The use of graphite in the refractory industry

Alexey Trisvetov
**What Refractories are?**

**Refractory products** are nonmetallic ceramic materials (may contain metals) that have a certain refractoriness – a pyrometric cone equivalent of $\geq 1,500 \, ^\circ C$.

**OR**

**Refractories** are products which are installed whenever high temperature ($\sim 600 – 2,000 \, ^\circ C$) exists.

Refractory materials are based on 6 oxides: \( \text{Al}_2\text{O}_3, \text{SiO}_2, \text{MgO}, \text{CaO}, \text{Cr}_2\text{O}_3, \text{ZrO}_2 \), their compounds and often in combination with carbon.

*Base material pyramid with the location of the refractory materials (according to H. Barthel)*
Progress in metallurgy demand new refractory materials and one way of improvement is to use carbon.

Main up-to-date types of secondary steelmaking processes:

- Chemical heating station
- Composition adjustment by argon sealed bubbling with oxygen blowing
- Heating advanced ladle treatment
- Hot metal desulphurisation station
- Ladle furnace
- Ladle treatment station
- RH technology (RH, RH-OB, RH-TOP)
- Vacuum arc degassing (VD)
- Vacuum oxygen decarburization (VOD and VD-OB)
Development of refractories is aligned with steel industry

Tendencies in carbon-containing basic refractories

Similar tendencies in production of steel and refractories

Source: 5th MagMin Conferenc. Sanjiv Bhushar

Based on UNITECR’99. Refractories at the Turn of the Millennium. Dipl.-Ing. Jakob Mosse, Dr. Günter Karhut
Graphite Market

Refractories are the largest single market for natural graphite

<table>
<thead>
<tr>
<th>World: Estimated consumption of natural and synthetic graphite by region and end-use, 2011 (kt)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrodes</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Refractories</strong></td>
</tr>
<tr>
<td><strong>Lubricants</strong></td>
</tr>
<tr>
<td><strong>Foundries</strong></td>
</tr>
<tr>
<td><strong>Graphite shapes</strong></td>
</tr>
<tr>
<td><strong>Batteries</strong></td>
</tr>
<tr>
<td><strong>Friction products</strong></td>
</tr>
<tr>
<td><strong>Recarburising</strong></td>
</tr>
<tr>
<td><strong>Others</strong></td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

Note: 1-Including synthetic graphite consumption in foundries, friction materials, refractories and recarburisers


By 2016, the graphite market for refractories could grow to **560,000 tpy**. Global refractories production was around **42.6 Mt ($22.9 Bn)** in 2011 and can grow to **59 Mt ($31 Bn)** in 2015. Only a small proportion of refractories contain graphite but the industry is the main consumer of natural material, particularly **flake**.
Graphite Market

Refractories production drives flake graphite demand

Refractories production compared with flake graphite supply (China)

The volume of production of carbon-containing refractories in the world can be estimated at 3.0-3.2 Mt. Installed magnesia-carbon production capacity in China reached 1.3 Mt in 2012, of which over 1 Mt was exported.

**Types of Carbon used**

Depending on the type and technology of refractory materials the following types of carbon can be used:

- **Fine-crustalline and amorphous graphite** (natural and synthetic)
- **Flake graphite**
- **Synthetic resin** (phenolics, furane, etc.) and pitch (coal-tar, petroleum)
- **Recycling carbon containing materials**
- **Anthracite**
- **Coke**
- **Carbon-black**
- **Exotic carbon** (3-D graphite, nano-graphite, graphite fiber etc.)
## Graphite-containing Refractories

