7. Refractories

7.0 Introduction

- Refractory materials: withstand temperatures > 1500 °C (cone inclination temperature)
- Highly refractory materials: withstand temperatures > 1800 °C

Necessary precondition: high melting point components (oxides, carbides, nitrides, borides, silicides and carbon / graphite; for mass production mainly the oxides SiO₂, Al₂O₃, MgO, CaO, Cr₂O₃ and ZrO₂) 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 (φ < 45 %) – porous (φ > 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 (SiO₂ ≥ 93 %), siliceous (85 ≤ SiO₂ < 93 %), low alumina fireclay (SiO₂ < 85 % and 10 ≤ Al₂O₃ < 30 %), fireclay (30 ≤ Al₂O₃ < 45 %), high alumina (Al₂O₃ ≥ 45 %)
- Raw materials quartzite, clays, kyanite (and other Al₂SiO₅ modifications), mullite
- Binary phase diagrams SiO₂-Al₂O₃ (with special regard to mullite) and CaO-SiO₂
- Temperature dependence and high-temperature behavior of SiO₂ modifications
- Silica refractories – sharp softening point, excellent thermal shock resistance (due to low thermal expansion) between 600 and 1500 °C (but phase modifications beyond this temperature range)
- Fireclay refractories – wide softening interval

7.3 Composition, properties and application of basic refractories

- Magnesia (MgO ≥ 80 %), magnesia-doloma, doloma, lime, magnesia spinel, magnesia chromite, forsterite, chromite, magnesia-zirconia, magnesia-zirconia-silica
- Raw materials magnesite and other carbonates, sea water
- Binary phase diagrams CaO-MgO, CaO-SiO₂, MgO-SiO₂, MgO-Al₂O₃, Mg₂SiO₄-Fe₂SiO₄, CaO-FeO, MgO-FeO, CaO-Fe₂O₃, MgO-Fe₂O₃, ternary phase diagram CaO-MgO-SiO₂ (with special regard to monticellite, merwinite and dicalciumsilicate)
Magnesia 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 (ZrSiO₄), 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 Al₂O₃-ZrO₂-SiO₂, for aggressive glass fiber melts)
- SiC refractories (excellent thermal shock resistance due to low thermal expansion and high thermal conductivity)
- Si₃N₄ (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. Al₂O₃ or ZrO₂ (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 SiO₂-Al₂O₃ 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 magnesia refractories on the other? Explain the difference in the softening behavior of silica refractories, fireclay refractories and magnesia refractories.

c.) Explain the practical relevance of the problem of Al₂O₃ in silica refractories and of B₂O₃ in magnesia refractories. Also explain the role of the CaO in silica refractories and in magnesia refractories.