical compositions and physical properties of the magnesia-chromite bricks used in the anode furnace linings* (BD – bulk density, CCS – cold crushing strength, AP – apparent porosity)
material consists of periclase (MgO), primary and secondary chromite spinel (Mg,Fe\textsuperscript{2+})\[Cr,Al,Fe\textsuperscript{3+}]O\textsubscript{4} and a small amount of calcia-magnesia silicate (CMS). A more detailed description of the different phases observed in these magnesia-chromite refractories can be found in the works of GOTO & LEE [11], and JONES et al. [12]. Figure 3b shows a BSE image of the as-delivered microstructure of MC2. This refractory type is based on pre-sintered grain fired at a temperature of about 2100 °C. After this first firing, the resultant product was crushed, ground, mixed with chrome ore and fired for a second time at a lower temperature. This material consists of presintered magnesia-chromite grains, periclase, primary and secondary chromite spinel and a small amount of CMS. Because of its higher density and strength as well as lower porosity, MC2 is characterised by an excellent thermal shock resistance and improved slag penetration resistance with respect to the traditional direct-bonded bricks.

When the furnaces were taken out of production for the planned relining and maintenance, an inspection of the new zoned refractory lining was carried out. Some parts of the lining were found to be in a very good condition. Therefore, it was decided to perform only a partial relining. Bricks from different locations of the replaced lining areas were collected for detailed examination as shown in Figure 2. After this partial relining the anode furnaces were put back into operation and performed well in the course of the next campaign. A careful examination of the refractory lining was performed after 11 months. The inspection revealed that the lining was in a very good condition; therefore it was decided not to shut down the furnaces for relining. Normal operation was continued while constantly monitoring the lining’s thickness by means of infrared equipment and other on-site techniques. Proceeding in this way, the furnaces campaign was extended with 5 months. At that time, a need for repairs of some ancillary metallurgical equipment appeared, therefore the anode furnaces had to be taken out of production as well. A decision was taken to use the non-operational period for maintenance and complete relining of the furnaces. The examination of the worn lining showed that the campaign could be still prolonged with a few more months without taking any risks. During the relining, bricks from specific locations of the worn lining were collected for detailed examination (see Figure 2).

In the course of the four-year investigation in total 22 bricks originating from the distinct wear regions were thus obtained. Table 3 summarises the performance of the three linings and indicates which samples were collected for investigation. The table also shows the residual refractory thickness expressed in per cent of the original thickness.

2.3 Sample preparation

Bricks from all areas were cut to slices (perpendicular to the refractory hot/cold face) with a thickness of approximately 2 cm and two small specimens, A and B (approximately 2 cm \times 2 cm each), were recovered with a diamond saw from each slice as shown in Figure 4. Afterwards, the samples were embedded in low-viscosity resin (Technovit 4004), ground with diamond plates and polished with diamond suspensions. Finally, carbon was deposited on their surface to provide a conducting layer for further examination.

2.4 Characterisation techniques

A JEOL JXA-733 microprobe coupled with an energy dispersive spectroscopy (EDS) system was used for semi-quantitative analysis. The semi-quantitative procedure (TRACOR) requires that the operator selects a priori the oxides or elements to be measured. Combinations of elements and oxides (e.g. Fe and MgO) are not possible in the present software configuration. With this electron-probe set up, only elements with atomic numbers \( \geq \) than that of Na can be determined. Since oxygen cannot be measured directly, it has to be calculated indirectly from the measured amount of elements and the selected oxide stoichiometry. A high resolution scanning electron microscope (Philips XL-30 FEG), equipped with an EDS detector system with an ultra thin window, was used for acquiring high-quality BSE images and for additional EDS analyses (using a semi-quantitative procedure from EDAX).

3 Results

3.1 Lining N1

As can be seen from Table 3, there are significant differences in the wear rate of bricks coming from distinct zones of lining N1 (entirely brick type MC1). For example, bricks recovered from zone 6 were only slightly worn, while bricks collected from zones T1 and T2 were extremely degraded. The refractories recovered from zones 1, 2, 4 and 5 were significantly affected, whereas the wear rate of the zone 3 bricks was intermediate.

