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(pg 65-)

BRIEF DESCRIPTIONS OF BASIC CLAY PROCESSING, BUT NOT VERY USEFUL FOR CLAY PROCESSING SECTION. NO EMISSIONS OR TRACE ELEMENT DATA.

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Natural and Synthetic Raw Materials for Classical Ceramics Manufacture

M. Bertolani

Istituto di Mineralogia e Petrografia, Università di Modena, Italy

Clayey raw materials (kaolin, fine clays and common clays) and the methods for their study and identification are discussed. Non-clayey raw materials, for bodies and glazes (quartz, feldspar and carbonates), for bodies only and for glazes only, and the methods for their study and identification are then considered.

A — CLAYEY RAW MATERIALS: KAOLINS, FINE CLAYS AND COMMON CLAYS

1 INTRODUCTION

Ceramic art was one of the first human activities. It began in the Neolithic age about 5000 years BC in Asia Minor, about 4000 years BC in Egypt and about 3000 years BC in Europe. The raw material used was clay, at first without additions, and prevalently pottery and vessels were formed and baked. The clay used in prehistoric ages was a common clay, which became red on baking. Ceramic colours to beautify the artefacts were already in use. Engobing, that is, the use of clay with a lower melting point to make the surfaces waterproof, was also used.

Later, additions to mixtures, of sand, calcite and calcined clay, were introduced. Similar conditions existed in Colombia at the end of the fifteenth century, at the time of the arrival of Amerigo Vespucci.

However, in China, before the year 1000, a refractory white clay which was very poor in iron, named kaolin (from the Kao-Ling hill, where the first deposit was found), was used. From the kaolin, together

with other pure raw materials, was produced a white, hard, translucent material: porcelain. This was used not only for vessels and pottery objects, but also for tiles; for instance, in the covering of the pagoda named the 'Porcelain Tower', built by the Emperor Jung Lo in the fourteenth century.

Therefore, clay, whether common or fine, is the main raw material for classical ceramics.

Petrographically, clay is a pelitic sediment formed by one or more clay minerals associated with non-clay minerals. Fine clays usually consist of a few prevalently clayey components; common clays are made up of many components.

According to particle size classification, clay is formed by particles with a diameter of $< 3{\cdot}9$ nm or 2 nm depending on the classification system used. At present, the clay fraction is generally considered as < 2 nm.

2 THE STRUCTURE OF CLAY MINERALS

Clay minerals are sheet silicates. The main structural element is a tetrahedron which contains silicon in the centre and oxygen at the vertices (Fig. 1). Aluminium can replace silicon in the centre of the tetrahedron. The union of the vertices of the tetrahedra forms tetrahedral layers (T) with hexagonal symmetry (Fig. 1).

Another structural element is an octahedron with trivalent (Al, Fe^{3+}) or bivalent (Fe^{2+}, Mg) ions in the centre and oxygen or (OH) at the vertices (Fig. 2). The union of octahedra forms hexagonal rings (Fig. 2) (octahedral layers = O).

If in three octahedra, only two have their centres occupied by trivalent ions, the structure is dioctahedral or gibbsitic (gibbsite is $Al(OH)_3$); if there are bivalent ions in the centres of all octahedra, the structure is trioctahedral or brucitic (brucite is $Mg(OH)_2$).

The union of tetrahedral and octahedral layers forms the sheet silicate structures. There are structures with two layers (T-O), three layers (T-O-T), three layers + one (T-O-T + O) and mixed layers.

3 THE MOST IMPORTANT CLAY MINERALS

Depending on the type of octahedral layer, clay minerals are classed as dioctahedral and trioctahedral.

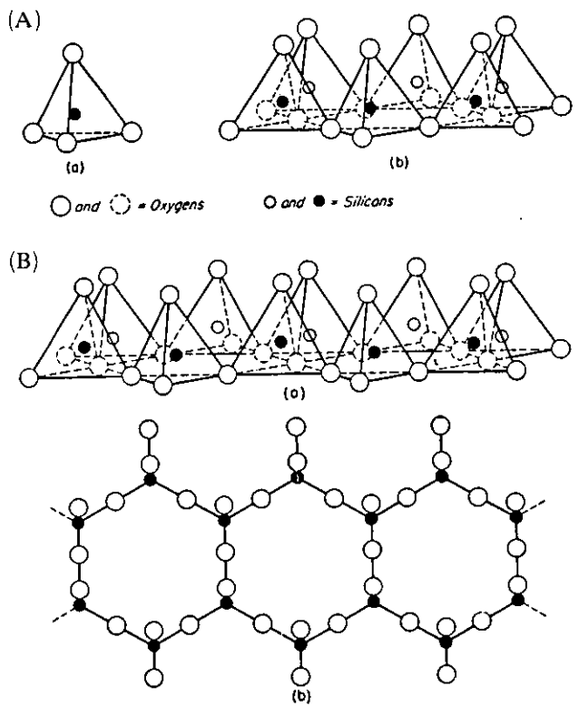

Fig. 1. Main structural elements of clay minerals. (A) Diagrammatic sketch showing (a) a single silica tetrahedron and (b) sheet structure of silica tetrahedra arranged in a hexagonal network. (B) Diagrammatic sketch of double chains of silica tetrahedra, as in the amphibole structural type of clay minerals; (a) in perspective (b) projected onto the plane of the base of the tetrahedra (source: Grim, 1953).

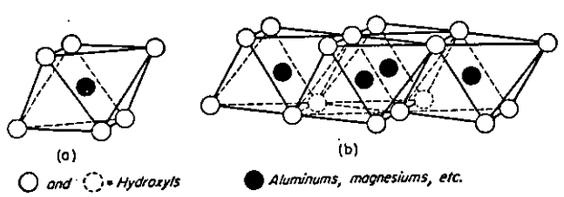

Fig. 2. Diagrammatic sketch showing (a) a single octahedral unit and (b) the sheet structure of the octahedral units (source: Grim, 1953).

The clay minerals are very abundant; here we will consider only the commonest and most important ones for the ceramic industry.

3.1 Two-Layer Sheet Silicates (T–O)

These have units 7·1 Å thick, and form two categories: dioctahedral and trioctahedral.

3.1.1 Dioctahedral Minerals

(a) *Kaolinite group.* Kaolinite, $Al_4(OH)_8Si_4O_{10}$, derives ordinarily from the transformation of feldspars and other aluminiferous silicates, e.g. micas. Dickite and nacrite have the same formula. Some varieties of kaolinite have lattice disorder (ball clay).

(b) *Halloysite group.* Halloysite has two different forms. One from, halloysite at 7 Å, has the same formula as kaolinite and a unit thickness of 7 Å. It is also called methalloisite. The other form has the same formula as kaolinite but has double the quantity of water: $Al_4(OH)_8Si_4O_{10}.4H_2O$. It is called halloysite at 10 Å. At 150°C, halloysite at 10 Å loses half of its water and takes on the characteristics of kaolinite and halloysite at 7 Å.

3.1.2 Trioctahedral Minerals

Serpentine group. The minerals of the serpentine group have the general formula $Mg_6(OH)_8Si_4O_{10}$. They contain also Fe^{3+} and Al. The principal types are:

Chrysotile (fibrous); the thickness of the double layer unit T–O is about 14 Å.
Antigorite (lamellar), has a unit thickness of about 7 Å.

Similar to serpentine is chamosite $(Fe^{3+}, Fe^{2+}, Mg, Al)_6(OH)_8$-$SiO_2Al_2O_{10}$. Its layer unit T–O is 7 Å.

3.2 Three-Layer Sheet Silicates (T–O–T)

Smectites, vermiculites and micas have this structural unit. The ground structures are those of pyrophyllite ($Al_4(OH)_4Si_8O_{20}$, dioctahedral) and talc ($Mg_6(OH)_4Si_8O_{20}$, trioctahedral).

3.2.1 Smectite Group

Dioctahedral smectites. Montmorillonite has the formula $(0{\cdot}5Ca, Na)_{0{\cdot}7}(Al_{3{\cdot}3}, Mg_{0{\cdot}7})(OH)_4Si_8O_{20}.nH_2O$. The thickness of the unit varies

from 12 Å for sodium montmorillonite to 15 Å for calcium montmorillonite. In montmorillonites there are weakly bound ions, called exchangeable ions, between the units.

Beidellite has the following formula: $(0{\cdot}5Ca, Na)_{0{\cdot}7}Al_4(OH)_4(Si_{7{\cdot}3}Al_{0{\cdot}7})O_{20}.nH_2O$.

Nontronite is similar to beidellite; it has iron in place of alumina: $(0{\cdot}5Ca, Na)_{0{\cdot}7}Fe_4^{3+}(OH)_4(Si_{7{\cdot}3}Al_{0{\cdot}7})O_{20}.nH_2O$.

Trioctahedral smectites. Saponite $(0{\cdot}5Ca, Na)_{0{\cdot}7}Mg_6(OH)_4(Si_{7{\cdot}3}Al_{0{\cdot}7})O_{20}.nH_2O$ is an important member of this group.

3.2.2 Vermiculite Group

These have, in general, large layers. The most common vermiculites are trioctahedral with the structure T–O–T. The general formula is $(Mg, Ca)_{0{\cdot}4}(Mg, Fe)_3(Si, Al)_4O_{10}(OH)_2.4{\cdot}5H_2O$.

3.2.3 Mica Group

Micas have T–O–T structure, and are of either dioctahedral (pyrophyllite) type or trioctahedral (talc) type.

Dioctahedral micaceous minerals. Sericite has the same composition and the same structure as muscovite: $KAl_2(OH, F)_2AlSi_3O_{10}$. However, it is always in very small sheets. It derives from transformation of many silicates, especially from sodium plagioclase. The thickness of the units is 10 Å.

Illite has the same appearance as sericite, but water replaces part of the potassium and part of the OH ions. This replacement causes lattice disorder. The chemical formula could be the following: $(K, H_2O)Al_2(OH, H_2O)_2AlSi_3O_{10}$. In the opinion of some authors, illite is formed by the overlap of micaceous and smectitic units.

Illite and sericite are among the commonest clay minerals.

Trioctahedral micaceous minerals. This group includes biotite $(K(Fe, Mg)_3(OH, F)_2Si_3AlO_{10})$ and phlogopite $(KMg_3(OH, F)_2Si_3AlO_{10})$, which are present in clays but are not as important as sericite and illite.

3.3 Three Layer + One Sheet Silicates (T–O–T + O)

3.3.1 Chlorites

Trioctahedral chlorites are important. These have a talc-type structure, and the general formula is $(Mg, Fe, Al, Cr, Ni, Mn)_3(OH)_2(Si, Al)_4O_{10}.(Mg, Fe, Mn, Al)_3(OH)_6$. The most frequent chlorites in clays are

penninite ($(Mg, Al)_3(OH)_2(Si_{3\cdot3}Al_{0\cdot7})O_{10}Mg_3(OH)_6$) and clinochlore ($(Mg, Al)_3(OH)_2Si_3AlO_{10}Mg_3(OH)_6$). In some varieties of clay (red beds), there are also iron-rich chlorites.

3.3.2 Mixed-Layer Clay Minerals

The close analogies among the different tetrahedral and octahedral units permit the formation of mixed-layer minerals, in which the layers are mixed either regularly or irregularly.

