

8. Oxide ceramics

8.0 Introduction

Oxide ceramics, single-phase or multiphase, are commonly understood to be ceramics with a microstructure consisting essentially of simple oxides. They can be designed for structural or functional applications. Ceramics consisting of complex oxides, formed e.g. by solid state reactions (titanates, ferrites etc.), and silicate ceramics (including mullite-based ceramics) are usually not treated in this group.

8.1 Alumina ceramics

- *Powder preparation*: bauxite (mixture of gibbsite $\gamma\text{-Al}(\text{OH})_3$, boehmite $\gamma\text{-AlO}(\text{OH})$ and diaspor $\alpha\text{-AlO}(\text{OH})$ with impurities SiO_2 , Fe_2O_3 and $\text{TiO}_2 \rightarrow$ Bayer process to extract the impurities; problem: agglomerates $\rightarrow$ powders must be milled, Na_2O content $\rightarrow$ powders must be refined).
- Bayer process: bauxite $\rightarrow$ hydrothermal digestion $\rightarrow$ ions in solution using NaOH under pressure 0.5 MPa at temperature 150-160 °C $\rightarrow$ transforms the hydroxides, cf. Table 1, into aluminate ions $\rightarrow$ solid impurities such as SiO_2 , Fe_2O_3 and TiO_2 remain undissolved $\rightarrow$ removed by filtration (“red mud”) $\rightarrow$ cooling $\rightarrow$ solution seeded with gibbsite $\rightarrow$ further gibbsite nucleates on the seed (precipitation step) $\rightarrow$ drying $\rightarrow$ agglomeration $\rightarrow$ calcination (1300-1400 °C) $\rightarrow$ water loss $\rightarrow$ high surface area, porous transition alumina phases, cf. Table 2 $\rightarrow$ above 1150 °C: $\alpha\text{-Al}_2\text{O}_3$ (corundum).
- Types of alumina powders: usual *calcined alumina* produced via the Bayer process contain 0.1–0.4 wt.% Na_2O $\rightarrow$ degrades many properties in demanding applications, since the Na^+ ion is highly mobile in an electric field and can be leached out during wet processing. Moreover, β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) can form on sintering $\rightarrow$ refined types: *low-soda*, *reactive* ($\text{Na}_2\text{O} < 0.1\%$), *tabular* (for refractories), *fused* (as abrasives, white and brown).
- Nanocrystalline alumina powder can be prepared via the sol-gel process from acid boehmite solutions (sols); alternative routes: precipitation, vapor phase synthesis, hydrothermal synthesis, pyrolysis, combustion, freeze drying, laser ablation; the primary products of all these processes are transition aluminas (mainly $\gamma\text{-Al}_2\text{O}_3$) and the calcining step, which is necessary for the formation of $\alpha\text{-Al}_2\text{O}_3$, is invariably accompanied by grain growth.
- Processing by solid state sintering (SSS) or liquid phase sintering (LPS): SSS aluminas are highly pure ($> 99.7\%$ Al_2O_3), used in the most demanding applications, e.g. as sodium vapor lamp envelopes; LPS aluminas are less pure (typically 80–99.7 % Al_2O_3), but also used for electrical and engineering applications as long as the liquid phase content is sufficiently low (e.g. microelectronic circuit substrates from 96 % Al_2O_3); lower-purity aluminas are used e.g. in electrical insulators but have poor high-temperature properties; role of MgO as a sintering aid in SSS and LPS.
- Properties and behavior: orientational values for different types of alumina ceramics ($> 99.7\%$ Al_2O_3 , 99 % Al_2O_3 , 80–95 % Al_2O_3) $\rightarrow$ cf. Table 3; elastic, thermal and thermoelastic properties (tensor coefficients) for $\alpha\text{-Al}_2\text{O}_3$ single crystals $\rightarrow$ [Pabst & Gregorová 2006] and [Pabst & Gregorová, in press]; alumina whiskers and fibers.
- Typical applications of alumina ceramics: wear parts (e.g. thread guides), electronic circuit substrates, filters and membranes, armouring and bioceramic implants.

