High Temperature Purification of Natural Graphite for Nuclear Applications

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2. Tsinghua University, China
Flake graphite in pebble matrix

<table>
<thead>
<tr>
<th></th>
<th>Specification</th>
<th>Mean value of 5 batches</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reference graphite ball</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>≥1.70, ≤1.77</td>
<td>1.72</td>
</tr>
<tr>
<td>Thermal conductivity (1000 °C, W/m K)</td>
<td>≥25.0</td>
<td>32.4</td>
</tr>
<tr>
<td>Corrosion rate (mg/cm² h)</td>
<td>≤1.3</td>
<td>0.79</td>
</tr>
<tr>
<td>Erosion rate (mg/h)</td>
<td>≤6.0</td>
<td>1.55</td>
</tr>
<tr>
<td>Number of drops b</td>
<td>≥50</td>
<td>≥50</td>
</tr>
<tr>
<td>Crushing strength (KN) c</td>
<td>≥18.0</td>
<td>23.7/21.2</td>
</tr>
<tr>
<td>CTE anisotropy (20–500 °C, αx/αy)</td>
<td>≤1.3</td>
<td>1.15</td>
</tr>
<tr>
<td><strong>Spherical fuel elements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diameter (mm)</td>
<td>59.6–60.2</td>
<td>59.6–60.2</td>
</tr>
<tr>
<td>Thickness of the fuel-free shell (mm)</td>
<td>≥4.0</td>
<td>4.0–6.0</td>
</tr>
<tr>
<td>U loading (g U/fuel element)</td>
<td>7.00 ±0.35</td>
<td>6.95</td>
</tr>
<tr>
<td>Free uranium fraction (U_free/U_total)</td>
<td>≤6.0 x 10⁻⁵</td>
<td>8.7 x 10⁻⁶</td>
</tr>
</tbody>
</table>

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Xiangwen Zhou et al. / Nuclear Engineering and Design 263 (2013) 456–461

64% Natural flake graphite
16% Artificial graphite
20% Phenolic resin
Flake graphite (FG) mine

Xinghe, Inner Mongolia, China, 2012
Requirements of graphite powder for HTR-PM pebbles

- The ash content should be less than 50 ppm.
- A total equivalent Boron content (EBC) value less than 1.00 ppm.
- .......

[^1]
Chemical purification of FG

Flake graphite
Crude ore

Beneficiation

Graphite

3-5% C

High purity flake graphite for Li⁺ BATTERY

95% C

99.9% C

MAX. 99.95% C

HCl, HF

High purity flake graphite for Li⁺ BATTERY

Hunan University
High temperature purification of FG

Flake graphite
Crude ore

Beneficiation

Graphite

3-5% C

95% C

Nuclear grade flake graphite

https://asbury.com/
Objective

1. Demonstrate the purification of raw flake graphite from different sources.
   – The current reserves of graphite mine for HTR-PM are insufficient. Stable graphite supply from new mines is needed in the near future.
Natural graphite

Flake graphite (FG)

Microcrystalline graphite (MG)

Ore → Milling → Beneficiation (floating)
→ Graphite (85-94%C, 100-50 Mesh)
→ Purifying (NaOH or HCl+HF)
→ G(99-99.9%C)

Mine → Graphite (85-94%C, <200 Mesh)
→ Purifying (high temp.)
→ G(99-99.99%C)
Microcrystalline graphite (MG)

Fig. 1 – (a) Distribution of natural microcrystalline graphite in China, (b) photograph of ore from Bayan Nur, (c) powder XRD pattern of natural microcrystalline graphite ore from Lutang of Chenzhou. (A color version of this figure can be viewed online.)
MG-based isotropic graphite

- Benefits of MG-based graphite include a higher thermal conductivity in green bodies, a high degree of graphitization, and a very low CTE value of around $3.0 \times 10^{-6}$/K.
- These indicate a large potential for nuclear applications.

Fig. 3 – Natural MG-based graphite. (a) Green body, (b) baked body, (c) final product after impregnation and graphitization. (A color version of this figure can be viewed online.)
Purification of flake graphite (FG) and microcrystalline graphite (MG)

- For flake graphite, chemical purification increases the carbon content to 99.9%.
- The impurities are often embedded in the crystals, in this case, beneficiation and chemical purification does not work well.
- High temperature purification at 3000°C increases the carbon content to 99.9%.
Objective

1. Demonstrate the purification of raw flake graphite from different sources.
   - The current reserves of graphite mine for HTR-PM are insufficient. Stable graphite supply from new mines is needed in the near future.