3.3.3 Ribbon-Like Sheet Silicates (T–O–T)

The tetrahedral and octahedral layers are parallel and not perpendicular to the *z*-axis as is normal. Hollows in the lattices therefore appear and water molecules enter these. Examples of this structure are sepiolite ($Mg_8(OH)_4Si_{12}O_{30}$) and palygorskite ($(Mg, Al)_5(OH)_2Si_8O_{20} + 4H_2O + 4H_2O$). The last four water molecules in palygorskite are free in lattice hollows.

3.3.4 Amorphous Clay Minerals

The best-known of these is allophane ($Al_{2-4}SiO_{5-8} \cdot nH_2O$).

4 KAOLINS, FINE CLAYS AND COMMON CLAYS

The minerals described above, alone or associated with other non-clay minerals, such as quartz, cristobalite, feldspar, micas, calcite and dolomite, form the clay raw materials.

4.1 Kaolins and Kaolinitic Clays

These are clay materials formed prevalently by kaolinite, dickite, halloysite or amorphous aluminium silicates of the allophane type. A very good kaolin must contain very small quantities of other minerals, among which the most frequent are: the inalterable mineral, quartz, which often exists in primary rocks such as granites and rhyolites (quartz can also be secondary, derived from hydrothermal action); feldspar, often present as untransformed remains; and muscovite.

Kaolins can have a hydrothermal or weathering origin. Hydrothermal kaolins often contain alunite ($KAl_3(SO_4)_2(OH)_6$), which, if $> 2–3\%$ is present, does not allow ceramic use, as this mineral liberates SO_2 at a temperature of about 800°C, during sintering of the mixture. The

emission of SO_2 damages the plant by attacking the metallic rollers of monofiring furnaces.

Kaolins which contain other compounds in addition to kaolin minerals, even if they contain very little iron, are classified as kaolinitic clays.

Kaolins and kaolinitic clays show high melting and softening points. If halloysite is present instead of kaolinite, the properties change very little; however, the material shows greater shrinkage on drying.

Kaolin appears in the quarry as an earthy, white, light mass, often variegated with iron salts; therefore kaolin for fine porcelains must be washed before commercial use. Kaolinitic clays, on the contrary, are used untreated.

We have already mentioned Chinese kaolin. In Europe, the main kaolin and kaolinitic clay deposits are in Czechoslovakia, Great Britain, France and Germany. In Brazil there are very large sedimentary deposits. In the volcanic area of the Andes, deposits of hydrothermal kaolin are common.

4.2 Illitic Clays

Illitic clays are among the most frequent, but it is difficult to find illitic clays with low iron content. Fine illitic clays are therefore required for ceramic use, as they have lower softening and melting points than kaolinitic clays. Illitic clays are often associated with kaolinitic clays, both in hydrothermal and in weathering deposits.

4.3 Bentonites

These clays contain smectitic minerals as the principal compounds. They have a much lower melting point than other clays. They also have a high swelling power, and high plasticity and viscosity. Until recently, bentonites were avoided by ceramists; now, on the contrary, they are used in small quantities to give plasticity to over-lean mixtures in monofiring, and thus avoid breakage during drying and glazing. Bentonites often, but not always, derive from the argillation of volcanic glass. They are used as decolorants and as a drilling mud.

4.4 Common Clays

These are prevalently sedimentary, marine clays, which contain all the minerals from often heterogeneous catchment basins. Illite and sericite

are almost always present among clay minerals, and kaolinite, chlorite and smectite are often present. Whereas chlorite occurs in clayey sediments which have undergone low-grade metamorphism, smectite is characteristic of undisturbed clays.

Generally, kaolinitic clays are more refractory and less plastic. The smectitic clays are very plastic and meltable, and show high viscosity. The chloritic clays have intermediate properties.

Common clays ordinarily contain large quantities of iron. They can be divided into carbonate and non-carbonate clays. Calcite prevails in the carbonates, but in some cases dolomite occurs. Apart from carbonates, the other non-clay minerals present are quartz and feldspar. In red beds, iron oxides in the form of haematite and amorphous iron oxides are abundant.

Common clays are widespread all over the world. They are used for pottery, artistic ceramics and tiles, either porous or vitrified, and are always coloured.

4.5 Clay for Brick

All clays, sometimes with addition and mixtures, can be used for bricks. In many regions, continental alluvial clays, which contain a proportion of sand, are preferred.

5 METHODS FOR STUDY AND IDENTIFICATION OF CLAY MATERIALS

5.1 X-Ray Diffraction

The most efficient instrument for a first examination of clay raw material is the diffractometer. With this apparatus, all the crystalline minerals of a clay can be shown and the quantities of the individual compounds can be evaluated. The procedure is as follows. The finely ground specimen is placed in the tray. The work velocity, sensitivity and starting angle are set. Clay diffractometry normally lasts about 40 min. The diffractometer shows graphically the interferences (peaks) of the mineral present. The height of a peak is proportional to the amount of mineral present. Its position is shown by angular values which can be transformed into the lattice distance d. The copper wavelength is suitable for clay determination. Every crystalline mineral is characterized by a series of interferences, which are reported on cards where

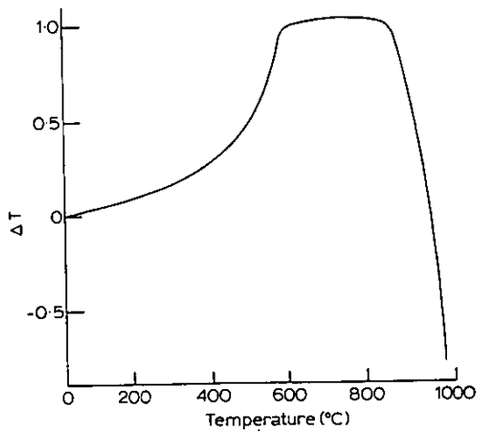

Fig. 8. Dilatometric curve for a clay containing illite, kaolinite, mica and quartz, heated at 1°C/min.

$\Delta l/l_{20}$, here Δl represents the difference in length and l_{20} is the length at 20°C. The result is a characteristic curve for each type of clay. It is very important to find the glaze–body fit (Fig. 8).

B — NON-CLAYEY RAW MATERIALS

6 FOR BODIES AND GLAZES

6.1 Quartz

Silica (SiO_2) has four natural phases: α quartz (rhombohedral); β quartz (hexagonal); tridymite (also hexagonal); cristobalite (cubic). The polymorphic system is partially monotropic and partially enantiotropic.

Only α quartz is of industrial interest. It is found all over the world in different ore types:

(a) in hydrothermal or pneumatolytic dykes related to acid magmatic complexes;
(b) in lenses related to metamorphic rocks or in metamorphites named quartzites;

(c) in sands of marine or lacustrine origin;
(d) in quartzitic sandstones, that is, sand cemented by diagenesis.

The easiest deposits to exploit are the sands, as they can be easily ground.

Quartz is a refractory mineral because it has a high melting point. It is used in some ceramic and refractory mixtures. It hardens glazes, although it increases the melting point. The change in volume corresponding to the phase transformation of quartz means that it is better not to use an excessive quantity of quartz in mixtures.

Silica also exists in amorphous form, in large amounts, in hydrothermal products of volcanic rocks.

6.2 Feldspars

Feldspars are also present in many magmatic, sedimentary and metamorphic rocks. They are of industrial interest, however, only in concentrated outcrops. K-Feldspar ($KAlSi_3O_8$) and Na-feldspar ($NaAlSi_3O_8$) are the feldspars normally used in ceramics. They are often found in pegmatitic dykes, in sedimentary sands and in low-grade metamorphic lenses of albitite.

K-Feldspar is found in nature in three phases: microcline (triclinic) orthoclase (monoclinic) and sanidine (monoclinic). The first two are present in intrusive and metamorphic rocks. Sanidine is characteristic of volcanic rocks, but is less used in industry, because it is rarely found in large quantities. It is possible to find sanidine in volcanic areas with hydrothermal activity.

Na-Feldspar (albite; $NaAlSi_3O_8$) forms a mixture with Ca-feldspar (anorthite; $CaAl_2Si_2O_8$) in all ratios: this is the plagioclase series. In this series, sodium-rich members are important in ceramics.

Feldspars are ceramic fluxes. K-Feldspar has a higher melting point than that of Na-feldspar, but a wider softening range. It is the classic feldspar of porcelains. Na-Feldspar is the most used in the grès tile industry.

Feldspathoids are also used as fluxes in ceramics, in particular nepheline ($NaAlSiO_4$), which exists in alkaline rocks in Canada and Scandinavia. It is separated from the rock by flotation.

There is also, although it is extremely rare and expensive, a lithium feldspathoid, petalite ($LiAlSi_4O_{10}$), which has very high fluxing power.

In glazes, feldspars increase the coefficient of expansion, but also increase solubility; therefore they must be used at not more than 8%.

In many regions, feldspars are deficient; therefore for some time either intrusive or volcanic rocks have been used; these are rich in quartz–feldspar and poor in iron. It is very important to know the ratio between quartz and feldspar so that the exact amount of the two minerals can be added to the mixture and the glaze.

6.3 Carbonates

Many clays naturally contain amounts of carbonates, and can therefore be used for production of tiles with a porous body. However, in some regions, it is difficult to find carbonate clays; therefore, to obtain porous ceramics, either carbonate or wollastonite must be added to the mixtures.

The most common carbonate is calcium carbonate, which, as a mineral, is named calcite. We find it in limestones and marbles, which are very common rocks. Limestones are scarce only in exclusively volcanic areas. In place of calcium carbonate, dolomite (calcium and magnesium carbonate; $CaMg(CO_3)_2$) can be used. In some regions, there are mountain chains of dolomite, which can have organic or evaporitic origin.

Calcite and, to a lesser degree, dolomite, are used in glazes, but in small amounts. They are, in fact, moderate fluxes and produce an expansion lower than that of feldspar. Carbonates give opacity; they are used in percentages from 4 to 15%.

7 FOR BODIES ONLY

Clays, quartz and feldspars are the most commonly used in classical ceramic raw materials; but often other natural or synthetic substances are used to obtain particular characteristics. These raw materials include:

- Talc ($Mg_3(OH)_2Si_4O_{10}$): this is used in porcelains, especially in insulator porcelains. Its use has been extended to white body tiles. Talc is a typical metamorphic mineral; it is found all over the world where there are mafic and especially ultramafic rocks, which have a high magnesium content. It is a very soft, greasy, translucent mineral.
- Sillimanite, kyanite and andalusite have the same chemical formula ($Al_2Si_2O_5$). They are of metamorphic origin. They are

common, but rarely form large outcrops. Sillimanite is the most used mineral, especially in refractories and in high-resistance porcelains.

- Wollastonite ($CaSiO_3$) has three phases: monoclinic para-wollastonite, triclinic wollastonite and triclinic pseudohexagonal pseudowollastonite. This mineral is used in porcelains to increase their resistance and to limit shrinkage. It is a contact metamorphic mineral. It is common, but rarely occurs in large amounts.
- Degasifier additions. Ceramic technology for the tiles industry has led to the introduction of rapid monofiring. The previously requested time of 20 h for the two firings has gone down to about 30 min. This causes inconvenience for red mixtures formed from common clays: rapid vitrification prevents volatiles (H_2O, CO_2) from discharging and oxygen from entering the tile, so that the inside becomes black (black core) with large bubbles. Degasifying materials are added to avoid this inconvenience. The most commonly used are lapilli and volcanic slags, ground basalts, non-carbonate sands and blast furnace slags. Kaolinite clays and calcined clays are also used.