8.2 Zirconia ceramics

- *Powder preparation:* zircon (ZrSiO_4) $\rightarrow$ dissociates at temperatures $> 1750\text{ }^\circ\text{C}$ into zirconia and silica; plasma flame decomposition at $> 6000\text{ }^\circ\text{C}$ $\rightarrow$ zirconia ZrO_2 solidifies first, then silica SiO_2 forms a glassy coating on the zirconia dendrites and can be removed by leaching with NaOH $\rightarrow$ after washing zirconia is removed from the residue by centrifugation; alternatively – thermal decomposition at temperatures $2100\text{--}2300\text{ }^\circ\text{C}$ $\rightarrow$ zircon + liquid silica; thermal decomposition can be modified by chlorination $\rightarrow$ lower temperature ($800\text{--}1200\text{ }^\circ\text{C}$) $\rightarrow$ volatile products $\rightarrow$ distilled and condensed; ZrCl_4 hydrolized with water $\rightarrow$ zirconium oxychloride $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$; very fine tetragonal zirconia (t-ZrO_2) can be precipitated directly by adding ammonia or oxychloride crystallized by cooling.
- Since the applications of zirconia require partial or full stabilization of the high-temperature polymorphs of zirconia (t-ZrO_2 and / or c-ZrO_2) stabilizing additives must be added, e.g. CaO , MgO (e.g. for partially stabilized zirconia PSZ) or Y_2O_3 , CeO_2 (e.g. for tetragonal zirconia polycrystals TZP); these can be introduced by coating zirconia powder in a solution (e.g. yttrium nitrate), but prolonged calcination required for homogenization $\rightarrow$ coarse powders; when yttrium is introduced as YCl_3 directly into the oxychloride solution before precipitation ($\rightarrow$ co-precipitation of a $\text{Y}_2\text{O}_3\text{-ZrO}_2$ solid solution after adding YCl_3) one obtains mixing of the resultant oxides at the atomic level $\rightarrow$ drying and calcining (short time $\rightarrow$ fine powders), milling and spray-drying (Tosoh process).
- *Pure zirconia polymorphs:*
 - *Monoclinic* (m-ZrO_2 , 5.6 g/cm^3); thermodynamically stable from room temperature to approx. $950\text{ }^\circ\text{C}$.
 - *Tetragonal* (t-ZrO_2 , 6.1 g/cm^3); transforms from monoclinic upon heating at approx. $1150\text{ }^\circ\text{C}$ (transition start temperature) or back to monoclinic upon cooling at approx. $950\text{ }^\circ\text{C}$ (transition finish temperature) $\rightarrow$ *martensitic transformation* with large hysteresis and relative volume change approx. 5 %.
 - *Cubic* (c-ZrO_2 , 6.1 g/cm^3); transformation $\text{t} \leftrightarrow \text{c}$ at approx. $2300\text{ }^\circ\text{C}$ (hysteresis maximally $30\text{ }^\circ\text{C}$); c-ZrO_2 melts at approx. $2700\text{ }^\circ\text{C}$.
- *Phase relations in zirconia:* all engineering ceramic applications of zirconia require full or partial stabilization of the structure $\rightarrow$ most common stabilizers – Ca , Mg , Y , and Ce . $\rightarrow$ binary phase diagrams $\text{ZrO}_2\text{-CaO}$, $\text{ZrO}_2\text{-MgO}$, $\text{ZrO}_2\text{-Y}_2\text{O}_3$ and $\text{ZrO}_2\text{-CeO}_2$.
- *Processing, microstructure and properties:*

Partially stabilized zirconia (PSZ): two-phase ceramics with typical stabilizer contents of 2.5–3.5 wt.% MgO , 3.0–4.5 wt.% CaO or 5–10 wt.%, i.e. $> 3\text{ mol.}\%$, Y_2O_3 ; require a solution treatment (sintering at high temperature, up to $1800\text{ }^\circ\text{C}$ $\rightarrow$ supersaturated solid solution) followed by quenching and reheating (ageing $\rightarrow$ transformation toughened microstructure); optimal ageing $\rightarrow$ t-ZrO_2 nuclei in a cubic solid solution (interfacial tension responsible for stability) $\rightarrow$ nuclei grow and thus become metastable t-ZrO_2 ; transformation $\text{t} \rightarrow \text{m}$ connected with volume expansion and shape change (the latter being compensated either by twinning of the lens-shaped precipitates or by microcracking

around these precipitates). *Mechanical properties* of optimized PSZ ceramics: Young's modulus up to 200 GPa, Vickers hardness approx. 13 ± 5 GPa, bend strength up to 1000 MPa and fracture toughness up to $20 \text{ MPa}\cdot\text{m}^{1/2}$. Of course, apart from grain size and porosity these properties are strongly influenced by the grain boundary phase. The thermal shock resistance of PSZ is poor, due to high thermal expansion and low thermal conductivity (similar to fully stabilized zirconia).

