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1 Introduction: the variety of ceramic systems

1.1 Introduction

The international advanced ceramics industry is concerned with basic research and ceramic fabrication as well as manufacture of powders and fibres while the success of research can be measured by its application to large-scale economic production of ceramics which function in particular working environments. Advanced ceramic materials are defined in this introductory chapter and their variety and uses are explained. The ceramics industry is large and an indication of its volume production and monetary value is also given here. Finally, the recent discovery of high-temperature oxide superconductors has had a tremendous impact on worldwide ceramic activities and a section is included on the properties and potential applications of these advanced ceramic materials.

1.2 From traditional to advanced ceramics

Ceramics are the group of non-metallic inorganic solids and their use by man dates from the time of ancient civilisations. In fact, the word ceramic is of Greek origin and its translation (keramos) means potter's earth. Traditional ceramics are those derived from naturally occurring raw materials and include clay-based products such as tableware and sanitaryware as well as structural claywares like bricks and pipes. Also in this category are cements, glasses and refractories. Examples of the latter are chrome–magnesite refractories used in the steel-making industry and derived from magnesite ($MgCO_3$) and chrome ore. Advanced ceramics are developed from chemical synthetic routes or from naturally occurring materials that have been highly refined. A variety of names has been used to describe ceramic systems. Hence, advanced ceramics are also called engineering ceramics whereas the phrases 'special', 'fine' and 'technical' have all been used in connection with these materials. When their use depends on mechanical behaviour, advanced ceramics are sometimes referred to as structural components whereas electroceramics are a class of advanced ceramic whose application relies on electrical and magnetic properties. Books by Norton (1968) and Shaw (1972) contain further details on traditional ceramics whereas Morrell (1985) has described the classification of ceramic systems.

1.3 Structural and refractory applications of engineering ceramics

Structural components derived from engineering ceramics are used as monoliths, coatings and composites in conjunction with or as replacements for metals when applications rely on mechanical behaviour of the ceramics and their refractory properties, that is chemical resistance to the working environment. Physical properties of ceramics and metals are compared in table 1.1 some of their magnitudes are shown in tables 1.2 and 1.3. Nickel superalloys are currently the main high-temperature materials for components such as combustors in gas turbine engines (Meetham, 1986). They have melting points around 1573 K and a maximum working temperature near 1300 K. Cast iron parts in reciprocating (i.e. petrol and diesel) engines have properties shown in table 1.3. Compared with metals, ceramics are generally more resistant to oxidation, corrosion, creep and wear in addition to being better thermal insulators. They have higher melting points (table 1.4) and greater strength than superalloys at elevated temperature so that a major potential application, particularly for silicon nitride, is in gas turbine and reciprocating engines where operating temperatures higher than attainable with metals can result in greater efficiencies. This enhanced strength is shown in figure 1.1 for hot-pressed silicon nitride (HPSN), hot-pressed silicon carbide (HPSC), hot isostatically pressed silicon nitride (HIPSN), sintered silicon nitride (SSN), sintered silicon carbide (SSC), reaction-bonded silicon nitride (RBSN) and reaction-bonded silicon carbide (RBSC). Although ceramics offer improvements in engine efficiency, incorporation of silicon nitride over the past three decades has been slow, mainly because of the difficulty in reproducible fabrication of dense components to close dimensional tolerances.

Silicon nitride occurs in two phases, the α and the β forms. The β form, whose structure is shown in figure 1.2, consists of SiN_4 tetrahedra joined together by sharing corners in a three-dimensional network. It is

Table 1.1. *Relative properties of ceramics and metals (AE Development, 1985)*

Property	Ceramics	Metals	Ratio, property of ceramics: property of metal
Ductility	Very low	High	(0.001–0.01):1
Density	Low	High	0.5:1
Fracture toughness	Low	High	(0.01–0.1):1
Young's modulus	High	Low	(1–3):1
Hardness	High	Low	(3–10):1
Thermal expansion	Low	High	(0.1–0.3):1
Thermal conductivity	Low	High	(0.05–0.2):1
Electrical resistance	High	Low	$(10^6–10^{10})$:1

Table 1.2. *Physical properties for alloys, oxide and non-oxide ceramics (Briscoe, 1986)*