8 FOR GLAZES ONLY

We have already spoken about feldspars which are much used in glazes because they are good fluxes; but there are other stronger natural and synthetic fluxes, which will now be described.

8.1 Borates

These are natural products, which have very low solubility in water and easy fusibility. Those most used are the following:

- Ulexite ($NaCaB_5O_9.8H_2O$). This is frequently found in fibrous-radiate aggregates. Its formation is related to salt-lakes and to an arid climate. It is normally associated with other salts. In South America, deposits occur in Chile, north Argentina and Peru.
- Colemanite ($Ca_5(B_3O_4(OH)_3).H_2O$). This is often associated with ulexite and pandermite ($Ca_2(B_5O_6(OH)_7)$).
- Boracite ($Na_2B_4O_7.10H_2O$). This has the inconvenience of being soluble in water.

The salts of boron are very good fluxes and have low expansion. However, they limit the colouring possibilities, and > 20% B_2O_3 cause solubility in water.

Also, barytes ($BaSO_4$) is used in glazes; it increases the refractive index, but as it causes devitrification, < 5% should be used.

8.2 Zircon

Zircon ($ZrSiO_4$) is a very much used mineral in glazes, either as a hardener or as an opacifier. Zircon is one of the commonest accessory minerals of rocks. As an industrial mineral it is present either in primary ores, or in secondary deposits such as zirconiferous sand. Its opacifying power derives from its high refractive index.

The greatest zircon producer is Australia. Synthetic zircon oxide can substitute for zircon silicate. It is possible to use other minerals with high refractive index in the place of zircon; for example, rutile and anatase, two phases of TiO_2. Most anatase used in ceramics is synthetic, derived from ilmenite ($FeTiO_4$). Also, cassiterite (SnO_2) can be used as an opacifier.

Among the synthetic components of glazes, lead salts are very important. They are exceptional fluxes and raise the refractive index of the glaze, which becomes very brilliant. Lead salts do not give solubility to glazes and show constant viscosity at different temperatures. They permit all colorations. The main defects of lead are that it reduces greatly the hardness of glazes and is toxic. Lead can be used up to 50% (80% in the frit), and is normally added in the form of minium (Pb_3O_4). Instead of lead, some glazes have zinc, generally as the oxide (ZnO). Zinc salts are good fluxes and are good for fluidization. They produce low dilatation and opacity. However, glazes containing zinc may be attacked by acids, and zinc limits the possibilities of colouring. It is not convenient to use more than 2–5% for bright enamels, or up to 25% for opaque glazes.

9 METHODS FOR THE STUDY AND IDENTIFICATION OF NON-CLAYEY RAW MATERIALS

9.1 Quartz

Quartz can be identified by microscope, by diffractometer and chemically. The first two methods are more rapid.

Quartz is easily recognizable under the microscope by its transmittance, absence of cleavage, inalterability, middle-low birefringence and refractive index (about 1·55). The refractive index is determined using liquids whose index is known. It should be noted that, for a mineral and a liquid which have identical refractive index, the Becke line does not appear (Fig. 9). By using point counter, a quantitative determination of the quartz can be made.

The diffractometer permits exact quantitative determinations of quartz and shows other minerals which may accompany the quartz.

Chemical analysis is essential to determine the amount of iron in the quartz, which is an important value.

9.2 Feldspars

The diffractometer identifies, very well, the presence of feldspar in specimens, but does not distinguish potassium, sodium or sodium-calcium feldspar with certainty. This distinction is easier by microscope. In fact, using the method of liquids with known refractive index, potassium feldspar always shows an index lower than 1·54. Sodium feldspar shows the minor index slightly lower than or equal to 1·54, and

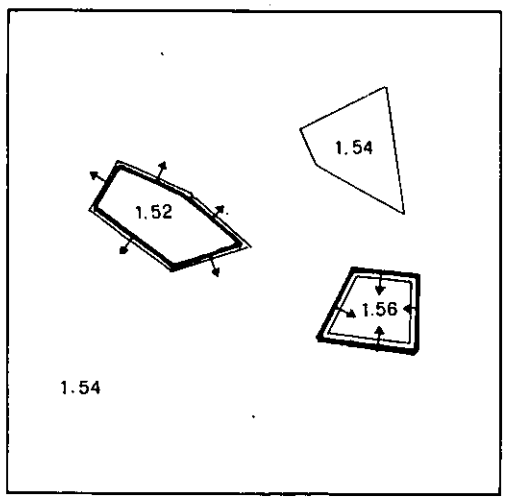

Fig. 9. Microscopic determination of the refractive index of minerals by use of the Becke line.

the major index higher than 1·54. Calcium–sodium feldspar (plagioclase) has all its indices greater than 1·54 (Fig. 9).

As well as using the refractive index, sodium and calcium–sodium feldspar can be distinguished, under the microscope, from potassium feldspar by their habitual sericitic alteration and the often present polysynthetic twinning, observable with crossed nicols. This twinning gives crystals an aspect characterized by illuminated and extinguished parallel stripes. The microscope allows a rapid examination of the mineral assemblage of quartz–feldspar sand.

Chemical analysis gives two important data: the amount of iron and the amount of alkalis (Na_2O and K_2O).

9.3 Carbonates

The microscope does not identify the type of carbonate present. Calcite, dolomite and magnesite have the same characteristics: high interference colours, good cleavage, and a strong difference in relief if observed relative to the ω axis or ε axis.

In contrast, identification by diffractometer is easy, because the interferences of these minerals have different lattice distances.

To find the quantity of carbonates in a raw material, the most rapid, although not the most exact, method is the gas-volumetric determination of carbon dioxide. This determination is done by use of a calcimeter; it does not identify the different carbonates, but is very practical and gives an immediate result even in a quarry. To achieve sufficient precision it is necessary to introduce conversion factors which depend on ambient temperature, atmospheric pressure and instrument calibration.

9.4 Talc

Chemical methods are not suitable for determination of talc, because it is naturally mixed with other magnesian silicates and carbonates, such as serpentine, chlorite and magnesite. These minerals are well identified by diffractometer. Also, a microscopic examination can be interesting, because talc is recognizable through its interference colours, which are only like those of muscovite.

Sillimanite, kyanite, andalusite and wollastonite are best identified by diffractometry; but are also well identifiable also under the microscope. Sillimanite in particular, which forms fine needles with straight extinction and rectangular section, is unmistakable.

The additive for rapid monofiring can be examined microscopically to determine the characteristics of the raw material. It is possible to verify the presence or absence of quartz (its absence is preferable), and whether the raw material is vitreous or crystalline, natural or artificial.

Clay additions are characterized by diffractometry.

9.5 Borates

Borates are not easy to identify because the most important datum is the content of B_2O_3, which requires a very difficult chemical determination. Diffractometry is suitable for mineralogical evaluation.

9.6 Zircon

Commercial zircon has very fine particle size, so that it is not resolvable by microscope. It is necessary therefore to use a diffractometer. Often the screen size is required, but particle size analysis of zircon is not easy because of the very small size of the product.

The same problem exists for anatase and cassiterite. For lead and zinc salts it is necessary to carry out chemical titration of the metal.

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Various storage and conditioning pits, deposits and towers are used in industry. In all of them clay is protected from outside weather conditions. It is continuously fed in at one point and extracted at another by means of conveying screws or excavating machines of various kinds. During storage, fine mists of water are sprayed on the newly exposed clay surfaces. The conditioned clay is usually transferred to a belt which conveys it to the plant to start the fabrication process.

Storage is very helpful in homogenizing the water distribution in clays. It is very likely that evaporation–condensation is the predominant mechanism of water transport in most industrial clay storage operations.

3 CRUSHING AND GRINDING

Crushing and grinding are done with the following aims:

(a) reduction of the clay particle size;
(b) intermixture of all the solid components of clays;
(c) destruction, as much as possible, of oriented clay textures;
(d) blending of the clay with a suitable proportion of water.

Another important function of these operations is to eliminate some unwanted components of clays, or — if this is not possible — to diminish their deleterious effects. Examples of these processes are the following:

(1) Elimination of pebbles, stones or hard lumps by means of stone separating mills.
(2) Magnetic separation of iron pieces or components which could be accidentally present in the clay.
(3) Fine grinding of hard limestone pebbles or lumps which have been excavated together with the clay. Particle reduction greatly helps in preventing lime blowing.

The crushing and grinding equipment is usually selected to match the requirements of the clay or clays to be used for brickmaking. A short description of the most widely used equipment will now be given.

3.1 Clay Crusher

The clay crusher is suitable for breaking and crushing small as well as large clay lumps which come directly from the pit and are therefore mixed with stones and other impurities. The clay is crushed to a maximum grain size of about 25 mm.

The crusher consists of a sturdy welded steel body which includes a hopper. A full carload of clay can be unloaded into this hopper. At the bottom of the hopper two rollers turn at fixed distances and at different speeds, thereby permitting very fine crushing. Each roller consists of a shaft with bolted rings placed side by side and supporting steel breaking knives. On rotation of the rollers, the knives of one roller penetrate into the groove of the corresponding ring on the other roller. Two sets of fixed scrapers, which are easily adjustable, ensure the continuous cleaning of the grooves. At the entrance of the hopper, over the rollers, a square-section shaft supports a set of interchangeable knives, which avoids the clay blockages, and ensures that the lumps are kept between the crushing rollers and continue to pass through them.

The clay crusher should be installed below ground level, in a concrete compartment. A rubber conveyor belt under the crusher transfers the crushed clay to a box feeder.

3.2 Box Feeder

The purpose of the box is to receive the ground clay coming from the clay crusher, and to feed it in a constant and suitable manner to the following preparation machines. The box may have two compartments, with adjustable shutter gates, to manage two kinds of clay simultaneously, or only one, as required. The conveyor belt consists of steel links and cambered slats. The belt speed can be adjusted at any time, even during operation, through a reduction gear box.

3.3 Stone Separating Mill

The stone separating mill is composed of a smooth and a grooved roller, which are running at different speeds. Clay containing limestone or other hard pebbles can be passed through this mill, where stones and lumps too large for crushing move to one end and are discharged separately.

3.4 Wet-Pan Mill

Perforated wet-pan mills are usually employed for the continuous wet grinding of plastic clays. Several sectors of the pan are slotted, the remainder being dead plates, on which rollers revolve and grind the clay. The rollers which pass over the perforated sectors of the pan squeeze the clay through the slots onto the collecting device below. The

output of the mill is related to the dimensions of the pan, the speed of rotation, and the proportion and size of openings in the pan. Although some size reduction takes place in wet-pan mills, breakdown is not so much by brittle fracture, as in dry-pan mills, as by plastic deformation of the moist clay by the rollers as they pass over the clay on the solid sectors of the pan, and when they squeeze it through the slots. The mixing action and the redistribution of water in the clay are not very effective when the charge remains on the pan for only a short time and it escapes rapidly from the mill via the slots in the pan. The smaller the proportionate area of the perforations in the pan, the more complete the distribution of the water tends to be. The clay escaping through the slots of the pan falls onto a cast iron plate from which one or two scrapers unload the ground clay and feed it onto a conveyor.

In some factories, water is sprayed on the clay in or before the wet-pan mill, so that the mill's powerful kneading action will infiltrate the water into the clay.

