The Role of Graphite in Refractories such as $\text{Al}_2\text{O}_3/\text{MgO}/\text{C}$
Overview

- AMG Mining – Short introduction
- History of refractory production in Europe
- Crucibles
- Refractories
  - High alumina refractories
  - $\text{Al}_2\text{O}_3$-$\text{MgO}$-$\text{C}$
  - MgO-$\text{C}$
- Summery of the graphite role in refractories
**AMG Mining - Company History**

1870  Start of industrial Graphite mining in Kropfmühl
1877  Patent for a „Method to purify Graphite“
1916  Change into a public company
1916  First deliveries to the pencil industry
1980  Development of water based Graphite-Dispersions
1984  UF Graphite: Standard in PM Industry
1998  Acquisition of RW silicium GmbH
1999  Start of expandable Graphite production in Týn
1999  Introduction of SGB Graphite
2008  80% of GK shares were bought by AMG
2012  First increase to 93,59 %, then squeeze out
2012  Restart of mining in Kropfmühl
Worldwide companies AMG

AMG Advanced Metallurgical Group N.V. (Netherlands)

100 %

Graphit Kropfmühl

100 %

Advanced Materials Division

100 %

Engineering Systems Division

Germany
- Silicon metal
- Natural and synthetic graphite

Germany
- Specialty alloys for titanium and superalloys
- Coating materials
- Vanadium chemicals
- Metals-based powders

US
- Ferrovanadium
- Ferronickel-molybdenum

UK
- Aluminium master alloys
- Chromium metal
- Ferrotitanium
- Metals-based powders

Brazil
- Tantalum oxide
- Niobium oxide
- Aluminium master alloys

France
- Antimony trioxide

Germany
- Vacuum furnace systems
- Own & Operate heat treatment facilities

US/Mexico
- Own & Operate heat treatment facilities
Turnover AMG Mining 2012

- Refractory | 3.2%
- Powder metallurgy | 7.9%
- Pencils | 2.8%
- Lubricants | 10.3%
- Heat insulation | 25.7%
- Trading | 8.9%
- Batteries | 2.3%
- Carbon brushes | 11.8%
- Chemistry | 7.3%
- Dispersions | 4.8%
- Formed parts | 2.5%
- Foundry | 2.1%
- Friction pads | 8.4%
- Gasket | 1.9%
History – graphite in crucibles

The melting of metals in crucibles has a long history, beginning in ancient Egypt and still continuing its traditions in today’s modern world. The first crucibles in the very advanced civilisation made in Egypt were based on silicates free of graphite.

It is not clear when people first found out the advantages of mixing clay with graphite for crucibles. The German scientist Georgius Agricola was the first who made a report on the Passauer / Hafnerzeller crucibles for melting metals before the year 1556.

The addition of graphite to pottery made it water proof even without glaze and better heat conductive. We can assume that the very first production of clay bounded graphite crucibles had taken place in the “Kropfmühl” area.

In history, the celtics used graphite for production of ceramics already 2500 years ago.
Refractories

Market Size for Graphite in Refractories

- 2011: About 485,000 t graphite for 3.2 Mio t C-containing refractories
- 2 main groups at the center of attention:
  A) Crucibles:
      Main parts: Clay/tone, graphite
  B) Refractory stones (magnesite carbon stones)
      Main parts: Magnesite + coal materials
Refractories

Graphite containing crucibles

- Specs: Good thermal and el. conductivity
- Used in furnaces fired with fuel, electricity or induction, mostly for light non-ferrous metals
- Service temperature up to 1600 °C

Raw materials used in mixes for crucibles:

<table>
<thead>
<tr>
<th>Clay bonded</th>
<th>Carbon bonded</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-28% binder (refractory clays)</td>
<td>12-25% binder (refractory clays, pitch/phenolic resin)</td>
</tr>
<tr>
<td>6-10% Si</td>
<td>3-5% Si</td>
</tr>
<tr>
<td>15-25% SiC</td>
<td>38-45% SiC</td>
</tr>
<tr>
<td>40-50% Graphite</td>
<td>25-35% Graphite</td>
</tr>
</tbody>
</table>

- Isostatic pressing or screw-in (plastic) process
- Glaze formation during service protects graphite against oxidation
Graphite containing crucibles

- Specification for mostly used natural graphite:
  - C = 85-94%, other important parameters: crystallite size, flake size and thickness, BET
  - Relative fraction of edge sites strongly influences oxidation
  - Ash composition and melting point