Material	Specific gravity ($\mathrm{kg\,m^{-3}}$)	Thermal expansion coefficient ($10^{-6}\,\mathrm{K^{-1}}$)	Thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)
Alumina	4000	9	20
Toughened zirconia polycrystals	5800	10	2
Sintered silicon carbide	3100	4.5	40
Sintered silicon nitride	3100	3.2	12
Hot-pressed silicon nitride	3100	3.1	30
Window glass	2200	9	1
Aluminium alloys	2800	22	146
Nimonic superalloys	8500	15	16

possible to replace silicon by aluminium and maintain charge neutrality in the crystal lattice by substitution of nitrogen with oxygen. The resulting solid solutions in the Si–Al–O–N system are known as β'-sialons (K. H. Jack, 1986) whose structures are identical with β-Si_3N_4 over the composition range $Si_{6-b}Al_bO_bN_{8-b}$ $(0<b<4)$. They exhibit mechanical behaviour similar to β-Si_3N_4 and have some features of aluminium oxide. However, in contrast with Al_2O_3, which consists of six-coordinated Al,

Table 1.3. *Mechanical properties of cast irons, oxide and non-oxide ceramics (Lackey et al., 1987)*

Material	Young's modulus GPa	Fracture toughness (MPa $m^{1/2}$)	Fracture strength at room temperature MPa
Alumina	380	2.7–4.2	276–1034
Partially stabilised zirconia	205	8–9 at 293 K	
		6–6.5 at 723 K	600–700
		5 at 1073 K	
Sintered silicon carbide	207–483	4.8 at 300 K	96–520
		2.6–5.0 at 1273 K	
Sintered silicon nitride	304	5.3	414–650
Hot-pressed silicon nitride	304	4.1–6.0	700–1000
Glass ceramics	83–138	2.4	70–350
Pyrex glass	70	0.75	69
Cast irons	83–211	37–45	90–1186

Table 1.4. *Melting point and maximum working temperatures of ceramics (Lay, 1983)*

Material	Melting point or decomposition temperature/K	Maximum working temperature/K In oxidising atmosphere	Maximum working temperature/K In reducing atmosphere
Alumina	2323	2173	2173
Stabilised zirconia	2823	2473	
Silicon carbide	2873	1923	2593
Boron carbide	2723	873	2273
Tungsten carbide	3023	823	2273
Reaction-bonded silicon nitride	2173	1473	2143
Boron nitride	2573	1473	2473
Titanium diboride	3253	1073	>2273

β'-sialon contains Al that is four-coordinated by oxygen and this results in an enhanced Al–O bond strength compared with the oxide. Unlike Si_3N_4, β'-sialons can be densified readily by pressureless sintering and they have been put into commercial production by Lucas Cookson

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Syalon Limited. Syalon components shown in figure 1.3 include automotive parts such as valves, valve guides and seats, tappets, rocker inserts and precombustion chambers in addition to weld shrouds, location pins, extrusion dies, tube drawing dies and plugs.

Aluminium titanate is used as port liners in some automobile engines because its low thermal conductivity (2 W m^{-1} K^{-1}) reduces heat flow to the cylinder block and hence the amount of cooling required. Glass ceramics have applications (table 2.1) in cooking utensils, tableware, heat exchangers, vacuum tube components and missile radomes. Partially stabilised zirconia was developed in 1975 at the Australian Commonwealth Scientific & Industrial Research Organisation (CSIRO) and is nowadays manufactured by Nilcra-PSZ Limited. This material is particularly suited for withstanding mechanical and thermal shock because of its high fracture toughness (table 1.3). Examples are dies for

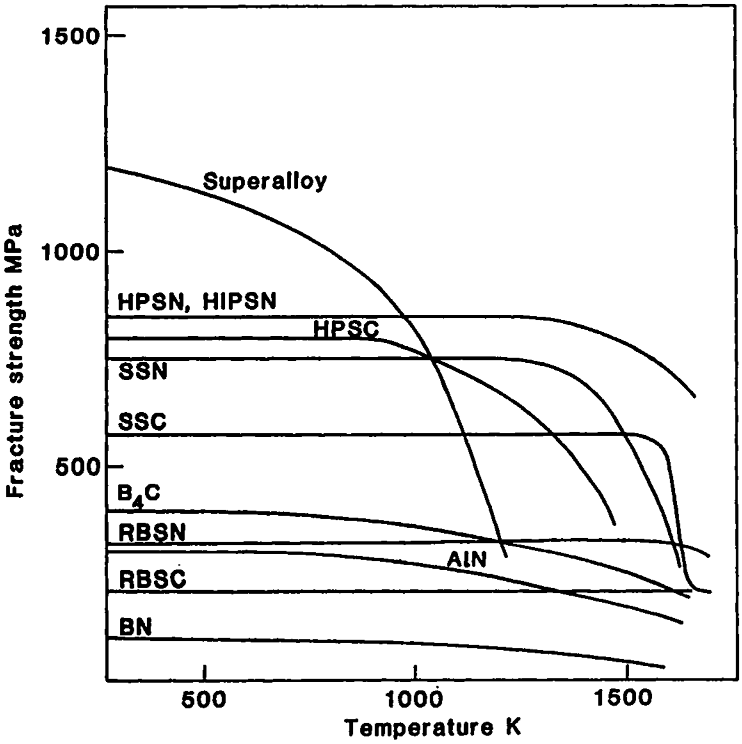

Figure 1.1. Variation of strength with temperature for non-oxide ceramics (Heinrich, 1985).