### Carbon and Graphite Bricks

<table>
<thead>
<tr>
<th>Carbon-containing Refractories</th>
<th>Carbon brick</th>
<th>Part-graphite brick</th>
<th>Graphite brick *)</th>
<th>Carbon microporous brick</th>
<th>Carbon super-microporous brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main raw materials</td>
<td>Termoanthracite, petroleum coke, flake graphite</td>
<td>Termoanthracite, synthetic graphite</td>
<td>Petroleum coke, pitch coke</td>
<td>Termoanthracite</td>
<td>High-density termoanthracite</td>
</tr>
<tr>
<td>Type of bound</td>
<td>coal tar pitch</td>
<td>coal tar pitch</td>
<td>coal tar pitch</td>
<td>coal tar pitch</td>
<td>coal tar pitch and phenol resin</td>
</tr>
<tr>
<td>Additions</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>SiC (few), Si-powder</td>
<td>SiC (a lot of), Si-powder</td>
</tr>
<tr>
<td>C content, %</td>
<td>≥ 92</td>
<td>≥ 94</td>
<td>≥ 99</td>
<td>≥ 60</td>
<td>≥ 60</td>
</tr>
<tr>
<td>SiC, %</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3-10</td>
<td>5-15</td>
</tr>
<tr>
<td>Al2O3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0-12</td>
<td>0-12</td>
</tr>
<tr>
<td>SiO2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0-5</td>
<td>0-5</td>
</tr>
</tbody>
</table>

*) – These types of refractories are graphitized – are performed in the Acheson resistance furnace or by graphitizing with direct current flow in the continuous graphitizing furnace

### Applications

- Ladle treatment: Large-shaped carbon and graphite blocks are installed as lining in the lower part of a blast furnace.
- In alumina production, the lining of the electrolysis tank is out of carbon and graphite bricks which are rammed with carbon ramming mixes.
- In the bottoms of furnaces that produce Si, FeSi, FeMn etc.
# Graphite-containing Refractories

## Oxide-Carbon Refractories

<table>
<thead>
<tr>
<th>Carbon-containing Refractories/ Main raw materials (except carbon components)</th>
<th>Carbon content</th>
<th>Type of carbon into refractories/ Type of graphite</th>
<th>Carbon content in graphite and flake size of graphite</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO-C (MC-type) Magnesia-carbon / Sintered and fused magnesia, antioxidants (Al, Mg, Al-Mg, B₄C etc.)</td>
<td>3 - 35</td>
<td>Flake graphite (3-25%), pitch (2-3%), synthetic resins (3%), carbon-black (1-2%)</td>
<td>C 86 – 99%, as a rule - 90-95% / -100 ÷ +50 mesh (-150 µm ÷ +300 µm). At times it used special types of graphite e.g. mark - SV: +50 mesh 5% max. / -100 mesh 50-80% - 150 mesh 20-40%.</td>
<td>The application in iron and steel industry: working linings of basic oxygen furnace, electric arc furnace, casting arc, tap hole surrounding and sleeves, purging elements for BOF and EAF.</td>
</tr>
<tr>
<td>Al₂O₃-MgO-C (AMC-type) Alumina-Magnesia-carbon MgO- Al₂O₃-C (MAC-type) Magnesia-Alumina-carbon / White and brown corundum, tabular alumina, AM-spinel, sintered bauxite, antioxidants.</td>
<td>5 - 15</td>
<td>Flake graphite (4-12%), pitch (2-3%), synthetic resins (3%), carbon-black (1-2%)</td>
<td>C 92 – 94% / as a rule -100 mesh (-150 µm)</td>
<td>The application in iron and steel industry: working linings of casting ladle in wall.</td>
</tr>
<tr>
<td>Al₂O₃-SiC-C (ASC-type) Alumina-Silicon carbide-carbon Al₂O₃-C (AC-type) Alumina-carbon / White and brown corundum, AM-spinel, sintered bauxite, SiC, antioxidants (Al, Si, etc.)</td>
<td>5 - 35</td>
<td>Flake graphite (3-32%), pitch (2-3%), synthetic resins (3%)</td>
<td>C 92 – 94% / as a rule -100 mesh (-150 µm)</td>
<td>The application in iron and steel industry: working linings of torpedo ladle and hot-metal ladle.</td>
</tr>
<tr>
<td>CaO-MgO-C Magnesia-dolomite-carbon/ intered and fused magnesia and dolomite</td>
<td>7 - 30</td>
<td>Flake graphite (5-27%), pitch (2-3%), synthetic resins (3%)</td>
<td>C 92 – 94% / as a rule -100 mesh (-150 µm)</td>
<td>The application in iron and steel industry: working linings of casting ladle (VAD and VOD).</td>
</tr>
</tbody>
</table>
Graphite-containing Refractories

Oxide-Carbon Refractories in Micro-pictures

Microphotography of MgO-C bricks after using (zoom 1000×, transmitted light)