3.5 Roller Mills

A belt conveys the clay from the wet-pan mill to the first roller mill, which contains a pair of rollers, rotating at the same speed. The gap between the smooth rollers in this roller mill should be wider than in the second one. The second roller mill is of the same type and dimensions as the first, but each roller shaft is equipped with a separate pulley. The independent drive of each roller allows the use of equal or different speeds, depending on the quality of the clay. In normal use, the rollers run at different speeds, and the gap between the rollers is narrower than in the first mill. Under these conditions, the particles are broken down by a combination of crushing, shearing and rubbing actions. This kind of milling is very beneficial in reducing the grain size of any limestone which may be present in the clay.

4 NATURAL TEXTURES OF CLAYS

It is fairly common to find clays with a more or less consolidated stratified texture. A frequent feature of these textures is that the grain size of the particles varies perpendicularly to the lamination plane.

It may be observed in some clays that each individual lamella, if separated from the lamellated texture, is clayey on its upper face and silty on its lower face. This texture corresponds to a cyclic sedi-

mentation process, and contains in itself a detailed record of the conditions in which the clay deposit was formed.

Lamellated, but scarcely consolidated, textures are frequent in brickmaking clays. Consolidated clays or shales of various kinds are also used in brickmaking, but only by those factories with the proper equipment to perform a thorough grinding.

Shales have been formed by the joint or separate action of heat and pressure on clay strata. During the transformation of clay into shale, the clay particles lose part of their lattice water. The loss of hydroxyl ions in adjacent particles results in a strong interaction between them, the net result of which is a hardening of the material and the loss of its plasticity. The lost plasticity can be partly recovered by

(a) the natural process of weathering, or
(b) the artificial process of a long wet milling.

Deep shales are very compact, have a slaty appearance and have very low plasticity. Superficial shales, which have been subjected to weathering, are soft and crumbly. When mixed with water, they develop a substantial amount of plasticity. In general, properly processed shales are very valuable raw materials for brickmaking.

It should be emphasized that texture is an important feature of clays which should always be taken into consideration in their appraisal as raw materials for brickmaking. Clays of highly lamellated and consolidated textures are difficult to distintegrate by mechanical means, and this is important because such undestroyed textures are sources of defects in brickmaking.

5 MIXING OF CLAYS

It is not uncommon for brickmakers to face the necessity of mixing two or more clays together, either because they are won jointly from the same quarry or because they are deliberately mixed to make a desired body. This operation, in spite of being so common, is always difficult and troublesome, unless powerful mechanical means are on hand.

Two clays intermix easily either if both are dry and finely ground or if both are dispersed in water. These are the two limiting states in which the system has its highest mobility. Conversely, two clays intermix with difficulty if each one of them, separately, has been previously moistened to an intermediate state.

The mechanical behaviour of a clay, as a function of its moisture content, can be easily observed with the aid of a Brabender plastograph. This instrument measures and registers the clay consistency by measuring the torque on an electrical motor connected to a double-shafted mixer. Knives of various shapes can be adapted to the shafts. The sample container is charged with dry powdered clay and the electrical motor is set on operation. Under these conditions, a zero value for the consistency is set up on the dial. Water is then added at a constant rate, and the clay consistency is continuously recorded as its water content increases.

Figure 1 is a typical curve of clay consistency as a function of moisture, determined in such a dynamic test. In this curve, three stages are clearly distinguished: (a) an initial stage, in which only a very small increase of consistency takes place; (b) an intermediate stage, corresponding to a sudden consistency increase; and (c) a final stage, in which the consistency falls very abruptly.

In the first stage, water films of variable thickness surround the clay particles and groups of particles; this gives the macroscopic effect of granulation.

In the second stage, free water is interspersed between the clay particles, and the capillary attractions, as a result of the water surface tension, result in a cohesion that increases rapidly to a maximum.

In the third section, water is added in amounts greater than that corresponding to maximum cohesion; this makes the interparticle water films thicken. The increase in the water film thickness weakens the interparticle attractions, and the wet body starts to behave as a liquid. Under these circumstances, the consistency drops rapidly and approaches a zero value.

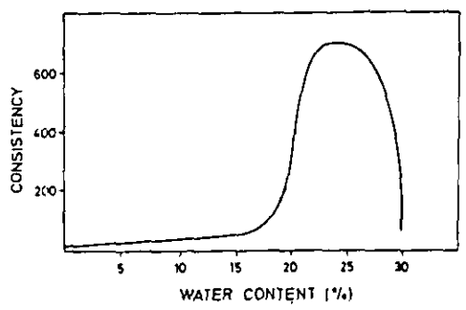

Fig. 1. Consistency of clay.

The mobility of the clay is high when it is either in a dry powder form or in a suspension form, and is low when the clay has an intermediate moisture level that corresponds to the plastic state.

The difficulty of mixing two clays is great when both of them are very plastic, and have the optimum water content for maximum cohesion (Fig. 1). Clays with low cohesion, e.g. those rich in a sandy fraction, are easier to mix.

5.1 Mixing of Clays in the Quarry

In winning the clay, it is advisable to work all the strata together, to give the winning a mixing character.

If the entire clay bed is sectioned at a time, with a batter, all the clay varieties existing in it will be mixed together in proportions that correspond to the thicknesses of the respective strata. The mixing action will be more efficient if the clay bed is planed following parallel planes very close to each other.

6 MOISTENING THE CLAY

In moistening the clay, two objectives are sought:

(1) to provide the clay with the necessary amount of water so as to achieve a given consistency;
(2) to ensure that all the water contained in the clay is in its most stable condition.

Water is transported in clay by several mechanisms, some of which operate in a liquid phase and others in a vapour phase. Each of these mechanisms is prevalent in one or another stage of moistening. The overall moistening process is at least as complex as the drying process.

In brickmaking it is common practice to increase the moisture of clays step-wise, the starting level being, of course, the moisture content of the freshly won clay.

6.1 Water Content of the Freshly Won Clay

The moisture content of fresh clay varies greatly from one deposit to another, but it is rather constant within the same deposit. If the winning of clay from a clay face is done daily in a regular manner, normal interaction with weather conditions is not sufficient to cause significant

10

Processing of Advanced Bulk Ceramic Materials

J. Kriegesmann

Fachhochschule Rheinland-Pfalz, Abt. Koblenz, FB Keramik, D-5410 Höhr-Grenzhausen, Federal Republic of Germany

After classification of advanced ceramics according to two different principles, the processing of bulk advanced ceramic materials is described. The following sequence can be found:

powder preparation; shape forming; drying; removal of the binder; prefiring; firing; final machining.

Study of the different shape forming and firing methods demonstrates that there are two objects in processing of advanced ceramics: high densities and close tolerances. It seems very difficult to combine both objects.

1 INTRODUCTION

Ceramic materials are currently undergoing a significant technical development; new areas of applications are being reported and there seems to be no end to this development in sight. These involve new applications in numerous fields of engineering, some of which were previously considered inconceivable, rather than application of traditional ceramics in the building industry or as items of tableware. Naturally, it was impossible to exploit these new applications using traditional ceramic materials such as earthenware, stoneware or porcelain. On the contrary, entirely new materials, specially adapted to individual areas of application, were needed. Thus the new term 'advanced ceramics' has recently been created to express the high-performance requirements of these new engineering materials.

2 ADVANCED CERAMIC MATERIALS

Composition is one principle which characterizes a ceramic body. Therefore it is useful to classify ceramic materials according to their characteristic main phases.[1] The various groups of advanced ceramic materials are summarized in Table 1. In this chapter only the monolithic ceramics of oxide and non-oxide types are treated. Thus the bulk advanced ceramics consist of only one dominant phase.

The classification given in Table 1 takes the compositions of the ceramics into account. Thus it is reasonable for researchers and ceramics producers to use this classification. For users of ceramics, however, the application of a material is more characteristic than its composition.[2] Thus in Table 2 advanced ceramics are classified according to their applications. It should be noted that the two proposed classifications are not always comparable. For instance, porcelains for technical use, such as insulators or evaporating boats, are traditional ceramics according to the characterization of Table 1 but advanced ceramics according to the classification of Table 2.

Naturally, not all of the main groups and subgroups can be dealt with in this chapter. Only some aspects of bulk advanced ceramics for structural use will be discussed.

3 PREPARING POWDER COMPOSITIONS

The composition of the raw materials has a strong effect on the properties of the final product. On the one hand, homogeneity of the mixture should be considered, and, on the other hand, particle size distribution, reactivity and purity of the various components must be carefully controlled. For fabrication of advanced ceramics synthetic powders are generally used. As the powder preparation methods have been treated by Suyama[3] for this volume, they can be omitted from the discussion in this chapter.

It should be noted, however, that as opposed to the raw material mixtures for traditional ceramics the powder compositions for advanced ceramics do not generally contain special plastic components such as clay, which permit the powder mixtures to be formed to a desired shape without additional shape-forming aids. Thus, as a rule, the raw material mixtures for advanced ceramics must contain, in addition to the basic powder, organic agents and sintering aids to obtain a sufficient plasticity. The quantities and types of the organic binders

TABLE 1
Classification of Advanced Ceramics According to their Characteristic Main Phases

Main groups	*Subgroups*	*Examples*
Oxide ceramics	Simple oxides	Alumina Magnesia Beryllia Titania Zirconia (FSZ, TZP)
	Complex oxides	Perovskite Spinel Garnet Titanate Magnetoplumbite Beta-alumina
Non-oxide ceramics	Elements	Graphite PCD[a]
	Nitrides	Silicon nitride Aluminium nitride Boron nitride Sialon Alon
	Carbides	Silicon carbide Boron carbide
	Borides	Boron carbide Boron nitride
	Silicides	Silicon nitride Silicon carbide
Composites	Transformation toughened ceramics	PSZ[b] ZTA[c] ZT-mullite ZT-spinel
	Fibre and whisker reinforced ceramics	CFC[d] SiC whisker reinforced alumina
	Coatings	Glaze CVD-coating[e] PVD-coating[f] Coating by plasma spraying

[a]Polycrystalline diamond.
[b]Partially stabilized zirconia.
[c]Zirconia toughened alumina.
[d]Carbon fibre carbon.
[e]Chemical vapour deposition.
[f]Physical vapour deposition.

TABLE 2
Classification of Advanced Ceramics According to their Characteristic Applications

Main groups	*Subgroups*	*Examples*
Chemical ceramics	Chemotechnical	Crucibles Filters
	Active	Catalysers Sensors
Structural ceramics	Mechanical engineering ceramics	Extrusion nozzles Seal rings Ball bearings
	Cutting ceramics	Cutting tools
	Grinding ceramics	Grinding wheels
Reactor ceramics		Fission materials Breeding materials Moderators Regulating rods
Electro-ceramics	Passive	Insulators
	Active	Capacitors Heating resistors Electrolytes Electrodes Oxygen sensors Piezo-ceramics Superconductors
Magneto-ceramics	Soft magnets Permanent magnets	Coil cores Loudspeakers
Optoceramics	Passive	Na-vapour lamps
	Active	Lasers Electro-optical transformers
Bioceramics	Implantations Dental ceramics	Protheses Artificial teeth

strongly depend on the chosen shape-forming method. Thus the role of the binders will be discussed in the next section.