extrusion of copper and aluminium tubes, diesel engine cam follower faces, valve guides, cylinder liners and piston caps, wear and corrosion-resistant nozzles in papermaking equipment, wear resistant inserts such as tabletting dies as well as scissors and knives.

Not all ceramic components require high-temperature strength. The high Young's modulus (550 GPa) of titanium diboride, TiB_2, makes it useful for armour plating (Knoch, 1987) whereas ceramics are suitable materials in seals because of their chemical resistance (table 1.5). Hence sintered silicon carbide is used for mechanical seals and sliding bearings whereas boron nitride, which is not wetted by glass and liquid metals, constitutes break rings in the horizontal continuous casting process for steels. Boron carbide, a harder ceramic than SiC, is suited to wear-resistant applications such as grit blasting nozzles whereas Si_3N_4 is also

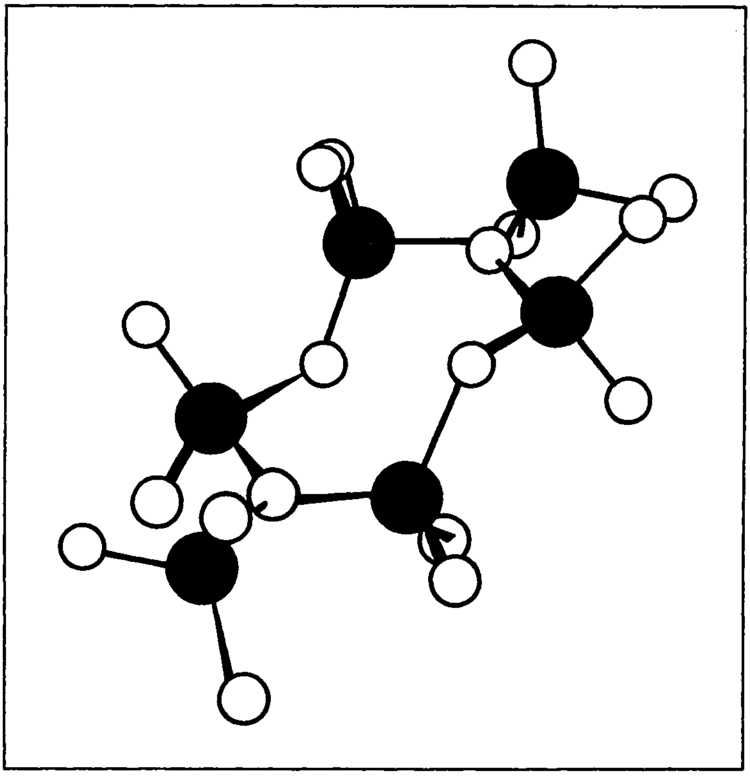

Figure 1.2. Crystal structure of β-Si_3N_4 and β'-$(Si,Al)_3(O,N)_4$. ●, metal atom, ○, non-metal atom (K. H. Jack, 1986).

used as ball bearings. An established industrial use for engineering ceramics is as cutting tools for steels where high-temperature hardness of sialons and zirconia toughened alumina together with their low reactivity towards metals are desirable properties; this application has recently been reviewed by D. H. Jack (1986).

Worldwide markets for ceramic coatings in 1985 have been estimated at around 1100 US$M (Charles H. Kline, 1987) and their breakdown is shown in figure 1.4. About 45% of this market is in optical coatings,

Table 1.5. *Resistance of ceramics towards acids and bases (Lay, 1983)*

Material	Resistance to acids	Resistance to bases
MgO, ThO_2	Lowest	Highest
BeO	↓	↓
Al_2O_3, Cr_2O_3, ZrO_2		
SiO_2, TiO_2, SiC, B_4C, Si_3N_4	Highest	Lowest