Microphotography of Al2O3-MgO-C bricks (zoom 50×, reflected light)
Graphite-containing Refractories

Oxide-Carbon Refractories in **Macro-pictures**

1. MgO-C bricks in vacuum packing
2. Installation of MgO-C bricks
3. MgO-C bricks
4. MgO-C bricks after using

Using of MgO-C bricks
Graphite-containing Refractories

Functional Refractory Products for Steel Casting
# Functional Refractory Products for Steel Casting

<table>
<thead>
<tr>
<th>Type of refractories / Main raw materials (except carbon components)</th>
<th>Applications and Carbon Content</th>
<th>Type of carbon into refractories</th>
<th>Carbon content in graphite / flake size of graphite</th>
</tr>
</thead>
</table>
| Al₂O₃-C (AC) and Al₂O₃-ZrO₂-C (AZC) materials / White corundum, tabular alumina, zirconium oxide, zirconia mullite, SiC, antioxidants (Al, Si etc.) | **Tundish Stopper**  
body: C ~ 20 – 40%, head: C ~ 5 – 20%  
**Subentry Nozzle**  
Seat area: C ~ 5 – 15%, body: C ~ 20 – 30%  
**Ladle Shroud**  
Seat area: C ~ 15 – 20%, body: C ~ 25 – 40%  
**Tundish Nozzle**  
Seat area: C ~ 15 – 25%, body: C ~ 20 – 30%  
**Slide Gate**: C ~ 5 – 7%  
**Collector Nozzles**: C ~ 5 – 10% | Flake graphite, synthetic resins (~3%) | 90-99% / -100 ÷ +50 mesh (-150 µm ÷ +300 µm) |
| ZrO₂-C (ZC) material / zirconium oxide, antioxidants (Si, SiC etc.) | **Subentry Nozzle**  
Slag line: C ~ 15 – 22%  
**Ladle Shroud**  
Slag line: C ~ 15 – 22% | | |
| MgO-C (MC) and MgO-Al₂O₃-C (MA-spinel-C) materials / fused magnesia, AM-spinel, antioxidants (Al, B₄C etc.) | **Tundish Stopper**  
Head: C ~ 15 – 20%  
**Subentry Nozzle**  
Seat area: C ~ 15 – 20%  
**Ladle Shroud**  
Slag line: C ~ 25 – 30%  
**Tundish Nozzle**  
Seat area: C ~ 15 – 25%, body: C ~ 20 – 30%  
**Slide Gate**: C ~ 5 – 7% | | |

There is an Important factor of anisotropy (length: width of flake) - about 1:50, as affect the thermal shock resistance of refractory products.
Graphite-Containing Crucibles

**The Crucibles** are refractory, coarse ceramic vessels with good thermal conductivity and relatively low electrical resistance. The crucibles are used in various furnaces to melt metals and alloys and/or keep them hot. The crucibles are most commonly used in the light metal and non-ferrous metal sector.

Flake graphite is the preferred type of graphite for use in crucibles, although amorphous graphite can also be used. Flake graphite burns more slowly, has low combustibility, high thermal resistance and the orientation of the flakes can increase the strength of the finished crucible. Graphite is often used to give specific results, for example it can be used in crucibles for foundry induction heaters to provide special electrical properties.

<table>
<thead>
<tr>
<th>Type of crucibles / Main raw materials (except carbon components)</th>
<th>Carbon content</th>
<th>Type of carbon into crucibles</th>
<th>Carbon content in graphite and flake size of graphite</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay bond / Refractory clay (22-28%), SiC (15-25%), Si (6-10%)</td>
<td>40 - 50</td>
<td>Graphite (30-50%)</td>
<td>Flaked graphite: C 85 – 94% / +100 mesh (+150 µm).</td>
<td>Molding type - plastic pressing, isostatic pressing</td>
</tr>
<tr>
<td>Carbon bond / Refractory clay (12-25%), SiC (38-45%), Si (3-5%)</td>
<td>28 - 40</td>
<td>Graphite (25-35%), pitch (3-5%) or synthetic resins (3-5%)</td>
<td>Flaked graphite: C 85 – 94% / -150 mesh (-100 µm).</td>
<td>Molding type - Isostatic pressing</td>
</tr>
</tbody>
</table>
Unshaped Carbon-Containing Refractories

The following components are used in Unshaped Carbon-Containing Refractories (UCCR):

- flaked graphite (C-containing ~ 85-94%),
- pitch (2-4%),
- synthetic resins (2-3%),
- carbon-black (1-2%),
- anthracite.