- “thick” graphite flakes from Zimbabwe
- “thin” flakes from Madagascar
Refractories

Al$_2$O$_3$-C (AC) high alumina refractories with ZrO$_2$

- Widely used as the lining materials in blast furnaces and electric furnaces

**Important spec:**
- Corrosion behavior in the melts of smelting reduction with the iron bath
- Thermal shock during filling and emptying

**Studied compositions:**

<table>
<thead>
<tr>
<th>Specimens</th>
<th>AC1</th>
<th>AC2</th>
<th>AC3</th>
<th>AZ1</th>
<th>AZ2</th>
<th>AZ3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ (%)</td>
<td>76.75</td>
<td>74.60</td>
<td>72.45</td>
<td>71.58</td>
<td>68.35</td>
<td>66.02</td>
</tr>
<tr>
<td>SiO$_2$ (%)</td>
<td>11.20</td>
<td>10.40</td>
<td>10.12</td>
<td>10.17</td>
<td>9.50</td>
<td>8.14</td>
</tr>
<tr>
<td>C (%)</td>
<td>4.05</td>
<td>7.20</td>
<td>9.50</td>
<td>9.90</td>
<td>9.80</td>
<td>9.80</td>
</tr>
<tr>
<td>ZrO$_2$ (%)</td>
<td>0.12</td>
<td>0.51</td>
<td>1.50</td>
<td>3.00</td>
<td>6.00</td>
<td>9.00</td>
</tr>
<tr>
<td>CCS (MPa)</td>
<td>41.95</td>
<td>44.74</td>
<td>45.88</td>
<td>42.53</td>
<td>43.65</td>
<td>41.50</td>
</tr>
<tr>
<td>MOR (MPa)</td>
<td>15.45</td>
<td>16.68</td>
<td>17.81</td>
<td>15.36</td>
<td>14.45</td>
<td>15.66</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>5.38</td>
<td>4.52</td>
<td>4.03</td>
<td>4.18</td>
<td>4.92</td>
<td>5.14</td>
</tr>
</tbody>
</table>

**Refractories**

**Al$_2$O$_3$-C (AC) high alumina refractories with ZrO$_2$**

**Testing**

- Corrosion behaviors: rotary immersion and quasi-static immersion in electric resistance furnace
- Experimental temperatures were between 1400 °C and 1650 °C.
- The atmosphere above the molten bath was maintained at 30% CO, 60% N$_2$ and 10% CO$_2$ by volume.
- Slag composition: 10.0% FeO, 35.3% CaO, 33.2% SiO$_2$, 8.0% MgO, 11.0% Al$_2$O$_3$, 2.5% TiO$_2$. Iron bath formed by pig iron scrap, 4.16% C, 0.53% Si, 0.32% Mn, 0.10% P and 0.034% S.

-Dependence of the corrosion rate of refractories on the FeO content in melts, test temperature 1500 °C

- The refractories containing ZrO$_2$ exhibit a good anti-corrosion characteristic, especially in the melts of FeO concentration above 6%.

- Graphite carbon contained in the refractory is an active reducing agent of the iron oxides. The graphite of the Al$_2$O$_3$-C refractories was oxidized by the iron oxides of the melts. Pores and cracks are formed in the reaction zone.
Al₂O₃-C (AC) high alumina refractories with ZrO₂

SEM: AC2, immersed in slag and iron bath, test temperature 1773 K, rotary speed of refractory in melts 15 r/min.

Al₂O₃-C refractories are composed of corundum, mullite, Al₂O₃ and graphite.

EDS data: graphite carbon was oxidized over 90% and no graphite carbon was found in the interface between deteriorative layer of the refractory and slag film.

Corrosion mechanism of AC refractories in the smelting reduction melts with iron bath:
1. graphite oxidization
2. deteriorative layer formation.

The deteriorative layer of Al₂O₃-C refractory was corroded greatly by the smelting reduction melts.

Lot of new compounds formed by reaction with slag, such as CaSiO₃, TiO₂, FeSiO₃, Al₂SiO₅ and Fe₃C.
Refractories

\( \text{Al}_2\text{O}_3-\text{MgO-C (AMC)} \) refractories for steel ladle lining

**Important spec:**

- Residual expansion during the usage
- Temperatures from 1600 to 1750 °C, resistance against turbulence of steel bath during heating/purging
- Thermal shock during filling and emptying
- Corrosion contact with basic steel ladle slags

- AMC: Superior chemical and thermodynamic stability characteristics when compared to high alumina and doloma steel ladle refractories, but also excellent thermal and mechanical properties.
- Influence of alumina/carbon ratio and magnesia / silica contents on the refractories corrosion resistance.