4 SHAPE-FORMING METHODS

Consolidation of the powder mixtures is achieved by the shape-forming processes, which should essentially accomplish three different requirements:

(1) The powder mixture should be given a shape which approaches the desired shape as closely as possible, to exclude or at least reduce final machining.
(2) The powder particles should come very close to each other to achieve high consolidation of the green body, because this gives low shrinkage and high final density, on firing.
(3) The costs for the shape-forming methods should be kept low. This can be achieved not only through high piece rates or continuous processing but also through cheap tool manufacturing.

As there is no technique that accomplishes all of these requirements properly, many different shape-forming methods are used, the most common of which are summarized in this section.

Pressure sintering techniques ('hot pressing' and 'hot isostatic pressing') combine consolidation and densification in one step. Using these techniques, high densifications can be achieved. Thus primarily they should be regarded as densification processes, and therefore they will be discussed in Section 6.1.

4.1 Extrusion Moulding

Extrusion moulding can be used for fabrication of elongated shapes with high aspect ratios, such as tubes or rods. An extruded column streams off the die relief and is cut lengthwise by a special cross-cutting tool according to the desired linear extension. As the extruder can work continuously, series production is possible.

Using this technique, an operational disadvantage is caused by the dimensional limitations in the shape, as only those shapes can be produced that have constant cross-sections. On the other hand, very complex cross-sections can be extruded; for instance, the fabrication of thin-walled honeycomb structures is possible.

Both the recipe of the organic additives and the processing parameters should be chosen in such a way that the column flows laminarly but keeps dimensionally stable after leaving the die.

The pressure needed for extrusion is transmitted to the flow either via a worm (screw) or via a piston. The principles of the worm extruder and the piston extruder are shown in Fig. 1.

The advantage of the worm extruder is the fact that the flow of the column is absolutely continuous. The resistance to wear, however, is very low because of both the abrasive ceramic powders and the immense frictional forces on the worm. Therefore the worm material must meet high requirements, and materials such as cemented carbides should be used. The frictional pressures can be reduced through additional plasticizers or lubricating agents. Moulding defects are typical for worm extrusion; these originate from the slip planes between the ceramic mass and the internal walls of the extruder or from the slip planes within the mass. The latter defect is caused by different velocities of neighbouring parts of the mass. Those moulding defects which depend only on the manner of operation of the worm extruder can be reduced by a proper choice of organic agents.

Piston extruders compared with worm extruders are much less susceptible to wear. Moulding defects do not occur so often because of the simpler flow configurations. However, the process is, strictly speaking, not continuous, as the piston must be drawn back after each forward feed.

A critical part of both types of extruders is the die relief (orifice). High pressures exist in the region of the die, where stiffening of the

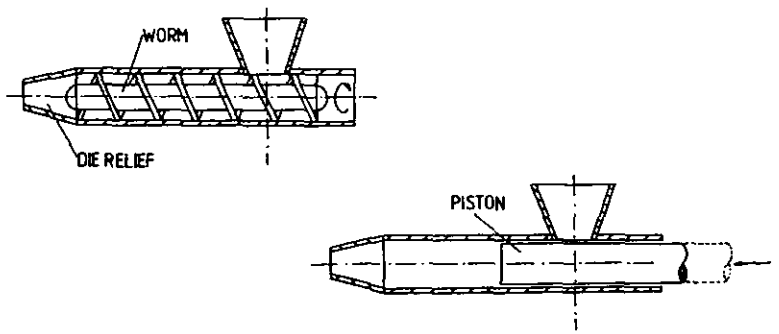

Fig. 1. Principles of worm (left) and piston (right) extrusion.

ceramic mass can occur through dilatancy effects. This is particularly critical if agents based on organic solvents are used. It is easier to use thermoplastic binders.

It can be concluded that a proper extrusion of masses for advanced ceramics is not easy to achieve, although the process seems to be so simple.

4.2 Uniaxial Pressing

Uniaxial pressing is used for parts with length to transverse dimension ratio of less than three. It is accomplished by the compaction of a powder mixture into a rigid die by applying pressure along a single axis through upper and lower punches (or pistons). The principle of uniaxial pressing is shown in Fig. 2.

If only one punch is used at the top and one at the bottom, very simple parts such as rods or bars can be fabricated. If parts with steps, such as seal rings, are to be produced, the process is conducted with tools which have at least two separately guided punches for both top and bottom. The principle of uniaxial pressing is demonstrated in Fig. 3.

It is important for presses with separately guided punches that the powder particles move along the pressing axis during the whole pres-

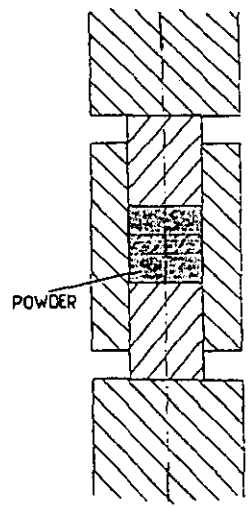

Fig. 2. Principle of uniaxial pressing.

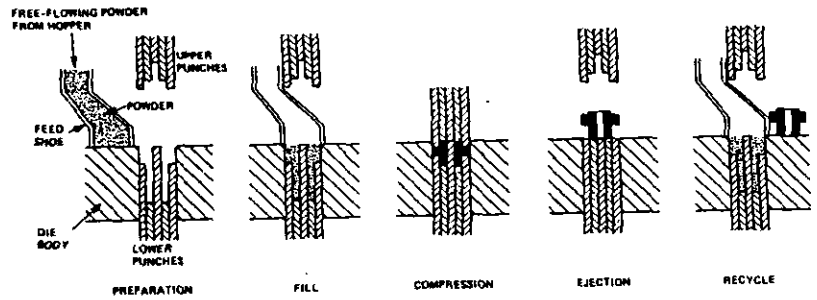

Fig. 3. Pressing stages for fabricating complex shapes.[4]

sing cycle. Any mutual sliding of already compressed parts of the mass should be avoided in the final stage of the pressing cycle, as a defect caused in this way does not disappear during the firing process.

If thin-walled parts are to be fabricated, the uniaxial pressing process should not be used. Also, the process does not permit undercuts and holes perpendicular to the pressing axis. As notch sensitivity of the green body is high, sharp edges should be avoided.

Uniaxial pressing is hardly flexible; if there is only a slight deviation from the desired shape or from the desired shrinkage, new tools have to be used. As a rule, the tools are complex with regard to the design; they should be composed of wear-resistant materials such as cemented carbides.

Uniaxial presses permit high piece rates provided that the powder mixture is pourable, which makes filling of the press mould easier. However, the granules should be so weak that they can be destroyed during the pressing cycle, as otherwise a remnant of the original granule structure would remain even after firing. These rings of pores are weak areas of sintered bodies.

A high pressure, of at least 100 MPa, is necessary to guarantee high green density. An important problem which must be overcome in uniaxial pressing is non-uniform green density. Density variations within green compacts may result in distortions or cracking during firing. Density variations are caused by the friction between the powder and the die wall and between the powder particles. The often observed differences between longitudinal and transverse shrinkage during firing are based on non-uniform green density. In any case, compared with extrusion pressing, uniaxial pressing gives rise to a less distinct texture.

The binder systems used for the powder mixtures are based on either organic or aqueous solvents. If spray drying is chosen for granulation, water should be used as solvent; otherwise, explosion-proof spray driers must be used. Aqueous suspensions containing non-oxide powders should be handled very quickly, as the powders are extremely susceptible to oxidation because of their fineness. For organic solvents, kneading machines which can be heated can be used, as they permit volatilization of the solvent. The consolidated powder mixtures should then be ground by a jet mill and used as pourable powder. The binder systems should contain lubricating additives. On the one hand, they reduce wear of the tools, and, on the other hand, they permit a better mutual sliding of powder particles to increase consolidation.

4.3 Cold Isostatic Pressing

Cold isostatic pressing (CIP; not to be mistaken for hot isostatic pressing, or HIP; see Section 6.1), is one of the shape-forming methods for complex geometries. It involves application of pressure equally to the powder from all sides. Thus problems of non-uniformity seem to be overcome by using this technique. The isostatic pressure acting on the specimens is transferred via an essentially non-compressible fluid (water with a rust inhibitor, glycerine or hydraulic oil) in a pressure vessel. Isostatic presses may permit pressures of more than 600 MPa. The principle of cold isostatic pressing is illustrated in Fig. 4.

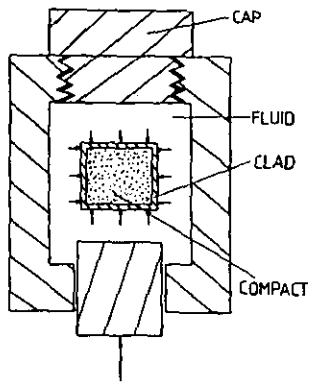

Fig. 4. Principle of cold isostatic pressing.

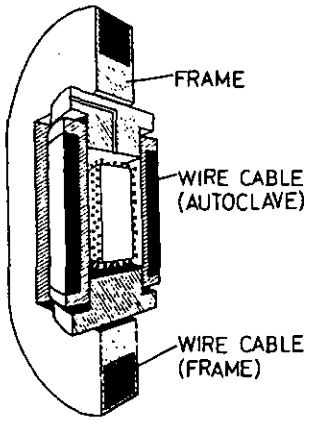

Fig. 5. Cold isostatic press; design ASEA.

Cold isostatic presses must guarantee safe working. Additionally, opening and closing of the vessel should be possible without difficulty. Figure 5 shows an appropriate design of a cold isostatic press. The cylindrical vessel is concentrically covered by strong steel wires to stress the vessel compressively even during the pressing cycle. In the same way the frame is covered to protect the bottom and the cap of the press. The pressure vessel is pulled out of the frame, for charging or discharging of the press.

The powder is enclosed in a flexible liquid-tight rubber cladding, as otherwise the pressure fluid would penetrate into the pressed article during the process. After filling, the cladding is closed by a seal plate, which may be modified to a complex mandrel according to the desired shape. The powder-containing cladding is immersed in the fluid within the vessel. The pressurized fluid transmits the pressure to the surface of the cladding. During powder compaction the cladding deforms, and it springs back after the pressure is released. Thus the pressed parts can easily be removed from the cladding.

For isostatic pressing the same granulated powder mixtures should be used as for uniaxial pressing, as it is important, in either shape-forming process, to achieve homogeneous filling of the mould. Isostatic pressing allows a uniformly distributed density, because no important frictional losses between powder and cladding wall occur. Additionally, a greater degree of compaction is achieved, as cold isostatic pressing generally permits higher pressures. Thus the primary advantage of

isostatic pressing compared with any other shape-forming method is an improved quality of the green compacts' microstructures. However, even isostatic pressing cannot prevent friction between the powder particles, which may result in an immense pressure drop inside the compact, even if lubricating additives are used. Therefore density gradients also occur in isostatic pressed compacts.

Mould-making for isostatic presses is much simpler than for uniaxial pressing, if a model exists that is enlarged according to the expected shrinkage. Additionally, many compacts can be fabricated simultaneously, depending on the size of the isostatic press, whereas generally only one compact can be produced within each cycle, by uniaxial pressing. Nevertheless, the production rate of cold isostatic pressing is usually low, as filling and discharging of the cladding takes a considerable time in each cycle. Thus, as a rule, cold isostatic pressing should only be used for samples or job lots.

Although isostatic pressing permits complex shapes to be produced, the main problems of this technique are limitations in close tolerances and in surface finish. Limitations arise from the flexibility of the cladding. If, however, pipes, tubes, nozzles or crucibles are pressed, close tolerances and good surface finishes are required mainly for the interior surfaces. This demand may be realized, if a mandrel of hardened steel is adapted in the cladding.