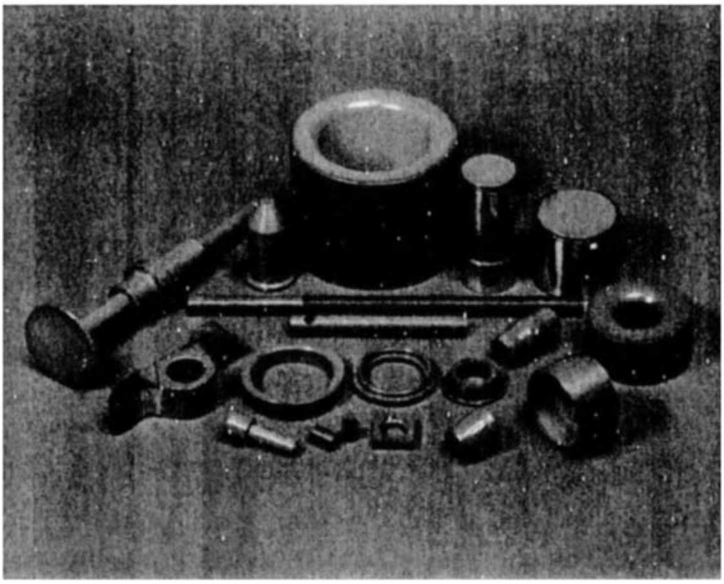

Figure 1.3. Examples of Syalon components. (Courtesy of Lucas Cookson Syalon Ltd.)

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the remainder for thermal, wear and corrosion resistance. For example the thermal barrier coating in figure 1.5 contains an outer ZrO_2 layer on the combustion chamber from the RB211 gas turbine engine (Meetham, 1986) and produced an increase in combustor lifetime because of a reduction in substrate temperature by 50 K.

Bioceramics are a class of advanced ceramics that require high strength. Thus, alumina for artificial hip joints, hydroxyapatite for surgical implants, calcium phosphate as an aid to rejuvenation of bone and carbon surgical implants are used in this area which has been reviewed by Boretos (1987).

Physical data for traditional and advanced ceramics are dispersed throughout the technical literature but a useful source is available (American Ceramic Society, 1987) which collates this information for some materials described in later chapters of this book.

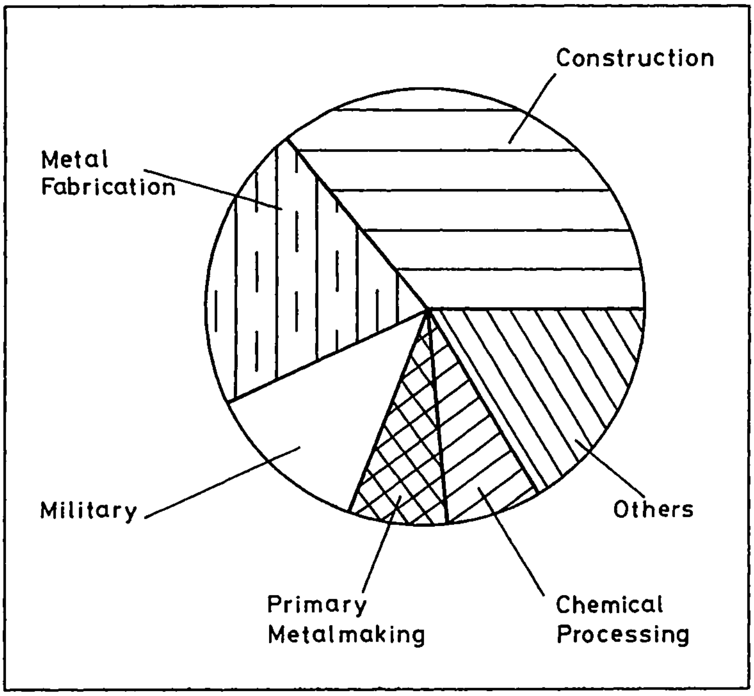

Figure 1.4. World market for ceramic coatings by end use industries, 1985 (Charles H. Kline and Company, 1987).

