1
Introduction to Classic Ceramics

1.1
Ceramics through the Ages, and Technological Progress

Throughout the ages of humankind, materials have been the overwhelmingly crucial determinant of the competitiveness of individuals and societies. Today, a better understanding of the atomic and molecular structure of materials is becoming indispensable for the development of new materials, and the improvement of existing materials. As a result, materials are being tailored to meet specific applications to address pressing industrial and societal challenges in the highly competitive contemporary world. In this process, ceramics technology plays a particularly important role, and hence has emerged as a driver of technological progress in many industrial sectors.

It is a widely accepted paradigm that such technological progress takes place in a highly competitive environment where only a limited amount of the required resources exist. Hunger for raw materials has always been a strong driving force in world history. Throughout the history of humankind, the information contained within each newly developed or significantly improved material or technology has increased exponentially. Figure 1.1 suggests that the knowledge required to make pottery – that is, the mining/collecting, processing, forming, and firing of clay, including the knowledge and skill to construct and operate kilns and flues – were orders of magnitude higher than those needed to fashion rather simple tools and implements from bone or stone. The quantification of the "technology information content," plotted logarithmically on the ordinate of Figure 1.1, is – of course – highly subjective. Nevertheless, it suggests that the knowledge acquired in pottery making has later been put to use to mine, dress, and smelt ore, and to purify and alloy metals. As is evident from the figure, technological development stagnated in the Western societies during the Dark and Middle ages, but eventually took off dramatically during the Renaissance and the emerging Age of Science. Since the rate of change in materials technology is ever-accelerating, the increase in information content – that is, entropy – leads to an ever-decreasing technological half-life of newly invented materials and technologies. The consequences of this effect have been estimated and projected onto future economical and societal trends of developed and developing nations

Classic and Advanced Ceramics: From Fundamentals to Applications. Robert B. Heimann

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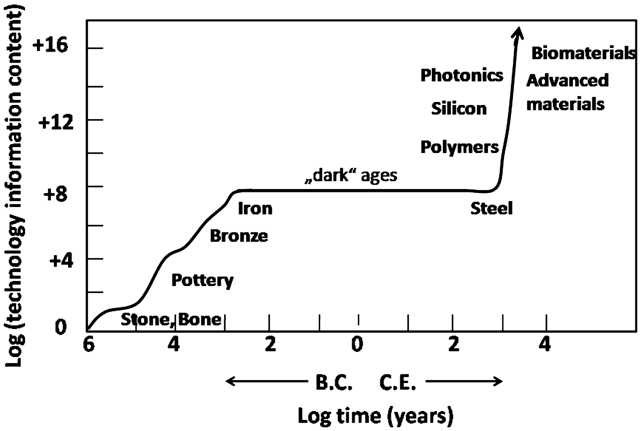

Figure 1.1 Materials development over time: increase of technology information content. Adapted from Hench (1988).

(see, for example, Hench, 1988; Franklin, 1990; Heimann, 1991; Marchetti, 1997; Heimann, 2004).

The rate of change in the information content of advanced materials duplicates the equally fast rate of information and technology transfer within societies of the developed world (Heimann, 1991). As pointed out by Hench (1988), a positive feedback mode connects the two rates, leading to an autocatalytic relationship between materials and technology. This relationship thrives in technological niches that compete with each other for survival and growth, and is controlled by complicated mechanisms involving small random effects which, however, can accumulate and become magnified by positive feedbacks (Arthur, 1990).

Ceramics *sensu strictu* are the oldest man-made materials. By definition, they are inorganic, nonmetallic, silicate-based materials, insoluble in water and many acids and alkalis, and contain at least 30% crystalline compounds. In general, ceramics are shaped at ambient temperature from a specific raw materials mix by a large variety of forming techniques and tools (see, for example, Brownell, 1976), and obtain their typical properties by firing beyond 800 °C (Hennicke, 1967).

While at the dawn of civilization naturally available "ceramics" such as hard rock and flint were utilized for tools (Figure 1.2), with the advent of fire it became apparent that soft and pliable clay and loam raw materials could eventually be changed into hard, durable shapes that were capable of holding liquids, and consequently these were used as storage containers and cooking pots. This development is thought to have been triggered by the transition from hunter–gatherer to agrarian societies. Through the firing process, clay minerals generated by the weathering of granitic rocks could be transformed back into something resembling an artificial "stone" (Heimann and Franklin, 1979). Later, construction materials such as bricks, tiles, and pipes were produced from fired clay. As early as 1600 B.C., the technology of glazing of bricks was known and exploited by the Babylonians.