Tetragonal zirconia polycrystals (TZP): in principle single phase polycrystalline t-ZrO₂ ceramics (typically with 2–3 mol.% Y₂O₃); in practice, Y-TZPs may contain significant amounts of c-ZrO₂, including some microstructural features associated with PSZ → distinction between Y-TZP and Y-PSZ is diffuse; Y-TZP can be obtained by sintering (LPS) at 1450 °C for 2 h (very similar for Y-PSZ, but ageing temperatures and times are more critical here); main advantage of TZPs over Mg-PSZ – lower sintering temperature → finer grain size → higher strength; Y-TZP with 2 mol.% should be pure t-ZrO₂, while most TZP ceramics with > 2.5 mol.% Y₂O₃ contain c-ZrO₂ (with a grain size typically larger than that of t-ZrO₂) → transition to PSZ ceramics (with > 3 mol.% Y₂O₃), where c-ZrO₂ is the prevailing phase → yttria content is critical in determining transformability and toughness; Ce-TZP ceramics with 12–20 mol.% CeO₂ are similar to Y-TZP ceramics and also densify via LPS. *Mechanical properties* of optimized TZP ceramics: extremely high toughness values for Ce-TZP (up to $30 \text{ MPa}\cdot\text{m}^{1/2}$) and very high strength values for Y-TZP (up to 1300 MPa); Young's modulus approx. 205 GPa, Vickers hardness approx. 10 ± 3 GPa; available monocrystal values (tensor coefficients) of elastic, thermal and thermoelastic properties → [Pabst & Gregorová 2006] and [Pabst & Gregorová, in press].

- *Particle size and shape effects*: m-ZrO₂ is the thermodynamically stable polymorph at room temperature, but metastable t-ZrO₂ can be retained if the particle size is below some critical value (approx. 0.3–0.5 μm); rounded particles exhibit lower transformability than faceted ones.
- *Strength / toughness relations*: peak strength does not coincide with peak toughness, due to inelastic deformation and R-curve behavior; the strength of very tough ceramics is transformation controlled rather than flaw size controlled → less variability in strength → higher Weibull modulus; damage tolerant and processing insensitive materials → design for engineering applications based on a yield stress criterion.
- *Low-temperature degradation and hydrothermal ageing*: in TZP ceramics spontaneous t→m transformation occurs (from the surface) at 150–250 °C → strength degradation or complete material disintegration; this surface degradation is worse in the presence of water vapor and aqueous solutions; the exact mechanism of this low-temperature degradation and degradation due to hydrothermal ageing is not known (probably leaching of Y₂O₃ plays a key role); below a critical grain size (0.4 μm) no degradation occurs → probably the degradation is a combined effect of grain size, Y₂O₃ content and distribution, density (porosity) and flaw size (microcracks); strategies to improve the resistance to low-temperature degradation / hydrothermal ageing are grain size reduction or Al₂O₃ additions; special concern: degradation of biomedical grade zirconia in the human body environment (i.e. in contact with body fluids) → material failure → collapse of the market for zirconia implants (femoral heads) in 2001; 1 h of autoclave treatment at 134 °C has the same effect as 3–4 years in vivo; at the moment

the only realistic alternative to the classical material for these applications (alumina) is the use of optimized alumina-zirconia composites.

- *Superplasticity*: polycrystalline ceramics with fine grain size (below a few μm) can be deformed with high strain rates at elevated temperatures to very large strains (up to several hundred %) without rupture; main mechanism: grain boundary sliding (not dislocation flow) $\rightarrow$ superplastic behavior (plays an important role in hot pressing).

Alumina-zirconia composite ceramics: two-phase mixtures of $\alpha\text{-Al}_2\text{O}_3$ and TZP; addition of zirconia to alumina increases the fracture toughness of alumina (zirconia-toughened alumina, ZTA), while addition of alumina to zirconia reduces the low-temperature degradation and degradation due to hydrothermal ageing (alumina-containing tetragonal zirconia, ATZ); typical compositions are Y-TZP with 20 wt.% Al_2O_3 (ATZ) and Al_2O_3 with 15 wt.% Y-TZP (ZTA), but many other compositions, including the 50-50 composition, have been prepared and studied; in ZTA composites the critical size for the $t \rightarrow m$ transformation is larger than in pure (i.e. “single-phase”) zirconia (TZP) ceramics, since the stiff alumina matrix (elastic modulus 400 GPa versus 200 GPa for zirconia) constrain the $t\text{-ZrO}_2$ particles, preventing transformation; the critical size decreases with increasing volume fraction of dopant-free (i.e. unstabilized) zirconia, probably due to the lower effective elastic modulus of the composite with increasing zirconia content. The addition of (dopant-free) zirconia has also a significant effect on the microstructure of alumina: small additions (< 1 vol.% ZrO_2) $\rightarrow$ fine grain size of alumina, larger additions (> 3 vol.% ZrO_2) $\rightarrow$ isometric grain shape of alumina. Optimally prepared AZ composites exhibit a monotonic increase in fracture toughness from both sides of the binary phase diagram ($\text{Al}_2\text{O}_3\text{-ZrO}_2$), with a maximum at the 50-50 composition; since the microstructure of ZTA may contain $t\text{-ZrO}_2$ as well as $m\text{-ZrO}_2$, the toughening mechanism in some ZTA is believed to be a combination of transformation toughening and microcrack toughening (with the latter, of course, implying strength reduction); for ATZ ceramics (with essentially $t\text{-ZrO}_2$) transformation toughening prevails and extremely high strengths are reported (up to 2500 MPa); ZTAs are commonly used as cutting tools, allowing more severe conditions in high speed metal cutting than conventional alumina cutting tools; for biomedical applications ZTA ceramics are advantageous because the degradation due to hydrothermal ageing is effectively restricted when the zirconia content is below the percolation threshold of approx. 16 vol.%.