2. Demonstrate the high temperature purification of microcrystalline graphite from different sources.

3. Show the chemical and structural mechanism involved in the high temperature purification.
High temperature purification experiments

Samples:
- FG from 6 sources within China:
  - JiXi, Bayan Nur, Xinghe, LuoBei, Nanshu, Pingdu.
- MG from 4 sources within China:
  - Chenzhou, Bayan Nur, Yongan, Panshi

Two process:
1. Lab: 3000 ºC for 30 min in a lab graphitization furnace;
2. Industry: Around 3000 ºC for hours in an Acheson furnace with a presence of Halogen (Freon).

Purity measurement: INET
- The ash content and total equivalent Boron content (EBC) was measured by INET at Tsinghua.
Results

1. Ash content and total EBC.
2. Chemical component evolution during purification.
3. Change in material structure during purification.

• Preliminary data
Ash content (3000 °C)

**Ash content of FG**

- **Bar chart** showing ash content in ppm for different locations.

**Ash content of MG**

- **Bar chart** showing ash content in ppm for different locations.
Ash content (3000 ºC)

- Why do these elements remain?
- Carbide-forming elements

<table>
<thead>
<tr>
<th></th>
<th>Melting point(ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₄C</td>
<td>2763</td>
</tr>
<tr>
<td>CaC₂</td>
<td>2160</td>
</tr>
<tr>
<td>TiC</td>
<td>3160</td>
</tr>
<tr>
<td>MoC</td>
<td>2687</td>
</tr>
<tr>
<td>WC</td>
<td>2785-2830</td>
</tr>
</tbody>
</table>
Measurement of total EBC

- Elements with high EBC: B, Cd, Dy, Eu, Sm, Gd…

<table>
<thead>
<tr>
<th>元素</th>
<th>吸收截面</th>
<th>碲当量因子</th>
<th>元素</th>
<th>吸收截面</th>
<th>碲当量因子</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>63.6</td>
<td>0.0084</td>
<td>Li</td>
<td>71.0</td>
<td>0.1457</td>
</tr>
<tr>
<td>B</td>
<td>759</td>
<td>1.000</td>
<td>Mn</td>
<td>13.3</td>
<td>0.0034</td>
</tr>
<tr>
<td>Ba</td>
<td>1.2</td>
<td>0.0001</td>
<td>Mo</td>
<td>2.70</td>
<td>0.0004</td>
</tr>
<tr>
<td>Cd</td>
<td>2450.0</td>
<td>0.3014</td>
<td>Na</td>
<td>0.53</td>
<td>0.0003</td>
</tr>
<tr>
<td>Cl</td>
<td>33.2</td>
<td>0.0133</td>
<td>Ni</td>
<td>4.6</td>
<td>0.0011</td>
</tr>
<tr>
<td>Co</td>
<td>37.2</td>
<td>0.0090</td>
<td>Si</td>
<td>0.16</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cr</td>
<td>3.1</td>
<td>0.0008</td>
<td>Sm</td>
<td>5820.0</td>
<td>0.5513</td>
</tr>
<tr>
<td>Cu</td>
<td>3.8</td>
<td>0.0009</td>
<td>Sr</td>
<td>1.28</td>
<td>0.0002</td>
</tr>
<tr>
<td>Dy</td>
<td>930.0</td>
<td>0.0815</td>
<td>Th</td>
<td>7.0</td>
<td>0.0004</td>
</tr>
<tr>
<td>Eu</td>
<td>4400.0</td>
<td>0.4124</td>
<td>Ti</td>
<td>6.1</td>
<td>0.0018</td>
</tr>
<tr>
<td>Fe</td>
<td>2.55</td>
<td>0.0007</td>
<td>U</td>
<td>7.6</td>
<td>0.0004</td>
</tr>
<tr>
<td>Gd</td>
<td>49000.0</td>
<td>4.4380</td>
<td>V</td>
<td>5.06</td>
<td>0.0014</td>
</tr>
<tr>
<td>K</td>
<td>2.1</td>
<td>0.0008</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EBC (3000 °C)

- The total EBC should be less than 1.00 ppm.
Ash content and EBC (3000 °C+Halogen)

FG
- Ash content of FG
- Total EBC of FG

MG
- Ash content of MG
- Total EBC of MG

Hunan University
Summary

• Carbide-forming elements are difficult to remove by high temperature treatment.
• Natural graphite powder can be purified to nuclear grade by high temperature treatment with the presence of Halogen.
Weight loss due to impurity evaporation