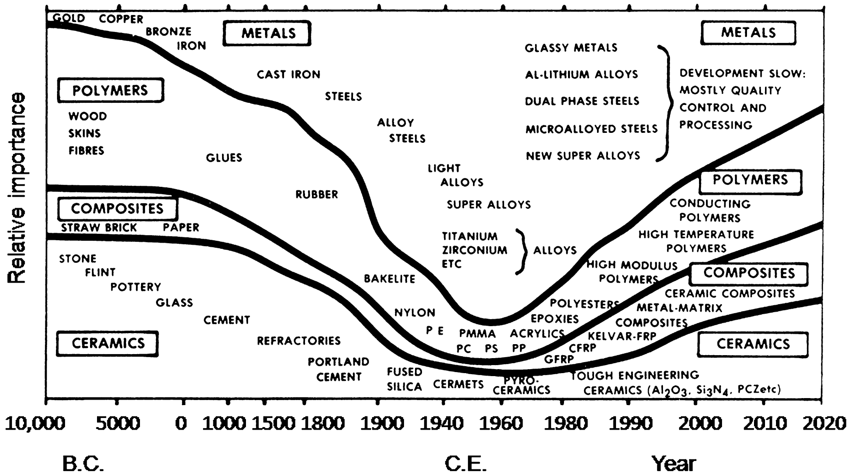

Figure 1.2 Historical timeline of development of materials (Froes, 1990).

The early history of the ceramic technology is difficult to assess in both geographical and temporal context. Arguably, among the first objects fashioned from clay were maternal goddess images such as the famous Upper Paleolithic "Venus of Dolni Věstonice," Moravia, and fragments of animal and human figurines dating from between 25 000 and 29 000 years ago (Klima, 1962). Near the end of the Mesolithic (13 000–12 000 B.P.), hunter–gatherers living in Japan independently rediscovered ceramic technology, but this time applied it to manufacture the world's oldest known ceramic vessels of the Jōmon culture (Chard, 1974; Sherratt, 1980). Very recently, still earlier remnants of ceramic technology were found in a cave in southern China and dated to between 18 300 and 15 430 cal B.P (Boaretto *et al.*, 2009). Since ceramic shards are well preserved in most soils, they are of overriding importance in archeology to date, and distinguish prehistoric cultures by the unique and enduring physical and stylistic features of their pottery. Highlights in ceramic art and technology are the Greek Attic red-on-black and black-on-red vases of the sixth and fifth centuries B.C., the Roman Terra sigillata ware (first century B.C. to third century C.E.), Chinese Song (960–1279 C.E.) and Ming wares (1368–1644 C.E.), as well as the European developments surrounding the inventions of Faience and Majolica (late fifteenth to early sixteenth century C.E.), soft-paste (Sèvres, France) and triaxial hard-paste (Meissen, Saxony) porcelains of the eighteenth century C.E., and soapstone porcelain and bone china in eighteenth-century England. The art, structure and technology of these ceramics have been magnificently researched and displayed in the seminal work "Ceramic Masterpieces" by Kingery and Vandiver (1986). The British development lines in particular were described by Freestone (1999) and Norton (1978).

In parallel, a second line of development emerged concerned with technical refractory ceramics for applications in ancient metal-working activities, including

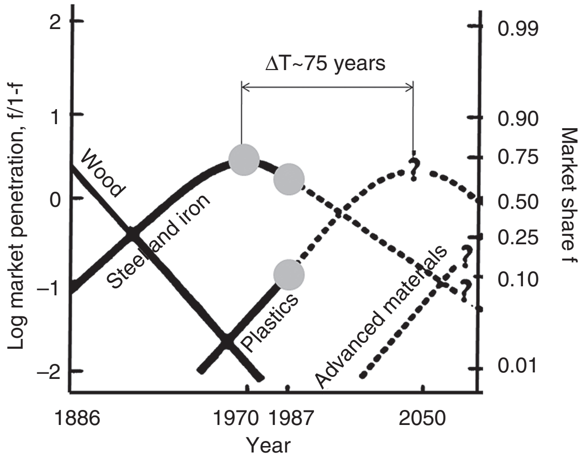

Figure 1.3 Logistic substitution of structural engineering materials between 1886 and 2050 plotted according to the Marchetti–Nakicenovic model (Marchetti and Nakicenovic 1979; Marchetti, 1997). The maxima of the evolutionary curves are spaced about 75 years apart (i.e., 1.5 times the Kondratieff cycle).

tuyères, kilns, furnace linings, smelting and casting crucibles (Rehren, 1997), glass smelting pots, and saggars for firing delicate – and hence high-priced – pottery (Freestone and Tite, 1986).