Figure 5 shows BSE images of samples recovered from zones 1 and 2. The samples recovered from these zones are heavily infiltrated with metallic copper. The latter has filled most of the periclase grain boundaries together with forsterite (Mg\textsubscript{2}Si\textsubscript{4}O\textsubscript{10}) partially replacing the intergranular secondary chromite (Figure 5a). Forsterite is formed through the reaction:

\[
2[\text{MgO}]_{\text{Refr}} + (\text{SiO}_2)_{\text{Slag}} = [\text{Mg}_2\text{SiO}_4]_{\text{Refr}}
\]

Large cracks filled with copper and (to a lesser extent) with copper oxide were observed in these samples (Figure 5b). Copper oxide is mainly present as cuprous oxide (Cu\textsubscript{2}O), although a minor amount of cupric oxide (CuO) was also detected at the refractory hot face. Close to the hot face (Mg,Fe\textsuperscript{2+})\[Cr,Al,Fe\textsuperscript{3+}]O\textsubscript{4} magnesiochromite spinel grains
have grown and formed a network of interconnected (Cu,Mg,Fe$^{2+}$)[Cr,Al,Fe$^{3+}$]$_2$O$_4$ spinel grains incorporating copper in their composition. Nearly complete spinelisation of the refractory microstructure has taken place at the hot face due to the incorporation of periclase into the newly formed spinel (Figure 5c). Small amounts of silicate phase are enclosed in this expanding spinel phase (Figure 5c).

At higher magnification (Figure 5d) it can be seen that the silicate phase involves cuprous oxide grains scattered in a FeO$_x$-Al$_2$O$_3$-SiO$_2$ matrix.

BSE images of samples recovered from zone 4 (side wall, below the gas outlet) and zone 5 (side wall, below the burner inlet) are presented in Figure 6. The wear and penetration rates of these bricks correspond to the average values, which can be explained by their location in the lining. Oxygen rich copper has infiltrated the bricks in zone 4 causing the appearance of metallic copper with cuprous oxide inclusions (Figure 6a and 6b). On the other hand, in the samples from zone 5 (located below the burner inlet) only cuprous oxide was found, even in the interior of the brick. Some anode slag (CuO$_x$FeO$_y$) was observed to have penetrated the brick together with copper (Figure 6c). Spinel formation was highly pronounced in the bricks recovered from these zones. A small amount of fayalite (2FeO-SiO$_2$) crystals embedded in anode slag were detected in the newly formed spinel matrix (Figure 6d).

---

### Table 3: Summary of linings N1, N2 and N3 performance

<table>
<thead>
<tr>
<th>Lining</th>
<th>Collection zone (see Figure 2)</th>
<th>Brick type</th>
<th>Residual brick thickness (% of original thickness)</th>
<th>Overall refractory lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1 – old lining concept</td>
<td>1</td>
<td>MC1</td>
<td>30-35</td>
<td>11 months followed by complete relining</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>MC1</td>
<td>30-35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>MC1</td>
<td>45-50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>MC1</td>
<td>35-40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>MC1</td>
<td>35-40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>MC1</td>
<td>75-80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>MC1</td>
<td>20-25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T2</td>
<td>MC1</td>
<td>20-25</td>
<td></td>
</tr>
<tr>
<td>N2 – new lining concept: first trial</td>
<td>4</td>
<td>MC2</td>
<td>75-80</td>
<td>11 months – complete relining was not needed, only partial</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>MC2</td>
<td>75-80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MID</td>
<td>MC2</td>
<td>80-85</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TAP</td>
<td>MC2</td>
<td>60-65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>MC2</td>
<td>55-60</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T2</td>
<td>MC2</td>
<td>55-60</td>
<td></td>
</tr>
<tr>
<td>N3 – new lining concept: second trial</td>
<td>4</td>
<td>MC2</td>
<td>60-65</td>
<td>16 months followed by complete relining, but campaign could be still prolonged</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>MC2</td>
<td>60-65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MID</td>
<td>MC2</td>
<td>65-70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TAP</td>
<td>MC2</td>
<td>50-55</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T1</td>
<td>MC2</td>
<td>45-50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T2</td>
<td>MC2</td>
<td>45-50</td>
<td></td>
</tr>
</tbody>
</table>

---

Fig. 5
BSE images of samples recovered from zone 1 and zone 2 – MC1, lining N1; F – forsterite (2MgO·SiO$_2$), Sil – silicate phase, Sp – in situ formed spinel phase [(Mg,Fe,Cu)(Fe,Cr,Al)$_2$O$_4$]
Vesely Petkov et al.: Optimisation of an Anode Furnace Lining Using Distinct Magnesia-Chromite Refractory Types

3.2 Lining N2

The refractories from zone 6 (furnace roof, near the charging mouth) are only occasionally in contact with copper or slag (tilting of the furnace for slag skimming, splashes during oxidation and reduction steps). Therefore, the wear and penetration rate of the bricks collected from this zone is lower than the average level.