It should be noted that the spark-plug insulator industry has managed to overcome the main problems of hot isostatic pressing by the use of thick-walled rubber cladding. The rubber material is flexible enough to transmit pressure without irregular deformation. Also, high production rates are possible.

4.4 Slip Casting

Slip casting is one of the old shape-forming techniques used for traditional ceramics. It has been introduced to advanced ceramics as well, because it permits the formation of complex geometries.

Slip casting is conducted with ceramic particles suspended in fluids containing polar molecules (slip) and cast into multipart porous moulds. Generally, the fluid is water and the mould consists of plaster. Because capillary forces within the pores cause a partial vacuum, the mould extracts the fluid and forms a compact of close-packed particles along the mould walls which grows into the slip. Two different slip casting methods may be distinguished: drain-casting and solid casting.

In the more common drain-casting, the slip is left in the mould until the desired thickness of the compact is built up, then the remaining slip is drained from the mould. Figure 6 illustrates the drain-casting process. Solid casting involves keeping the slip in the mould during the whole process, to achieve a solid casting. After drying the casting is removed.

The main features of slip casting are both high solids content and low viscosity, which cannot, however, be regarded as independent of each other. Ideally, the solids content should be as high as possible and the viscosity of the slip as low as possible. For fluid slips the green density of the finished casting increases with increasing solids content. On the other hand, an increase in solids content results in an increase in viscosity, which impairs castability. Bubbles may remain in the casting if viscosity is high, because high viscosity might cause some regions of the slip not to flow back. This means that for viscous slips the green density of the castings decreases with increasing solids content. Figure 7 shows the typical effect of solids content on the green density of the casting. Additionally, formation of bubbles originates from entrapped air.

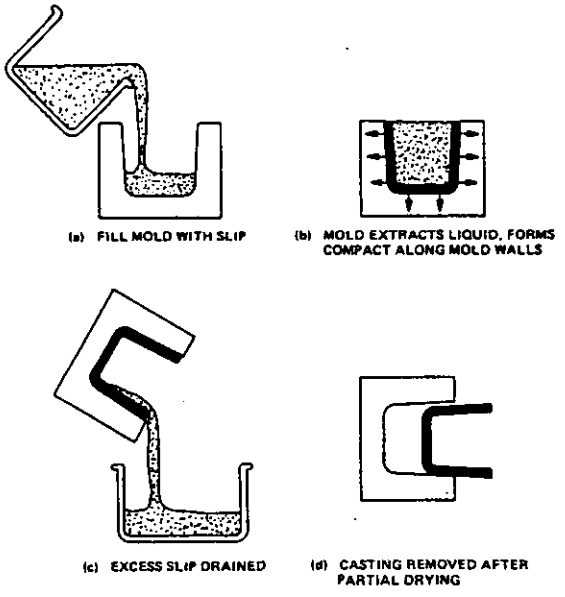

Fig. 6. Principle of the drain-casting process.[6]

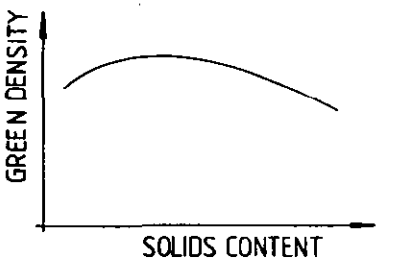

Fig. 7. Typical effect of solids content on the green density of the casting.

Therefore air should be removed by an evacuation treatment before the casting procedure.

The viscosity of the slip can also be influenced by special liquefiers. However, in general, the pH value affects the viscosity more distinctively. Usually, two minima of viscosity exist, one in the acidic and one in the basic range. It should be noted that pH value must not be controlled by using alkalis, if ceramics for high-temperature structural use are produced, as alkalis reduce high-temperature strength.

Basic slips often show thixotropic effects; thus they tend to become pasty whenever they are not moved. Therefore the slip should be vibrated by an excentric during both mould filling and fluid extraction. Thus thixotropy can be utilized to reduce the viscosity of the slip through vibrational movements. In this way, the green density of the casting can be increased. On the other hand, strong vibration may cause segregation so that fine particles tend to accumulate near the surface of the mould. Accumulation of small particles may also occur because the flow of the fluid caused by capillary forces carries finer particles preferentially.

As opposed to clay-containing powders some powders for advanced ceramics, for example, silicon carbide or silicon, do not shrink at all during the drying process. The casting sticks to the mould. Therefore removal of the casting is not possible if no separation medium is used. Well-tried separation media are alginates, e.g. ammonium alginate.[7,8] There are two ways of coating the surface of the mould, either directly, by brushing over the surface, or indirectly, by dissolving the alginates in the fluid (water) followed by segregation at the mould surface. Combinations of the processes are also possible.

The quality of the casting strongly depends on settling rate. This should be low, to give a homogeneous microstructure, a high green

density and as few casting defects as possible. On the other hand, efficiency is strongly affected by the settling rate. For slow rates the moulds should possess fine open pores.

The primary disadvantages of slip casting are a limited production rate because of long settling and drying times, an immense space requirement for the moulds and difficulties in achieving close tolerances and good surface finish. As the pores of the mould become increasingly choked, capillary forces decrease gradually. This increases moulding time but also changes the quality of the casting. Additionally, the surface of the mould is finally destroyed by the powder particles, which generally are abrasive. After about 10 castings the mould must be renewed. For all these reasons slip casting should only be used for samples or job lots.

4.5 Injection Moulding

Injection moulding is regarded as the most modern shape-forming method for advanced ceramics, although it had already been proposed for ceramic processing in 1949.[9] Using this method complex shapes can be fabricated.

Injection moulding involves forcing a deformable mixture of powder, additives and binders through an orifice via a narrow passageway into a tool cavity.[10] The pressure used is about 200 MPa. Figure 8 demonstrates the principle of this technique.

Injection moulding is a common technique in the plastics industry to make all types of complex-shaped articles. Injection moulding of a

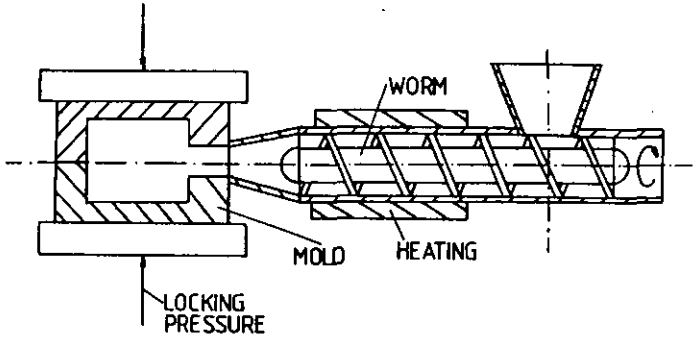

Fig. 8. Principle of the injection moulding process.

ceramic mass is basically comparable to injection moulding of plastics. Even the same equipment can be used, except that the dies must be made of harder, more wear-resistant metals.

Injection moulding can also be compared with extrusion moulding. By extrusion moulding the extruded column is synonymous with the shape, whereas the extruded column is forced into a die for injection moulding. For both techniques the pressure can be transmitted either by pistons or by worms.

Injection moulded parts may have holes, undercuts and differences in wall thickness. Also, tolerances of less than 0·1 mm are possible. This technique is therefore regarded as the most flexible shape-forming method. On the other hand, tool design is extremely complicated and thus expensive. Therefore it is only reasonable to use this fine technique, if a large-scale series production is going to be conducted.

The maximum content of binder is fixed by the intermediate grain volume of the powder. Provided that effective green density (i.e. density of the powder mixture except the binder) is 60%, the binder content may be 40 vol%, if the binder fills the whole intermediate grain volume. The binder should be free-flowing to enclose all powder particles without increasing the distance between them. Therefore the process is conducted at temperatures of 150–200°C using thermoplastic resins. The powder particles must not be agglomerated without intermediate binder. Flow resistivity should also be low, to give a steady flow during the process and to avoid wear. The binder used should permit good dimensional stability of the compact after moulding. During cooling, a static pressure should remain on the green body to react against thermal-induced stress caused by non-uniform shrinkage.

The high binder content should be baked out slowly. This may take more than a week. Reducing the baking time is possible through decreasing the wall thickness. The thickest part within the batch of compacts is the rate-limiting factor.

It can be concluded that the process of injection moulding, including powder processing, is immensely complicated. Thus much empirical knowledge is necessary if this technique is to be used successfully.

4.6 Tape Casting

Green compacts made by tape casting look like thin flexible foils with large areas. Tape casting involves casting a slurry onto a moving carrier surface, such as a steel or plastic band, which is lubricated with fish oil,

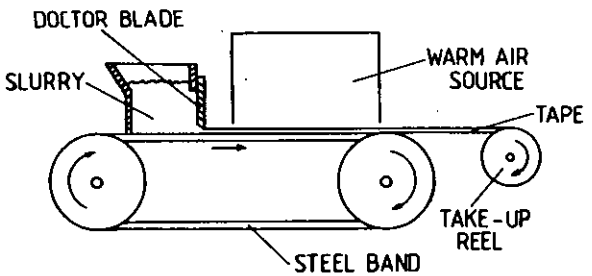

Fig. 9. Principle of the tape casting process.[11]

and spreading the slurry to a controlled thickness of 0·2–1·5 mm with the knife edge (i.e. doctor-blade) of a blade (doctor-blade process). The slurry, containing binders, plasticizers and organic or aqueous solvents, is then carefully dried, cut into strips and removed from the carrier surface. The tapes can either be rolled up on a take-up reel or directly segmented.[12] Figure 9 demonstrates the principle of this technique.

The main problem which needs to be overcome in tape casting is the drying process, where the solvent is volatilized. The speed of the band and temperature distribution must be strictly controlled. If the tape is dried either too little or too much, sticking of the tape to the band occurs.

At first sight, the tape forming method seems to be restricted to flat articles, but as the tapes can be punched, silk screen printed (for instance with a paste containing a metal powder) and laminated by pressing the tape segments onto each other, immensely complex shapes can be fabricated.

Tape casting is well established for production of electronic or structural ceramics. For instance, it can be used for fabrication of electrically insulated substrates for thick-film and thin-film circuitry, multilayer chip carriers with current paths within the ceramic and heat exchanger modules. Figure 10 shows the assembly of a complex seal ring for a rotatory pump.[13]

4.7 Green Machining

Even if the best of all shape-forming methods is used to approach the desired shape as closely as possible, machining of some of the surfaces is frequently required to meet dimensional tolerances, achieve improved surface finish, or remove surface flaws.

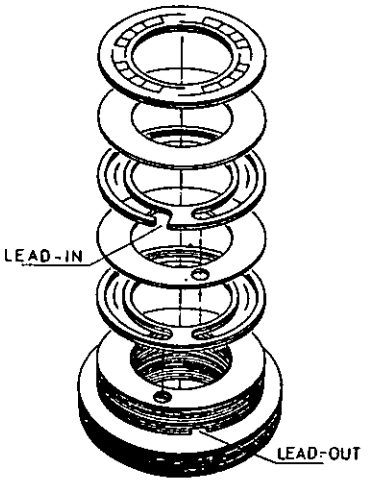

Fig. 10. A cooling channel containing seal ring shaped by tape casting followed by punching.[13]

The best surface finish and dimensional quality is achieved through final machining. An additional advantage of final machining is the fact that after densification the strength of the material is so high that there is only a slight problem of overstressing. On the other hand, after densification the material is so abrasion-resistant that material removal occurs very slowly and can only be done successfully by cutting tools which are harder than the ceramic being machined. Thus the disadvantage of final machining is its high cost. As a rule, the costs for machining often exceed 60% of the total costs.