As indicated in Figure 1.2, ceramics and ceramics-based composite materials played a very important role during the early technological development period of mankind until about 1500 C.E., when metals technology took over. This lasted until the 1970s, when the ubiquitous application of engineering polymers and their composites reduced the impact of metals (Figure 1.3). However, in parallel a second "ceramic age" emerged, highlighted by the development and practical use of tough engineering, functional, and other advanced ceramics. Today, the production volume of classic ceramics such as bricks, tiles and cement/concrete still drastically outperforms that of advanced ceramics. For example, the present world tonnage of cement produced is in excess of a staggering 2×10^9 tons annually (see Section 5.2.1). In contrast, the volume of advanced ceramic materials produced is ridiculously small, although owing to their high value-added nature their sales figures approach those of classic ceramics (see Section 6.2).

Around 1970, metal technology – exemplified by the most common construction materials of steel and iron – reached its maximum market penetration of approximately 75%, and then began to decline. Today, these materials are gradually being replaced by engineering plastics, the use of which is predicted to peak around the year 2050. Simultaneously, the use of advanced materials, including advanced ceramics, is on the rise and will presumably reach a market share of about 10% by the year 2050. This model is based on the logistic Volterra–Lotka equation (Prigogine and Stengers, 1984), that is a measure of the continuous competition

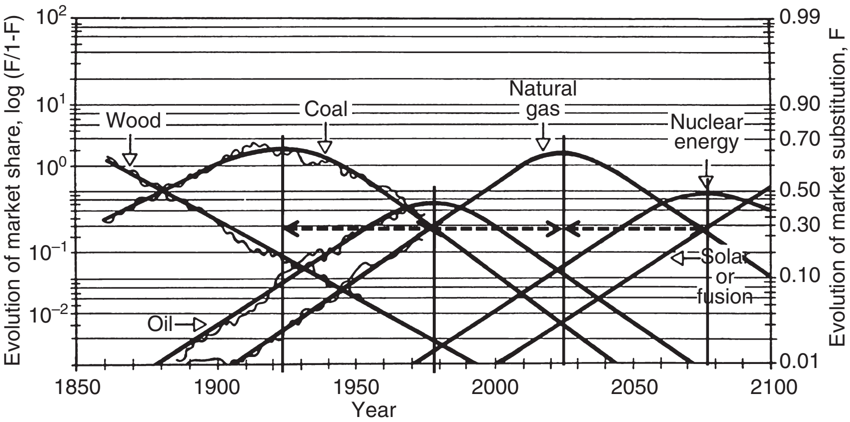

Figure 1.4 Global use of primary energy sources since 1850 (Marchetti, 1989, 1997). The maxima of the Verhulst logistic curves are spaced 50–55 years apart (Kondratieff cycles). Data beyond 1970 are extrapolated.

of materials and technologies, and the fight for technological niches (Heimann, 1991). The maxima of the overlapping logistic equations (Verhulst equations) are shown to be spaced approximately 75 years apart. This offset, however, does not match the well-known Kondratieff cycle of 50–55 years, which arguably is a series of recurring long-range economic cycles that have been shown to govern numerous evolutionary developments, including discoveries (inventions), innovations,[1] industrial production figures, and primary energy uses (Figure 1.4) (Marchetti, 1981, 1997; see also Heimann, 1991, 2004).

In order to underscore the overriding role that raw materials play in society, two additional scenarios will be juxtaposed: (i) the worldwide industry production; and (ii) the individual use of raw materials per capita and lifetime in present-day Germany. The major growth industries are considered to be energy production and distribution, the chemical industry, and microelectronics. The proportions of these industrial sectors of the total industry production worldwide for 1960 and 1990, and extrapolated to 2025, are shown in Table 1.1. While the energy-producing and chemical industries are assumed to remain constant, microelectronics are predicted to double between 1990 and 2025, whereas the metal-based industries (including processing and machining industries) will show a remarkable decline.

Figure 1.5 lists the tonnage of raw materials used per capita within a person's average lifetime of 70 years in contemporary Germany, representative of the raw materials "hunger" of a developed nation with a high technological and societal efficiency (Millendorfer and Gaspari, 1971; Marchetti, 1981).