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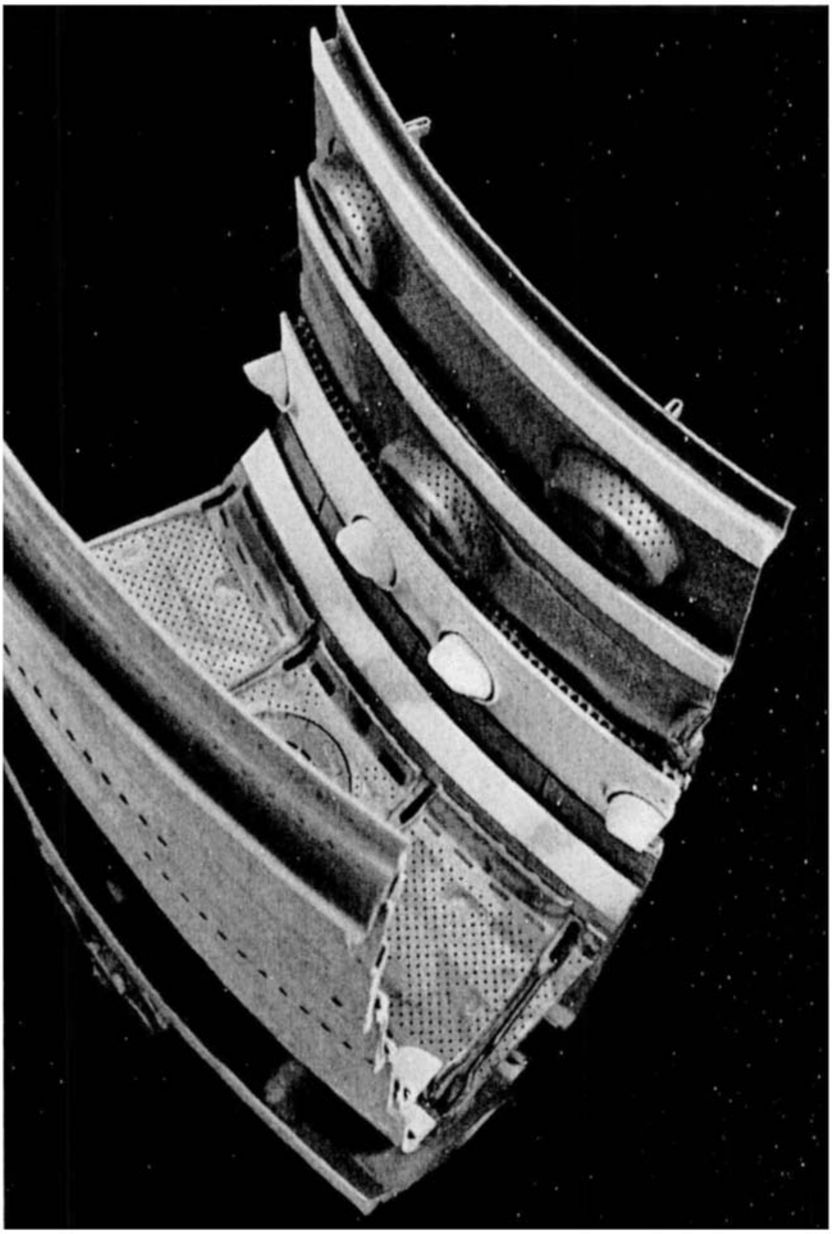

Figure 1.5. Thermal barrier-coated RB211 combustion chamber. (Courtesy of Rolls Royce plc.)

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1.4 Electroceramics

Electroceramics or electronic ceramics can be considered as materials whose uses rely primarily on their electrical or magnetic properties rather than mechanical behaviour although optical properties are important for opto-electronic devices. The electroceramics industry is a mature one and dates from the 1940s when insulating properties of Al_2O_3 were utilised in spark plugs but nowadays this is a rapidly expanding area of materials science and forms the largest sales sector (in monetary value) for advanced ceramics. Examples of electroceramics include zinc oxide for varistors, lead zirconium titanate (PZT) for piezoelectrics, barium titanate in capacitors, tin oxide as gas sensors, lead lanthanum zirconium titanate (PLZT) and lithium niobate for electro-optic devices; physical properties required for these applications are shown in table 1.6. In the case of packaging, ceramic substrates such as Al_2O_3 are used for supporting electronic chips and interconnections. The trend towards greater miniaturisation and densification of components demands substrates with high thermal conductivity and the magnitude of this property for packaging materials is listed in table 1.7.

European and North American consumption of electronic ceramics for 1985 are compared in table 1.8, while Bell (1987) has quoted Japanese sales of electroceramics for 1983 totalling around 1500 US$M. This industry is a large volume producer as shown in table 1.9 for a range of ceramic sensors whose operation is described in more detail by Kulwicki (1984). At the present time electroceramics such as piezoelectric knock sensors and thermistors for fuel gauges are being increasingly used in automobiles (Taguchi, 1987), while Tuttle (1987) has reviewed their application in opto-electronic devices. High-temperature oxide superconductors, a class of electronic ceramics that has been recently discovered, are described below.

1.5 High-temperature oxide superconductors

Superconductors are materials that have no electrical resistance. The phenomenon was discovered by Onnes (1911a, b) who observed a superconducting transition or critical temperature, T_c, of 4.2 K for mercury in liquid helium. A gradual increase in T_c values took place over the following 75 years and the highest critical temperature up to 1986, 22.3 K, was for films of an almost stoichiometric niobium–germanium