Therefore to save expense it is desirable to machine ceramic parts before final densification, when the material consists of loosely bonded particles. Depending on the binding agents, prefinal machining is possible not only after presintering but also during the green stage; the latter is more cost-effective.

Green machining can be conducted by a variety of methods, for example, drilling, form wheel grinding and profile grinding. Basically, it is possible to machine green bodies using tools of high-speed steel or cemented carbide, but this cannot generally be recommended, as the tools usually dull so rapidly that immense care is necessary to avoid damage of green parts. Thus more wear-resistant materials such as Ti(C, N)-coated cemented carbide, polycrystalline cubic boron nitride (BN, Borazon) or PCD (polycrystalline diamond) should be used.

4.8 Concluding Remarks on Shape Forming Methods

It has been pointed out above that none of the proposed shape-forming methods accomplishes all of the desired demands equally; each method has advantages and disadvantages. In Table 3 it is attempted to compare qualitatively some characteristics of the shape-forming methods described above (except green machining). It must be remarked, however, that this list is a rather subjective statement and simplifies the characteristics of the shape-forming methods extremely. On the other hand, Table 3 helps to summarize Section 4.

5 PROCESSING BETWEEN SHAPE-FORMING AND FIRING

The processing stage after shape-forming and green machining generally is drying. This cannot be integrated into the firing process, because residual moisture must not evaporate too quickly, or the compact would be inflated and destroyed. It should be noted that the drying chamber used should be explosion-proof if the compact contains an organic solvent.

Too-rapid evaporation should also be avoided during the baking-out process mentioned in Section 4.5. Therefore baking-out should be conducted in separate ovens. This process is necessary if the binder content of the compacts is high, as in injection-moulded or tape-cast green bodies, and if the firing atmosphere is not air or oxygen. As a rule,

TABLE 3
Comparison of some Characteristics of the Shape-Forming Methods (Complexity of Shape, Surface Finish, Texture, Series Production and Costs for Tools)

	Complex	*Surface*	*Texture*	*Series*	*Costs*
Extrusion moulding	6	4	6	1	4
Uniaxial pressing	4	2	5	3	5
Cold isostatic pressing	3	5	1	5	2
Slip casting	2	6	4	6	1
Injection moulding	1	1	3	2	6
Tape casting	5[a]	3	2	4	3

[a]Without additional punching, screen printing and laminating; otherwise, the complexity rank is 3 instead of 5.

baking should be conducted in air, because organic resins have to be removed without leaving any residue. The choice of baking-out temperature is critical for the compacts if non-oxide ceramics are to be fabricated. If the temperature is too low, the processing would take uneconomically long, and if temperature is too high, the fine powder particles tend to oxidize. After baking-out, handling of the compacts is very difficult, as they are extremely weak because of the loss of binder.

Sometimes the compacts are machined after a presintering stage, especially for reasons of economy, as presintered bodies are weaker than bodies after densification.

Table 4 contains typical temperature data for the three stages.

TABLE 4
Typical Temperatures for the Processing Stages between Shape-Forming and Firing

	Temperature (°C)
Drying	110
Baking-out	280
Presintering	1100

6 FIRING

The purpose of firing is to strengthen the ceramic compact. This kind of strengthening is a physical process, which is called sintering. The free energy change that gives rise to sintering is the decrease in surface area by the reduction of solid–vapour interfaces. The lowering of the surface free energy generally takes place with the coincidental formation of new solid–solid interfaces, which have lower energy levels. Thus adjacent particles grow together during the sintering process to become strongly bonded. Surface area changes are only possible if a material transfer occurs, which is caused by various mechanisms such as diffusion, viscous flow or vapour-phase reactions. Each mechanism can work alone or in combination with others to achieve strengthening. Table 5 summarizes the sintering mechanisms.

Both material transports and surface area changes modify the pore shapes of the compacts during sintering. If the centre of gravity of each particle within the compact keeps its position, neither densification nor

TABLE 5
Sintering Mechanisms[6,14]

Type of sintering	*Material transport*	*Driving force*
Vapour phase	Evaporation–condensation	Differences in vapour pressure
Solid state	Diffusion	Differences in free energy or chemical potential
Liquid phase	Viscous flow, diffusion	Capillary pressure, surface tension
Reactive liquid phase	Viscous flow, solution–precipitation	Capillary pressure, surface tension

shrinkage of the compact occurs. This is usually the case, if evaporation–condensation or surface diffusion controls the sintering process. If, on the other hand, the centres of gravity approach each other, the volumes of the compacts decrease gradually during sintering and the pores shrink. Shrinkage during sintering is controlled by any other sintering mechanism. Whether shrinkage is desired or not depends on the requirements for the ceramic articles. This will be demonstrated below.

Strengthening effects at elevated temperatures which are not regarded as sintering phenomena, such as reaction bonding and infiltration, also occur. These phenomena are also discussed below.

6.1 Densification

Many important properties, such as strength, Young's modulus, thermal and electrical conductivity, and chemical resistance, not only depend on the ceramic materials used for particular applications but are also influenced by the quality of microstructures of the materials. An important microstructural factor is porosity. Each pore reduces the effective cross-sectional area of a material, which generally results in deterioration of the properties. Therefore a ceramic material of a high standard should have a high degree of density. It should be noted, however, that powders used for advanced ceramics usually are less active because of their strong ionic or covalent bond. Thus, in most cases, it is very difficult to achieve ultimate density.

6.1.1 Pressureless Sintering (S)

The densification characteristics of ceramic materials can be strongly influenced by the ultimate temperature used for sintering (sintering temperature). Generally, density increases with rising sintering temperature. Powders for advanced ceramics usually need higher sintering temperatures than do powders for traditional ceramics.

Sometimes there are limitations on temperatures for the firing process, not only because of energy costs or related to the refractory material used for the kiln, but also because of specific material characteristics.

Small grain sizes are obligatory for the achievement of high strengths. Therefore a structural ceramic should not be overfired, as this may cause exaggerated grain growth, which is difficult to detect during routine inspection because extensive procedures are required, such as preparation of polished surfaces, etching to accentuate microstructure and examination by microscopy.

Some compounds are not stable at elevated temperature, e.g. silicon nitride decomposes at temperatures higher than 1500°C:[15]

$$Si_3N_4(s) \rightleftharpoons 3\,Si(g) + 2N_2(g) \qquad (1)$$

As temperatures near 1500°C are far too low for silicon nitride to give dense products, some precautions have to be taken to permit sintering at higher temperatures and to reduce weight loss and porosity in the sintered product. Above all, there has to be a stationary stable nitrogen atmosphere so that either nitrogen or silicon vapour transport out of the system is prevented.[16] Second, it is advantageous to sinter in a boron nitride crucible containing the sintering compacts and on a powder bed consisting of a mixture of silicon nitride, boron nitride and sintering additives.[17] Finally, a high nitrogen pressure (20–100 atm) reduces decomposition.[18]

Generally, the sintering activity of a compound can be increased by using fine powders with grain sizes below 1 μm. These powders are extremely expensive.

Using high temperatures and fine powders alone is often not sufficient to give high densities. As a rule, special sintering additives are necessary to promote shrinkage because of liquid-phase (e.g. MgO for Si_3N_4 ceramics) or solid-state sintering (e.g. TiO_2 for fine-grained MgO ceramics). In addition, sintering additives are needed to inhibit secondary recrystallization (exaggerated grain growth) (e.g. MgO for Al_2O_3 ceramics) or to exclude a competing shrinkage-free sintering mechanism (C for SiC ceramics[19] or for Cr_2O_3 ceramics).

For pressureless sintering, various types of kilns can be used. If the articles being fabricated are oxide ceramics such as alumina (Al_2O_3), and are to be produced serially, a gas-heated kiln that is running continuously should be used. In principle, continuously running kilns have fixed temperatures for each position within the kiln but there are temperature gradients between the positions. The products are moved through the kiln and pass a heating zone first, then the firing zone, where temperature is highest, and finally the cooling zone. The products can be moved through the kiln by rolling the charged kiln furniture over refractory rollers (roller kiln) or by pushing charged track-type kiln cars through a tunnel (tunnel kiln). Continuously running kilns must always be charged in the same way; otherwise, the temperature distribution within the kiln will become out of control. Therefore these types of kilns should be used only for series production. Table 6 contains the sintering conditions of some selected pressureless sintered ceramic compounds. The applications of the corresponding ceramic materials are listed as well.

Slightly less economical but more flexible are those gas-heated

TABLE 6
Typical Sintering Conditions for some Pressureless Sintered Ceramic Compounds, and Applications of the Corresponding Ceramic Materials

Compound	*Additive*		*Temperature (°C)*	*Atmosphere type*	*Application*
	Type	*Quantity (mass %)*			
Al_2O_3	MgO	0·2	1750	Air	Electronic
	Glass	< 10			Mechanical
	TiO_2	0·3			Textile
					Chemical
					Medical
Cr_2O_3	C	1	1750	Reducing	Steel
MgO	TiO_2	0·3	1650	Air	Refractory
BeO	TiO_2	0·3	1600	Air	Electronic
Si_3N_4	MgO	2–5	1800	N_2	Mechanical
	$Y_2O_3 + Al_2O_3$	6 + 2			
AlN	Y_2O_3	1	1800	N_2	Electronic
SiC	B + C	1 + 1	2050	Vacuum, Ar	Mechanical
	Al + C	1 + 1			
B_4C	C	1	2050	Vacuum, Ar	Mechanical

periodic kilns, such as hood-type kilns or shuttle kilns, which should be used for smaller lots.

For precisely controlled reducing atmospheres it is sometimes better to use an electrical heating system, although electric energy is more expensive than gas energy.

For non-oxide ceramics, generally periodic chamber kilns are used which are heated either inductively or via graphite resistance heaters. The water-jacketed chambers are gas-proof to guarantee definite atmospheres of argon, nitrogen or vacuum. Continuously running kilns are not common for non-oxide ceramics, possibly because the piece numbers for such ceramics are still too small.

6.1.2 Hot Pressing (HP)

The advantage of pressureless sintering as compared with the two sintering processes discussed below is good efficiency. On the other hand, it is exceptional, in pressureless sintering, if parts can be completely densified. Furthermore, an increased amount of sintering additives can result in the formation of heterogeneous phases at grain boundaries, which may impair the properties of the ceramics. For instance, structural non-oxide ceramics with an increased amount of heterogeneous phases, especially glassy phases, usually have poorer high-temperature properties, such as lower strength, lower creep resistance and lower oxidation resistance.

To overcome these problems, new firing techniques have been designed where the energy imparted to the compacts is not only thermal but also mechanical. There are some different possibilities for the pressure acting on the compacts at high temperatures.

Using the conventional hot-pressing technique, the compacts are densified uniaxially via graphite or boron nitride dies with pressures of up to 50 MPa. Hot presses can be heated either inductively or ohmically. Figure 11 shows a scheme of an induction hot press (the insulation and the chamber walls are omitted for this figure). Generally, hot pressing is uniaxial pressing (see Section 4.2) at elevated temperatures.