1) *Innovations* start new industries; *inventions* are discoveries that are at the base of innovations (Marchetti, 1981).

Table 1.1 Proportion (%) of growth for industries of the total industry production worldwide. Data from United Nations Yearbook (1998).

Industry	Year		
	1960	1990	2025
Energy	4.8	6.5	7.0
Chemistry	8.5	12.9	14.0
Microelectronics	1.9	10.3	**25.0**
Metal-based industries	26.5	23.0	**9.4**

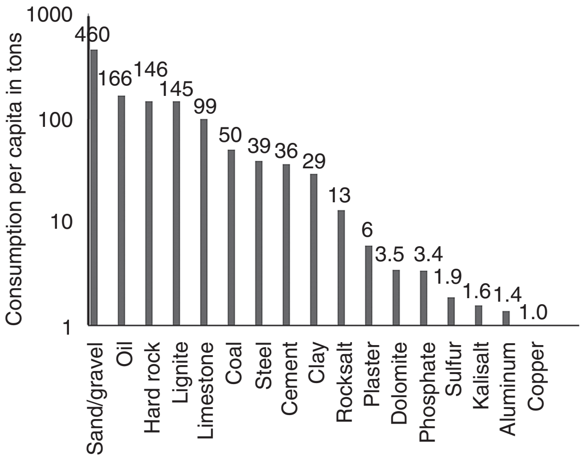

Figure 1.5 Per capita consumption of material resources in an average lifetime in Germany. Data from Bundesanstalt für Geowissenschaften und Rohstoffe (BGR), Hannover, Germany, Global-Report 2859, 1995).

1.2 Classification of Ceramics

A systematic treatment of inorganic–nonmetallic materials is best accomplished by considering a hierarchical approach, as shown in Figure 1.6. The first triangle of level 1 contains the three materials supergroups – metals, polymers, and ceramics – *sensu lato* that are distinguished by their differing chemical bonding relations. The second level of triangles shows at its apices the inorganic–nonmetallic materials classes n that is, ceramics *sensu strictu*, glasses, and hydraulic adhesive materials. These classes can further be subdivided into silicatic, oxidic, and nonoxidic materials (the third hierarchical triangle). Eventually, the chemical components characterize the individual properties (fourth hierarchical triangle). Figure 1.6 is

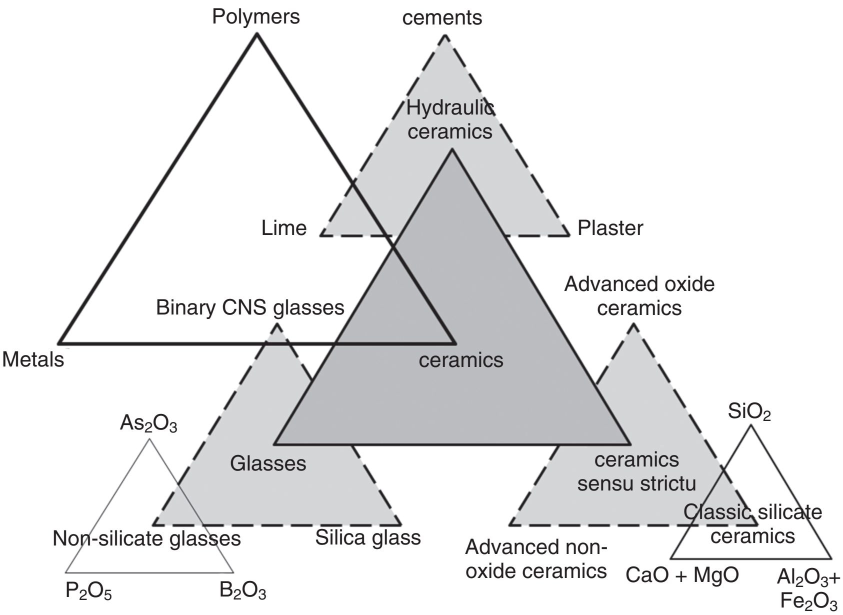

Figure 1.6 Four levels of hierarchical triangles relating different groups of materials. Level 1 (materials supergroups): metals, polymers, **ceramics**; level 2 (ceramics *sensu lato*): glasses, hydraulic ceramics, **ceramics *sensu strictu***; level 3 (ceramic subgroups): advanced oxide ceramics, advanced non-oxide ceramics, classic silicate ceramics; level 4 (phase diagrams): SiO_2, CaO + MgO, Al_2O_3 + Fe_2O_3.