- The carbon bond enables combinations of raw materials with varying expansion coefficient
- Usual compositions: 50-70% \( \text{Al}_2\text{O}_3 \), 15-30% MgO, 2-15% C, 0.3-3% others (\( \text{SiO}_2 \), \( \text{Fe}_2\text{O}_3 \), \( \text{TiO}_2 \))
Refractories

\(\text{Al}_2\text{O}_3\text{-MgO-C (AMC) refractories for steel ladle lining}\)

- Important spec: Residual expansion during the usage responsible for the formation of a monolithic refractory lining resulting in a decreased steel penetration through the refractory joints.

\(\text{Al}_2\text{O}_3/C (A/C) = 12.9\)

- Higher corrosion resistance for highest C content and smallest SiO2 content

- Present phases:
  - corundum \(\text{Al}_2\text{O}_3\)
  - mullite \(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2\)
  - periclase \(\text{MgO}\)

- Separate graphite phase with high refractoriness, \(\lambda\), low thermal expansion, low wettability by slag

- Wear results with rotary slag attack


High mullite conc. promotes Ca-aluminosilicat formation (eutectic at 1265 °C)

Periclase consumes mullite and contributes corrosion resistance to high basicity slags
Al$_2$O$_3$-MgO-C (AMC) refractories for steel ladle lining

A/C = 12.9

- Better packing of microstructure, smaller pore size
- Higher conc. of graphite lead to best packing

Graphit Kropfmühl
Refractories

Al$_2$O$_3$-MgO-C (AMC) refractories for steel ladle lining

- Slag test at 2.74 bin. basicity
- 2h / 1750 °C

SEM before test (20x)

A/C = 12.9

SEM after rotary slag test

A/C = 19.2
Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

**Important spec:**
- Used in basic furnace, electric arc furnace, and steel ladles

**Role of graphite**
- Carbon specs:
  - macrocrystalline flakes with 90-96% C, -100 to +50 mesh, 3-25%
  - carbon black for optimal pore filling 1-2%
  - pitch / phenolic resin for coaked binders (3%)

- Negative effects of oxidation of graphite: spalling and pore generation
  -> addition of antioxidants necessary

- Even better protection is possible by coating the antioxidant on top of the graphite particles
**Refactories**

**MgO-C (MC) refractories for basic/electric arc furnaces**

**Role of graphite**
- Corrosion resistance by less wettability with a molten metal
- Excellent thermal shock resistance by low thermal expansion & high thermal conductivity
- Low elasticity, due to the presence of graphite
- Structure-flexible bond characteristic – C-bond usually forms in service
- Carbon changes the infiltration depth from cm to the mm range by:
  - Reduction of Fe₂O₃ in the infiltrating slag to Fe -< increase of the eutectic temp. from 1300 °C to >1600 °C
  - Non wetting behaviour between oxidic slag and brick carbon

---

**Graphitic Content vs. Properties**

- Young's modulus
- Thermal conductivity
- Depth of slag penetration

**References**
Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

**SEM:** Anisotropy of thermal conductivity by flake orientation

Graphite flake alignment in MgO-C bricks, perpendicular (left) and parallel (right) to the bricks long dimension

W.E. Lee, http://core.materials.ac.uk
MgO-C (MC) refractories for basic/electric arc furnaces

SEM:

Formation of a dense zone due to reduction of MgO with C at high T which vaporized the Mg and precipitated it in the dense zone.

**MgO-C (MC) refractories for basic/electric arc furnaces**

Protection of the graphite in the dense zone: additions of metals like Mg, Al, Si

<table>
<thead>
<tr>
<th>Condition</th>
<th>Reaction</th>
<th>Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1380 K</td>
<td>MgO + Al + C</td>
<td>5. unreacted brick</td>
</tr>
<tr>
<td>&gt;1380 K</td>
<td>MgO + Mg + C</td>
<td>4.</td>
</tr>
<tr>
<td>(N₂)</td>
<td>MgO + AlN + C</td>
<td>3.</td>
</tr>
<tr>
<td>(CO, N₂)</td>
<td>MgO + MgAl₂O₄ + C</td>
<td>2.</td>
</tr>
<tr>
<td>&gt;2080 K</td>
<td>MgO + AlN + C</td>
<td>1. hot face</td>
</tr>
</tbody>
</table>


Example of reactions inside different zones of the basic oxygen furnace with Al addition
Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

Protection of the graphite in the dense zone: additions of metals like Mg, Al, Si

Typical microstructure of a MgO-C brick which contains Al and Si as antioxidants.