The highest temperature in the anode furnace is experienced near the two tuyere pipes through which air is blown in the first stage of the fire-refining process and propane in the second. The higher temperature leads to higher temperature change (amplitude) in comparison with the rest of the lining when the furnace is empty (i.e. cooler) during waiting periods. The heaviest infiltration of all was observed in the bricks recovered from this zone. The samples are abundant with cracks due to the higher thermal shocks experienced in this particular area. As a result, even some of the primary chromite grains were attacked and infiltrated by oxygen-bearing copper. The spinel growth in these samples was also at its heaviest.

Fig. 6: BSE images of samples recovered from zone 4 (a, b) and zone 5 (c, d) – MC1, lining N1; Per – periclase (MgO), F – forsterite (2MgO·SiO₂), Sp – in situ formed spinel phase [(Mg,Fe,Cu)(Fe,Cr,Al)₂O₄], Fay – fayalite (2FeO·SiO₂), AS – anode slag (CuO₂·FeO₂).

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3.2 Lining N2

The second set of industrially-worn bricks is comprised of the newly employed rebonded magnesia-chromite type (MC2), which was used for the first time in the anode furnace linings. Since the residual thickness of MC1 bricks (applied in the low wear regions – zones 3 and 6) was still high enough, they were not replaced during the partial relining. As can be seen from Table 3, the use of the higher-quality MC2 in the high wear zones was successful. This refractory type withstood to a large extent the corrosive and erosive action of the copper/anode slag melt. Similar phases were found in MC2 bricks compared with the phases encountered in MC1 bricks recovered from lining N1. The initially determined wear mechanisms affecting MC1 type essentially remain the same as well. However, their impact was less detrimental for the higher-quality refractories (MC2) used in the high wear zones of the new lining compared to the scale at which the medium-quality bricks (MC1) were affected.

Figures 7 and 8 show BSE overview images (low magnification – 25×) of “cold face” samples (type ‘B’ samples, see
Figure 4) – 4 to 5 cm away from the refractory hot face. Similarly to the bricks type MC1 recovered from the slagline area, a spinelisation of the refractory microstructure has taken place. Substantial levels of forsterite were observed in the samples coming from zones 4 and 5. Another common feature of these samples is that they were completely infiltrated by copper oxide. The images also show that the samples recovered from zone 5 contain more forsterite than the samples collected from zone 4. This is a result of the different conditions to which these zones are exposed. Zone 4 is situated below the gas outlet, while zone 5 is located below the burner inlet. The latter area is exposed to higher temperatures, which cause local overheating of the slag layer. This lowers the slag viscosity and accelerates the kinetics of the reaction of forsterite formation (6).

In all investigated samples a dense slag layer was observed along the joint with the adjacent brick (Figure 8). Apparently, slag and copper infiltrated the joints between bricks, causing the formation of a slag layer with copper inclusions. The layer disappears at a distance of 10 to 11 cm (registered by visual observation) from the hot face. We assume that this corresponds to the maximum depth of anode slag (and copper) penetration along the joints. A forsterite layer is always present between the frozen slag and the interior of the brick (Figure 8). The layer has formed as a result of reaction (6).

3.3 Lining N3

The third set of industrially-worn samples was also prepared from MC2 bricks. As can be seen from Table 3, the excellent performance of the newly employed refractories continued in the next furnace campaign. The results show that even after 16 months of service, the lining could still be safely used for a few more months. Figures 9, 10 and 11 show BSE images of the samples. A dense slag layer has formed at the hot face of the bricks collected from zones 4 and 5. Metallic copper is incorporated in the slag layer. The samples are completely infiltrated by copper oxide (white phase on the images). Forsterite was also observed in the bricks collected from these zones. As with the samples recovered from the same zones during the previous relining, the forsterite presence was more pronounced in zone 5 (see Figure 10a).

Figure 10b is a detailed BSE image clearly showing the abundance of forsterite in the brick collected from zone 5. Microprobe analyses performed on periclase grains near the hot face indicate that a considerable amount of FeO (up to 25 wt.-%) and some CuO (up to 5 wt.-%) diffused into the rim of the grains. This diffusion changed the colour of the rims making them lighter in BSE mode. The latter phenomenon was observed in all investigated samples.
A BSE image of a sample collected from zone TAP is presented in Figure 11. The slag layer on the hot face is thinner than in the previous samples, which can be explained by the refractory location in the lining. Bricks around the tap hole are in contact with slag only during furnace rotation for slag skimming. Nevertheless, a certain amount of forsterite has formed at the refractory hot face. A low level of open porosity is observed in this sample since most of its pores were filled by metallic copper (white phase on the image).