8.3 Other oxide ceramics

Apart from alumina and zirconia, the most important oxide ceramics are BeO (as a nuclear ceramic as well as for high-temperature crucibles, insulating parts and chip carriers), CaO (for refractory bricks, compounds and fibres), CeO_2 (for ion conductors, crucibles and oxygen sensors), MgO (for melting crucibles, insulators and refractory bricks), TiO_2 (for high-frequency capacitors and photocatalytic devices), UO_2 (as a nuclear ceramic), Y_2O_3 (for crucibles), ZnO (for varistors in voltage surge protectors) as well as a number of mixed oxides, most of them commonly treated as functional ceramics ($\rightarrow$ see Lecture 12), e.g. ferroelectric titanates with perovskite structure (e.g. BaTiO_3 and $\text{PbZrO}_3\text{-PbTiO}_3$), ferrites (with spinel, garnet or magnetoplumbite structure) and superconducting ceramics (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$), as well as Al_2TiO_5 (“tialite” ceramics with low or negative thermal expansion, an extreme anisotropy of the thermal expansion coefficient and a melting point of 1860 $^\circ\text{C}$). Silicate ceramics, including mullite-based ceramics, are treated as an extra group ($\rightarrow$ see Lecture 6). Table 4 gives the melting points and densities of selected simple oxides.

Table 1. Alumimum hydroxides.

Name	Formula	Crystal system
Gibbsite (hydrargillite)	$\gamma\text{-Al(OH)}_3$	Monoclinic
Bayerite	$\alpha\text{-Al(OH)}_3$	Hexagonal
Boehmite	$\gamma\text{-AlO(OH)}$	Orthorhombic
Diaspore	$\alpha\text{-AlO(OH)}$	Orthorhombic

Table 2. Alumina polymorphs.

Alumina (Al_2O_3) phase label	Crystal system
α	Trigonal (point group $\bar{3}m$), often described by a hexagonal unit cell
γ	Cubic
η	Cubic
χ	Hexagonal
δ	Tetragonal
θ	Monoclinic
κ	Orthorhombic

Table 3. Typical property values for different types of alumina ceramics (estimates based on extensive literature and data base studies).

Property	Al_2O_3 (> 99.7 %)	Al_2O_3 (99 %)	Al_2O_3 (80 – 95 %)
Density [g/cm^3]	3.96 – 3.99	3.8 – 3.9	2.6 – 3.8
Vickers hardness [GPa]	approx. 20	15 – 16	10 – 15
Fracture toughness [$\text{MPa}\cdot\text{m}^{1/2}$]	4 – 5	6	3 – 4
Young's modulus [GPa]	400	380 – 400	200 – 300
Poisson ratio	0.23		0.23
Compressive strength [MPa]	3000 – 4000	2500	2000
Bend strength [MPa] at 20 °C	400 – 600	350	200 – 300
Bend strength [MPa] at 1200 °C	100 – 150		50 – 100
Thermal expansion [10^{-6} K^{-1}]	8.5	8.0	7.0
Thermal conductivity [W/mK]	33	25 – 30	15 – 25

Table 4. Approximate melting temperatures and densities of selected oxides.

Oxide	Melting point [°C]	Density [g/cm ³]	Oxide	Melting point [°C]	Density [g/cm ³]
ThO ₂	3200	10.0	SrO	2430	4.7
HfO ₂	2900	9.7 (m) – 10 (t)	Y ₂ O ₃	2450	4.5
MgO	2850	3.6	Cr ₂ O ₃	2270	5.2
UO ₂	2800	11.0	Al ₂ O ₃	2050	4.0
ZrO ₂	2700	5.6 (m) – 6.1 (t, c)	BaO	1920	5.7
CaO	2600	3.3	TiO ₂	1840	4.2 (brookite) – 3.8 (anatase) – 4.3 (rutile)
CeO ₂	2600	7.1	SiO ₂	1720	2.65 (β-quartz) – 2.20 (silica glass)
BeO	2550	3.0			