Types of UCCR

- **Top-hole mixes** are used for the filling and sealing of blast furnace tapholes (C-contain ~ 8-25%).
- **Refractory Mortars** suited for the laying, mortaring and gluing of refractory bricks, prefabricated components and insulating products. CC-Mortars used for laying of blast furnace bottom (C-contain ~ 50-90%).
- **Plastic Mixes** are used for ramming of brick joint - for example in a blast furnace bottom (C-contain ~ 85-90), a basic oxygen furnace bottom (C-contain ~ 5-10%).
- **Refractory Castables** are systems Al₂O₃-SiC-C, MgO-C (C-contain ~ 5-10%).
- **Refractory gunning mixes** are used for application to the lining of oxygen converter (C-contain ~ 5-10%).
- etc.
The percentage of graphite may change properties of refractory materials

The state diagram of the $\text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{C}$ with zones of different properties

- Good Thermal Shock Resistance area
- Optimum Alternative area
- Good Corrosion Resistance area
The size of graphite particles may change the properties of refractory materials

Example #1

Relationship between content and particle size of graphite and slag corrosion (wear depth) of Al2O3-C brick

Example #2

Properties of the carbon brick samples (66% electro-calcined anthracite, 20% flake graphite, 8% Si, 6% activated alumina. Where are BD – bulk density, TC – thermal conductivity etc. – the important property of refractory materials.)

Source: UNITECR’99. The Effect of Particle Size and Carbon Content on Al2O3-C Brick Properties.

The chemical composition of graphite may change properties of refractory materials

**Example #1**
(influence of the ash amount)

Oxidative weight loss as a function of time for comparable MgO-C products with different purity graphite

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**Example #2**
(influence of chemical composition of ash)

Chemical composition of the ash of typical graphite

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O+K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount, %</td>
<td>53.4</td>
<td>28.0</td>
<td>0.38</td>
<td>11.9</td>
<td>1.27</td>
<td>2.48</td>
<td>1.90</td>
</tr>
</tbody>
</table>

Source: XXXVII International Colloquium on Refractories. High Purity Magnesias and Graphites in Magnesia-Carbon Refractories.

**Source:** XXXIX International Colloquium on Refractories. High Purity Magnesias and Graphites in Magnesia-Carbon Refractories.

There are other types of graphite influence on the refractories: the grain shape, the thickness of the grain, the method of introduction of graphite, graphite pre-processing; the various mechanisms of interaction of graphite on refractories and out. **There are various defense mechanisms of graphite oxidation.**
The Forecast for Graphite in Refractories

» The opposite trends. The increase of market for oxide-carbon refractories by BRIC- countries (mainly India and Brazil), increase the consumption of natural graphite. But decreasing consumption for refractories per ton of steel in the advanced economies may lead to decreases in consumption of graphite.

» The improving of quality. The reduction of refractories consumption per ton of steel demand improvements in quality of raw materials, including graphite.

» Unshaped refractories. The increase in consumption of unshaped refractory materials also may reduce the consumption of graphite. However there may be increases in the proportion of carbon concrete.

» New technologies. There may emerge new types of linings and applications (e.g., GrafTech International and their technology “Freeze Lining”) that will change the type of refractories used. This may lead to a decrease or an increase in the consumption of graphite (e.g. by replacing the natural graphite to the synthetic graphite).

» The exotic graphite. In the future applications of the nano-graphite and another exotic types of graphite will increase (e.g., 3D, graphite-fiber, etc.). This may significantly reduce the amount of carbon used in refractories.

» The graphite deposit for refractory companies. Due to the instability in raw material markets refractory companies are trying to secure themselves with raw materials (e.g., magnesite deposits of RHI, Magnezit Group, Magnesita S.A., etc.). As graphite is a basic raw material for oxide-carbon refractories, refractory players will buy or have already bought graphite deposits.

» etc.
Thank you for your attention!