As with the bricks recovered during the previous relining, a dense slag layer with copper inclusions was observed along the joints with adjacent bricks. Obviously, slag and copper infiltrated the joints between bricks, causing the formation of this layer. The latter disappears at a distance of 10 to 25 cm from the refractory hot face. The minimum depth of penetration along the joints (10 cm) was measured in bricks recovered from zone 4 while the maximum depth (25 cm) was registered in bricks collected close to the tuyeres zone (T1 and T2).

4 Discussion

In the course of the present study, 22 bricks in total were collected from distinct locations in the anode furnace linings for microstructural investigation. The first set of bricks (lining N1 – all MC1) included the formerly applied direct-bonded magnesia-chromite refractories while the second and the third sets (linings N2 and N3) included the newly employed rebonded magnesia-chromite bricks based on presintered grain (MC2). The study revealed that various chemical, thermal and mechanical (physical) degradation mechanisms influence the bricks in service.

4.1 Chemical wear mechanisms

4.1.1 Copper and slag components infiltration

All industrially worn samples collected during the three consecutive relinings were heavily infiltrated with metallic copper and copper oxide. Bricks recovered from zones 1, 2, 3, MID and TAP were mostly infiltrated with copper metal while bricks recovered from zones 4, 5, 6, T1 and T2 were predominantly infiltrated with copper oxide. The infiltration limit is located at a distance of around 20 cm from the hot face for most of the investigated bricks. However, this limit for bricks collected from the area close to the tuyeres zone reached 25 to 26 cm. The infiltrated copper oxide is mainly present as cuprous oxide (Cu₂O), although a minor amount of cupric oxide (CuO) was also analysed mainly at the refractory hot face.

The penetrating anode slag brings copper oxide, iron oxide and silica to the brick. It was noticed that in many samples copper oxide and iron oxide diffused in periclase and primary chromite grains. Another slag component (silica) has reacted with magnesia (from periclase) to form forsterite (see 4.1.3 for details).

The penetrating liquid phases penetrate the refractory through the open pore network and along the periclase grain boundaries. Once inside the brick they dissolve most of the intergranular secondary chromite spinel, partly replacing the direct-bonded (solid) structure of the refractory with a liquid-bonded one. The newly-formed, partially liquid-bonded microstructure is more susceptible to hot erosion and abrasion mechanisms resulting in accelerated refractory wear.

4.1.2 Spinelisation

The infiltrated slag imports iron oxide to the brick. The latter diffuses into the primary (and to some extent into the secondary) chromite spinel (Mg₆Fe₃)[Cr,Fe,Al₄]O₁₂. As a result of this diffusion, it is suggested that during refractory service, the primary chromite grains are continuously growing and sintering, thus forming a network of interconnected spinel grains (see Figures 5, 6 and 7). The consequence of this phenomenon is a more complex spinel composition, which is enriched in iron (wt.-%): 26 to 35 Cr, 22 to 27 Fe, 14 Mg, 9 Al, 0.5 Ca. Primary chromite in the as-delivered brick normally contains around 8 wt.-% Fe. The amount of Cr and Fe in the in-situ formed spinel phase varies strongly (26 to 35 % Cr, 22 to 27 % Fe), depending on the amount of diffused iron oxide. The amount of the other spinel components is nearly constant (± 1 %). The spinelisation process is highly pronounced in the slagline area (zones 4, 5, T1 and T2). As a result of this degradation phenomenon, a difference in the chemical composition (∆C) between the hot face and the interior of the brick emerges. This ∆C, together with some densification of the refractory hot face, makes the brick surface more prone to spalling.

4.1.3 Forsterite formation

A very limited amount of silicate phase (CMS) was detected in the as-delivered samples while large amounts of silicate phases (mainly forsterite) were found in many worn samples. This suggests that a significant quantity of anode slag has infiltrated the brick microstructure. The silica it contains penetrates the refractory, together with copper, copper oxide and iron oxide. Once inside the brick, silica interacts with magnesia (refractory component) to form forsterite following reaction (6). Forsterite formation is mostly outspoken in the slagline area (zones 4, 5, T1 and T2). The impact of forsterite formation on refractory
performance has been discussed in detail in previous work by the present authors [9]. The effect of this degradation phenomenon is a slight volume increase inside the bricks resulting in densification of the refractory microstructure, which may lead to cracking and spalling.