Table 1.2 The three main groups of silicatic ceramic materials (level 2 of Figure 1.6).

Material	Processing steps[a]			T_{max} (°C)	Time of invention
Ceramics *sensu strictu*	P	F	H	<1450	<6000 B.C.
Glasses	P	H	F	1500	<3000 B.C.
Cements (CBCs)[b]	H	P	F	>1500	Around 1850

a) P = powder production; H = heating; F = forming.
b) CBC = chemically bonded ceramic.

intended to show only the principle of the approach; in reality, such a succession of hierarchical triangles would be more complex. For example, the huge variation of chemical compositions inherent in silicate ceramics would require replacing the triangles by higher-dimensional shapes.

The three main groups of ceramics of level 2 are distinguished by their processing temperatures, the succession of processing steps (F = forming, H = heating, P = powder production), and the time of invention (Table 1.2).

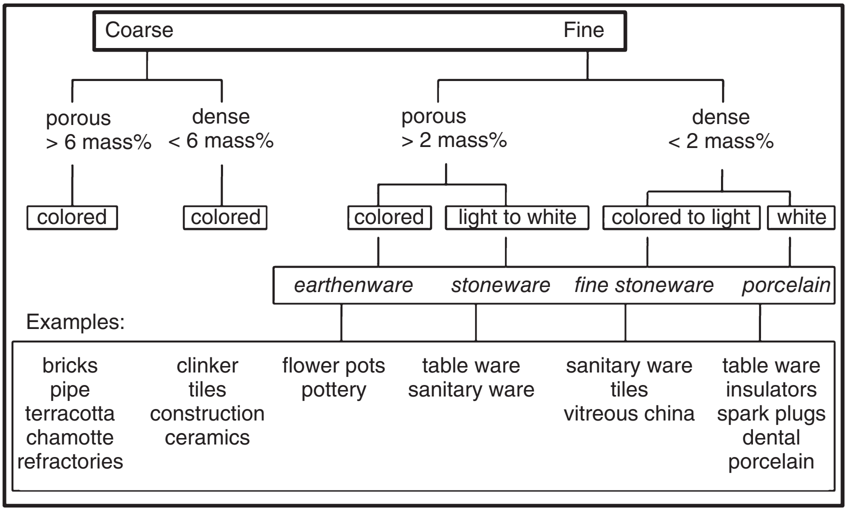

Figure 1.7 Classification of silicate-based ceramics (after Hennicke, 1967).

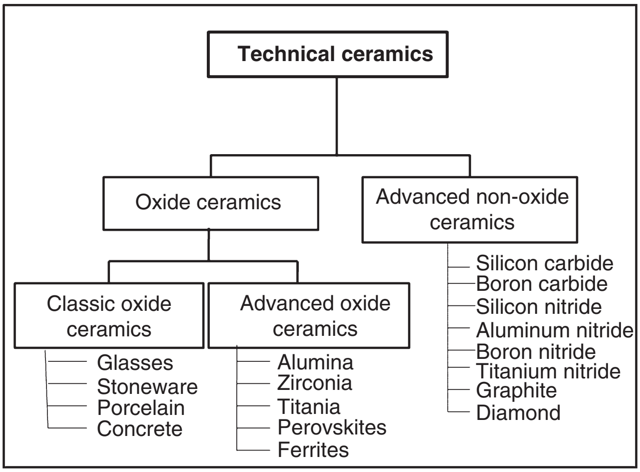

Figure 1.8 Classification of technical ceramics (level 3 of Figure 1.6).

Historically, silicate-based ceramics have been classified in various ways. One of the most useful schemes (Hennicke, 1967) divides different classic ceramic wares according to their starting powder grain sizes (coarse: >0.1 … 0.2 mm; fine: <0.1 … 0.2 mm), porosity of the fired product, water absorption capacity (<2 … >6 mass%), and color of the fired ceramic body (Figure 1.7).

A classification of the field of technical ceramics is shown in Figure 1.8.

In the chapters following this introduction, the path will be traced from natural silicate-based ceramic raw materials, rheological principles of clay–water interaction, and important ceramic phase diagrams to the mineralogy and chemistry of the ceramic firing process. A basic approach to cement and concrete will conclude the first part of the volume dealing with classic ceramics. Glasses, however, have deliberately been excluded from discussion as they do not comply with the definition of ceramics according to Hennicke (1967), as detailed above.

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