Low T  1100-2300 ºC  High T

Temperature (°C)

%
Hunan University

**FG from BAYAN NUR**

- **Gypsum**

- **Ora**
  - 800 °C
  - 1900 °C
  - 2100 °C
  - 2300 °C
  - 2500 °C
  - 2700 °C
  - 3000 °C

**FG from XINGHE**

- **Gypsum**

**2θ (°)**
• At low temperatures, the gypsum (CaSO$_4$·2H$_2$O) loses the crystallization water, causing a certain weight loss.
Formation of SiC

FG from BAYAN NUR

2θ (°)

10 20 30 40 50 60 70 80 90

FG from BAYAN NUR

2θ (°)

10 20 30 40 50 60 70 80 90

FG from XINGHE

Ora

800 °C

1900 °C

2100 °C

2300 °C

2500 °C

2700 °C

3000 °C

2θ (°)

10 20 30 40 50 60 70 80 90
Formation of SiC

MG from CHENZHOU

MG from XINGHE

2θ (°)

10 20 30 40 50 60 70 80 90

Ora

800 °C

1900 °C

2100 °C

2300 °C

2500 °C

2700 °C

3000 °C
Possible rule of Oxygen

- The weight loss on TG curve in the range of 1100-2100 °C may be attributed to the evolution of Oxygen, which produces CO$_2$, SO$_2$...

- Need to be confirmed by TG-FTIR or TF-MS.
Summary

• At low temperatures, the gypsum ($\text{CaSO}_4\cdot \text{2H}_2\text{O}$) loses the crystallization water, causing a certain weight loss.

• SiC formed above 1000 °C, and is then gradually removed at above 2300 °C.
Structural change of MG during high temperature purification

Mag = 1.00 K X
EHT = 10.00 kV
WD = 4 mm
Signal A = InLens
### Change in particle size

#### Crude ore

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean D</th>
<th>ΔD</th>
</tr>
</thead>
<tbody>
<tr>
<td>D90</td>
<td>47.412</td>
<td>47.825</td>
<td>47.879</td>
<td>48.021</td>
<td>47.385</td>
<td>47.061</td>
<td>47.597</td>
<td>0.368</td>
</tr>
</tbody>
</table>

#### 2800 ºC purified

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Mean D</th>
<th>ΔD</th>
</tr>
</thead>
<tbody>
<tr>
<td>D50</td>
<td>23.106</td>
<td>23.087</td>
<td>22.973</td>
<td>23.184</td>
<td>22.892</td>
<td>22.952</td>
<td>23.032</td>
<td>0.111</td>
</tr>
<tr>
<td>D90</td>
<td>47.781</td>
<td>48.102</td>
<td>46.836</td>
<td>48.992</td>
<td>45.543</td>
<td>45.625</td>
<td>47.147</td>
<td>1.393</td>
</tr>
</tbody>
</table>

- The particle size of MG slightly increases after high temperature purification.
Change in porosity

- MG is slightly porous.

![N₂ adsorption isotherms](image)

- The lower CTE of MG based graphite is probably related to its porous nature.

<table>
<thead>
<tr>
<th>Material</th>
<th>TR (×10⁻⁶/K)</th>
<th>AX (×10⁻⁶/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG</td>
<td>2.81</td>
<td>3.14</td>
</tr>
<tr>
<td>IG-110</td>
<td>4.06</td>
<td>4.35</td>
</tr>
</tbody>
</table>

Hunan University
MG from CHENZHOU

Before purification

After purification
MG from CHENZHOU

Before purification
MG from CHENZHOU

After purification

0.5 µm
MG from CHENZHOU

After purification

0.5 μm
Lattice order improvement

MG from CHENZHOU

MG from XINGHE

Ora

800 °C

1900 °C

2100 °C

2300 °C

2500 °C

2700 °C

3000 °C

2θ (°)

2θ (°)
T effect on lattice parameters

Graph showing the relationship between temperature (°C) and lattice constant $d_{(002)}$ (nm) along with graphitization degree (%). The lattice constant decreases as temperature increases, indicating a decrease in graphitization degree.

Specification for a standard procedure of X-ray diffraction measurements on carbon materials

Norio Iwashita a, Chong Rae Park b, Hiroyuki Fujimoto c, Minoru Shiraishi d, Michio Inagaki e
Concluding remarks

• Natural graphite powder can be purified to nuclear grade by high temperature treatment with the presence of Halogen.

• High temperature treatment up to 3000 °C not only removes impurities, but also helps to improve the lattice order and degree of graphitization of natural graphite.
Thank you!