4.2 Thermal and mechanical wear mechanisms

4.2.1 Thermal shock stress, thermal and mechanical fatigue

Temperature changes in case of irregularities and interruptions in normal furnace operation create stresses in the bricks, which can be absorbed only to a limited extent and lead to brick breakage as soon as the microstructural strength limit is exceeded. Thermal fatigue of the lining is due to the temperature changes occurring during consecutive batches (furnace full of molten blister versus empty furnace in waiting periods). The amplitude is typically in the interval 400 to 500 °C. The lining is also subjected to temperature changes according to the cycle of furnace rotation: i.e. the bricks are alternately down under the hot melt and up in the free (cooler) space of the furnace. The final result of the thermal fatigue is weakening of the microstructural layers on the hot face. Bricks from all investigated zones are equally exposed to this degradation mechanism. Causes for mechanical fatigue are the same as of thermal fatigue (e.g. furnace rotation resulting in changing brick load) but this phenomenon reaches also deep zones of the brick in the form of micro-fissures and macro-cracks, as a result of the heavy mechanical stress imposed on the lining (especially pronounced in zones 3 and TAP).

4.2.2 Hot erosion and abrasion

These phenomena are caused by the movement of the solid, liquid and gaseous content of the furnace and create a continuous wear on the hot face of the bricks from all zones except zone 6. The higher the temperature and the speed of movement of materials in the furnace, the more pronounced are these wear mechanisms. The effect of the latter is also accelerated by the chemical corrosion mechanisms described in the previous section.

5 Conclusions

The microstructural investigation of worn bricks recovered from several anode furnace linings generated the following conclusions with respect to the above-determined wear mechanisms:

The anode furnace lining can be divided in low wear (barrel and sidewalls above the slagline – zone 6), medium wear (barrel and sidewalls in contact with copper – zones 3, MID and TAP), high wear (slagline – zones 1, 2, 4 and 5) and highest wear (zones T1 and T2) areas.

Refractory degradation comes as a consequence of the combined action of chemical, thermal and mechanical drivers, which interact synergistically with one another, as shown in Figure 12.

It was found that various degradation mechanisms influence the refractory performance in anode furnaces (see

Figure 12). Depending on the region in the lining their relative importance may vary.

Firstly, the infiltrating copper, copper oxide and iron oxide continuously deplete the intergranular secondary chromite by dissolving most of it and partly replacing, in this way, the direct-bonded (solid) structure of the bricks with a liquid-bonded one. Since MC1 bricks possess higher level of porosity, a larger amount of copper and slag components infiltrated them. This led to a higher level of liquid bonding, which resulted in a higher wear rate compared to MC2 bricks. Secondly, a densification of the refractory hot face took place as a result of spinelisation and forsterite formation. Both phenomena are more pronounced in MC1 bricks resulting in a higher level of densification. This leads to compositional gradients (ΔC) in the bricks. The chemical wear mechanisms reduce the strength of the bricks and add to the susceptibility of the microstructure to further infiltration.

Apart from chemical wear causes, thermal and mechanical impacts increase the wear level. The thermal load is the result of thermal cycling, which adds further stresses (AT) to the refractory material (outspoken in zones T1 and T2). Mechanical stresses are the result of the erosive fluid, the abrasion of solids and the changing brick load (as a result of the furnace rotation). As Figure 12 shows, when already weakened refractory microstructures are exposed to additional thermal and mechanical loads, this gives rise to both continuous degradation (hot erosion and corrosion) and discontinuous wear (thermo-chemical spalling).

With respect to the optimisation of the refractory lining configuration it can be stated that this was a success. A zoned lining concept was proposed and installed with MC1
bricks used in the low and medium wear areas (barrel and sidewalls above the slag line, and in contact with copper – zones 3 and 6) and MC2 bricks applied in the high wear areas (zones 1, 2, 4, 5, T1 and T2) as well as in zones MID and TAP due to specific operational requirements. Fused-grain magnesia-chromite bricks with zirconia addition were used exclusively in the extremely high wear area (tuyere blocks). As a result of the fact that high-quality materials were used in the high wear zones, the overall wear rate could be limited and brought into accordance with the wear rate of the lower-quality bricks applied in the low wear zones. This enhanced performance resulted in a significant improvement of the overall lining lifetime – from 11 months to 16 months.

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