A=MgO; B=aluminium; C=silicon; D=merwinite (Ca$_3$MgSi$_2$O$_8$)

MgO-C (MC) refractories for basic/electric arc furnaces

- Further protection of the graphite particles by coating with Al

Shrinking – Core Model (SCM)
- The shrinking core model for an isothermal spherical graphite particle (B) which reacts with gas (A)
- There is a sharp boundary (the reaction surface) between the no reacted core of the graphite and the porous outer shell (ash layer).
- The gas film reflected the resistance to mass transfer of gas (A) from the bulk gas to the exterior surface of the particle.
- As time passes, the reaction surface moves progressively toward the center of the particle.
- According to the SCM model, three processes involving mass transfer of gas in gas film, diffusion of gas in porous layer and reaction of gas with solid (B) at reaction surface, are rate controlling steps.

Z. Ali Nemati et al., Tehran International Conference on Refractories, 4-6 May 2004
Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

- Further protection of the graphite particles by coating with Al

**Shrinking – Core Model (SCM)**

1. Oxidation increases exponentially with temperature because diffusion of oxygen and reaction of graphite with oxygen increase when temperature increases.

2. With increasing of the graphite content, the rate of weight loss increases due to the formation of a more porous oxidized layer, but the fractional weight loss decreases due to the increase of the initial carbon content. The weight loss increase is not, however, proportional to the enhancement of the graphite content. This may be attributed to the combined influences of the reaction front area change, CO/CO2 ratio change and inter diffusion coefficients variations.

3. Oxidation mechanism is pore diffusion, which means the diffusion of oxygen through decarburized layer is the process determining step.

4. With higher graphite content, the oxidation mechanism tends to slightly deviate from pure pore diffusion control. The gas volume variations due to the CO/CO2 ratio change may cause the slight shifting of the oxidation mechanism from pure pore diffusion to porous diffusion -external gas transfer mechanism.
**Refractories**

**MgO-C (MC) refractories for basic/electric arc furnaces**

Activation of graphite surface

1. **Graphite particles**
   - Mixing with an acid solution
   - Sonicating for 3h at RT & stirring for 24h at RT
   - Filtering
   - Washing with distilled water
   - Drying at 80 °C for 48h

2. **Surface modified graphite**
   - Mixing with Al precursor in an aqueous solution
   - Drying at 80 °C for 1h
   - Heat treatment at 300 °C for 1h

3. **Al-coated graphite**

Increased sedimentation stability of surface treated graphite in water after 3d

Refractories

MgO-C (MC) refractories for basic/electric arc furnaces

- Combustion tests at 500 – 1200 C for 1h

SEM morphologies and results of EDS analysis for modified graphite particles without and with coating by Al precursor:
(a) without coating layer and
(b) with coating layer.
**Refractories**

*MgO-C (MC) refractories for basic/electric arc furnaces*

- Combustion tests at 500 – 1200 °C for 1h

- Graphite without coating layer starts oxidizing at 700 °C and is fully reacted at 900 °C

- With coating: Oxidation starts at 900 °C and is fully oxidized at 1200 °C

- Further development of antioxidants: Binding resins that contain antioxidants attached to its polymeric chain in the form of complexation cations.

Refractories

Summary – Role of graphite

- Oxidation resistance
  - Graphite characteristics
    - Particle size distribution
      - Graphite impurities
    - Crystallinity
      - Macrocrystalline flakes
      - Microcrystalline powder
  - Presence of antioxidants
    - By mixing into the formulation
    - By coating onto the graphite

- Thermal shock resistance
  - Anisotropy of graphite flake
  - Thermal conductivity

- Wear resistance

- Structural strength
  - Infiltration depth of slag
    - Optimal pore filling by fine graphite or CB
    - Nonwetting of graphite by oxidic infiltrate
  - Bonding strength inside the C lattice
  - Adhesion of C (coke) lattice to the base material
  - Formation of favorable strong phases by reaction of the antioxidant at higher T

- Mechanical strength
  - Reduction of slag components with a low mp
  - Aspect ratio of graphite flake orientation

Refractory Specification
Thank you for your attention