

# 7. Refractories

## 7.0 Introduction

- Refractory materials: withstand temperatures  $> 1500\text{ }^{\circ}\text{C}$  (cone inclination temperature)
- Highly refractory materials: withstand temperatures  $> 1800\text{ }^{\circ}\text{C}$

Necessary precondition: high melting point components (oxides, carbides, nitrides, borides, silicides and carbon / graphite; for mass production mainly the oxides  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{ZrO}_2$ ) and avoidance of low-melting eutectics.

Requirements: mechanical stability and corrosion resistance at high temperature (materials for inner walls of furnaces and melters), high thermal resistivity (materials for outer walls of furnaces and melters) and sufficiently high thermal shock resistance (required for all materials).

Applicational areas: iron and steel production ( $< 70\%$ ), nonferrous metal industry ( $< 3\%$ ), cement industry ( $< 8\%$ ), ceramic industry ( $< 8\%$ ), glass industry ( $< 8\%$ ), chemical industry ( $4\%$ ), others ( $6\%$ ).

## 7.1 Classification of refractories

- Traditional criteria: acidic – basic – neutral, shaped (bricks) – unshaped (monolithics), dense ( $\phi < 45\%$ ) – porous ( $\phi > 45\%$ )
- Current classification according the EU standard norms EN 12475 (parts 1 – 4, issued 1998).

## 7.2 Composition, properties and application of silica-alumina refractories

- Silica ( $\text{SiO}_2 \geq 93\%$ ), siliceous ( $85 \leq \text{SiO}_2 < 93\%$ ), low alumina fireclay ( $\text{SiO}_2 < 85\%$  and  $10 \leq \text{Al}_2\text{O}_3 < 30\%$ ), fireclay ( $30 \leq \text{Al}_2\text{O}_3 < 45\%$ ), high alumina ( $\text{Al}_2\text{O}_3 \geq 45\%$ )
- Raw materials quartzite, clays, kyanite (and other  $\text{Al}_2\text{SiO}_5$  modifications), mullite
- Binary phase diagrams  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  (with special regard to mullite) and  $\text{CaO}$ - $\text{SiO}_2$
- Temperature dependence and high-temperature behavior of  $\text{SiO}_2$  modifications
- Silica refractories – sharp softening point, excellent thermal shock resistance (due to low thermal expansion) between  $600$  and  $1500\text{ }^{\circ}\text{C}$  (but phase modifications beyond this temperature range)
- Fireclay refractories – wide softening interval

## 7.3 Composition, properties and application of basic refractories

- Magnesite ( $\text{MgO} \geq 80\%$ ), magnesite-dolomite, dolomite, lime, magnesite spinel, magnesite chromite, forsterite, chromite, magnesite-zirconia, magnesite-zirconia-silica
- Raw materials magnesite and other carbonates, sea water
- Binary phase diagrams  $\text{CaO}$ - $\text{MgO}$ ,  $\text{CaO}$ - $\text{SiO}_2$ ,  $\text{MgO}$ - $\text{SiO}_2$ ,  $\text{MgO}$ - $\text{Al}_2\text{O}_3$ ,  $\text{Mg}_2\text{SiO}_4$ - $\text{Fe}_2\text{SiO}_4$ ,  $\text{CaO}$ - $\text{FeO}$ ,  $\text{MgO}$ - $\text{FeO}$ ,  $\text{CaO}$ - $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ - $\text{Fe}_2\text{O}_3$ , ternary phase diagram  $\text{CaO}$ - $\text{MgO}$ - $\text{SiO}_2$  (with special regard to monticellite, merwinite and dicalciumsilicate)

- Magnesite refractories – excellent high temperature stability (no phase transformations in MgO) but low thermal shock resistance (due to high thermal expansion)
- Environmental and hygiene issues related to chromite refractories

#### 7.4 Other refractories and special applications

- Fused or fusion-cast refractories (improved corrosion resistance due to closed pores)
- Zircon ( $\text{ZrSiO}_4$ ), zirconia (cubic, fully stabilized, or a mixture of cubic and monoclinic or metastable tetragonal, partially stabilized by MgO or CaO) and AZS refractories (fusion-cast  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ - $\text{SiO}_2$ , for aggressive glass fiber melts)
- SiC refractories (excellent thermal shock resistance due to low thermal expansion and high thermal conductivity)
- $\text{Si}_3\text{N}_4$  (expensive) and sialon (cheap) refractories (excellent thermal shock resistance)
- Pure carbon refractories (only in reducing environments)
- Oxide-carbon composite refractories (oxide: oxidation resistance, graphite: thermal conductivity, non-wetting and metal slag resistance)
- Pure oxide refractories, e.g.  $\text{Al}_2\text{O}_3$  or  $\text{ZrO}_2$  (no large volume applications, expensive)
- Highly porous refractories for thermal insulation purposes
- Whiskers (monocrystalline) and fibers (amorphous or polycrystalline) for thermal insulation purposes

**Complex exercise problem:** Use the *binary phase diagram* of the system  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  to discuss the influence of composition (raw materials selection) and processing on the phases and properties of silica-alumina refractories (silica, siliceous, low alumina fireclay, fireclay, high alumina). *Additional explicit questions:*

- a.) Discuss the opinions of different authors concerning the mullite problem.
- b.) What are the actual applications following from the different chemical and phase composition and properties of different silica-alumina refractories on the one hand and magnesite refractories on the other? Explain the difference in the softening behavior of silica refractories, fireclay refractories and magnesite refractories.
- c.) Explain the practical relevance of the problem of  $\text{Al}_2\text{O}_3$  in silica refractories and of  $\text{B}_2\text{O}_3$  in magnesite refractories. Also explain the role of the CaO in silica refractories and in magnesite refractories.