As the commonest advanced ceramic, alumina (Al_2O_3), can be completely densified by pressureless sintering, hot pressing is mainly used for non-oxide ceramics and composites (which are not dealt with here). Table 7 summarizes typical sintering conditions for some hot pressed compounds.

If one compares the data given in Tables 6 and 7, it can be concluded that the sintering additives are normally the same or at least comparable

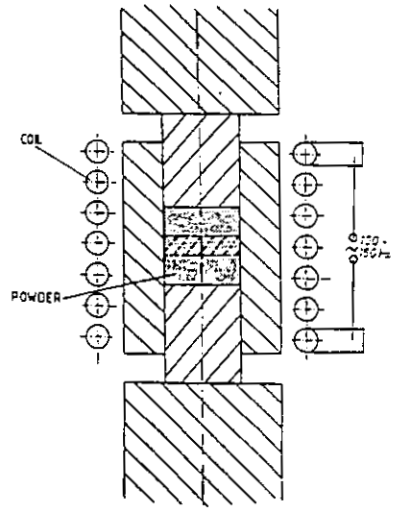

Fig. 11. Schematic diagram of a hot press.

TABLE 7
Typical Sintering Conditions for some Hot Pressed Compounds

Compound	*Additive*		*Temperature (°C)*	*Pressure (MPa)*	*Atmosphere*
	Type	*Quantity (mass %)*			
Si_3N_4	MgO	1–3	1750	30	N_2
	Y_2O_3	6–8			
SiC	B + C	0·3 + 1	2150	30	Vacuum, Ar
	Al	0·3			
B_4C	—	—	2100	30	Vacuum, Ar
BN (hexagonal)	—	—	2100	30	N_2

for both hot pressing and pressureless sintering, but the amount of sintering additives is generally lower for hot pressing. Hexagonal boron nitride can be densified only by applying pressure; obviously, a proper sintering additive has not yet been found for boron nitride. Figure 12 shows a scanning electron micrograph of a polished section of hot pressed silicon carbide (HPSiC).

Although hot pressing can give excellent properties, this technique is not used very often, because there are extreme disadvantages of

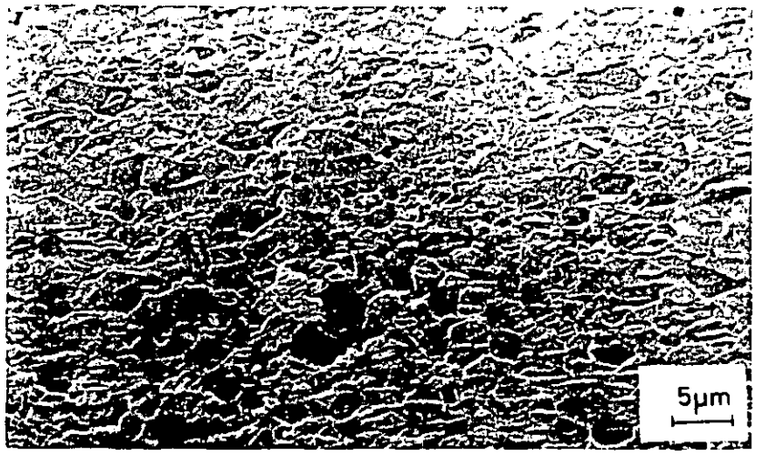

Fig. 12. Scanning electron micrograph of a polished section of hot pressed silicon carbide (0·3 mass % Al); etched with boiling Murakami solution; firing temperature 2150°C; pressure 50 MPa; density 99·7% of the theoretical value (99·7% TD).

economy. Generally, only a single part can be sintered within one cycle. From the energy point of view, it is detrimental that the die itself has to be heated up for each cycle. As a rule, the hot pressed compacts react with the die material; therefore, parts of the die have to be renewed after each cycle. Only simply shaped geometries are possible, thus more or less expensive final machining is necessary. Therefore hot pressing can be regarded as an expedient which is applied only if excellent properties are obligatory.

6.1.3 Hot Isostatic Pressing (HIP)

Even higher pressures (up to 300 MPa) are possible when using the technique of hot isostatic pressing. In this case, an external gas pressure is acting on the compact. Usually the gas is argon or nitrogen. The hot isostatic press consists essentially of an autoclave, which contains a molybdenum or graphite ohmic oven. Generally, hot isostatic pressing is isostatic pressing (see Section 4.3) at elevated temperatures.

As the pressure acting on the compacts is isostatic, articles can be fabricated without any texture. Compared with conventional hot pressing, the pressure used can be essentially higher, because it is not

TABLE 8
Typical Sintering Conditions for some Hot Isostatically Pressed Powder Compounds

Compound	*Additive*		*Temperature (°C)*	*Pressure (MPa)*
	Type	*Quantity (mass %)*		
Si_3N_4	Y_2O_3	3	1750	200
SiC	—	—	2000	200
B_4C	—	—	1900	200
BN (hexagonal)	—	—	1400	200

restricted to the strength of a die material. This means that sintering additives can be reduced even further. Table 8 summarizes typical sintering conditions for some hot isostatically pressed compounds. It is noteworthy that no additive is obligatory for sintering silicon carbide and that the sintering temperature for boron nitride can be immensely reduced.

Densification of a material would not be possible if the gas pressure were acting directly on the compact, as the gas would penetrate into the compact. To avoid blowing up, the compact must be placed in a gas-proof cladding, which is viscous or ductile at sintering temperatures and transmits the pressure from the gas to the compact. For temperatures higher than 1700°C the cladding consists of either silica glass or highly melted metals such as molybdenum or tungsten. If the temperatures are lower than 1500°C, it is even possible to use steel cladding, which would greatly reduce the costs. The principle of hot isostatic pressing of powder compacts is shown in Fig. 13.

Unfortunately, hot isostatic pressing of powder compacts generally cannot be regarded as economical, as the cladding technique is complicated and most cladding materials are expensive. Also, the initial costs for the equipment are extremely high.

There are, however, possibilities to use this modern technique very successfully, if two or even more firing stages are combined. A combination of pressureless sintering and hot isostatic pressing (HIPS) seems to be especially favourable. Using this technique, the compacts are first pressureless sintered up to closed porosity. This is usually achieved if compacts are densified to more than 95% of the theoretical density (Fig. 14). If there is still enough sintering activity (i.e. no distinct

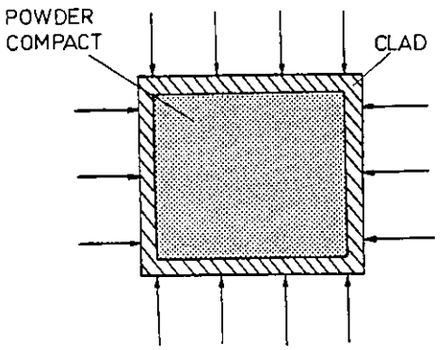

Fig. 13. Principle of hot isostatic pressing of a powder compact.

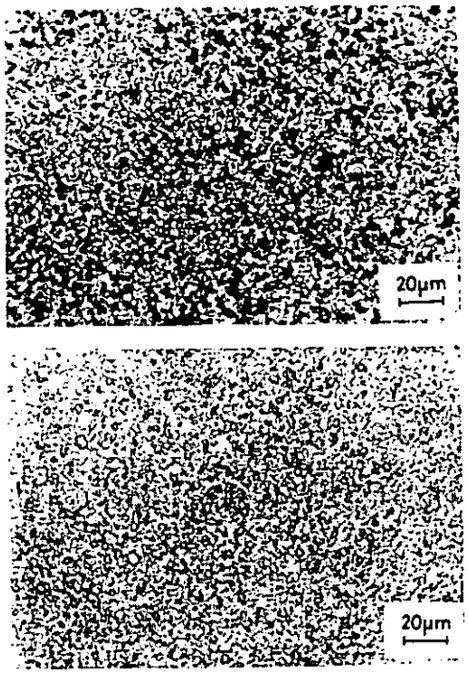

Fig. 14. Hot pressed silicon carbide (97% TD) (top) and post-densified by hot isostatic pressing (bottom); optical micrographs of polished sections etched with boiling Murakami solution.

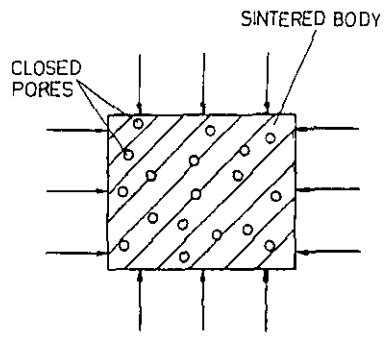

Fig. 15. Principle of cladless hot isostatic post-densification.

grain growth has occurred during pressureless sintering), the compact can be further densified — eventually up to theoretical density — without using a cladding. The principle of cladless hot isostatic post-densification is shown in Fig. 15.

This combination seems to be much more economical than the above-mentioned pressure sintering methods. It should be noted, however, that the quantity of sintering additives is comparable to those needed for the simple pressureless technique and is therefore higher than the quantity needed for both hot pressing and hot isostatic powder pressing.

Originally, pressureless sintering and hot isostatic pressing had to be performed separately in two different equipments. Nowadays, it is possible to conduct the two stages one after the other in a single piece of equipment. Cooling and reheating between the stages is no longer necessary.

Post-densification by hot isostatic pressing is used for all advanced materials being sintered, i.e. non-oxide ceramics, oxide ceramics, sintered metals, cemented carbides, composites, etc.

6.2 Strengthening without Undergoing Large Shrinkage

The purpose of the firing techniques discussed is to produce articles with guaranteed good properties; for instance, high strengths. This is only possible if the densification of the articles is high enough. However, there is a problem for highly densified articles that is typical for any ceramic material, whether traditional or advanced. If the densification of a ceramic is increased, the shrinkage is also increased. However, high

shrinkage also involves a wide range of tolerance for the sintered bodies. This is unfavourable, as advanced ceramics are to be used for technical applications where close tolerances are demanded. It is possible to achieve close tolerances through final machining, but as the costs for this are immensely high, machining of sintered parts should be restricted to the smallest possible extent. Problems of shrinkage are even more critical if the parts being fabricated are large.

Thus let us define a new main purpose of the firing technique: low shrinkage. Densification will now be regarded as secondary.

6.2.1 Pressureless Sintering Without Shrinkage ('Recrystallization'; R)

If the additives B or Al, or especially free carbon, are omitted for silicon carbide powder compacts (see Table 6) being pressureless sintered, shrinkage will be low although strong articles can be fabricated, which cannot simply be broken by hand. The reason is a change in sintering mechanism.

There are two sintering mechanisms, surface diffusion and evaporation–condensation, which are responsible for a strengthening effect without shrinkage. Thus if one of these mechanisms is acting alone, there is no shrinkage at all during the sintering process.

This can be achieved for silicon carbide by omitting the sintering additives and by a special 'bimodal' grain size distribution, which is characterized by both a coarse-grained powder with a narrow range of grain sizes and a fine-grained powder which ranges from micron to submicron grain size. Ideally, the coarse grains should be in contact with each other and the space between the coarse grains should be occupied by the fine grains. This is necessary, as the material will not gain a better density during the whole sintering process. Figure 16 (left) shows a schematic diagram of an idealized green body.

In silicon carbide an evaporation–condensation mechanism occurs during the firing process, although the concentration of gaseous SiC molecules is extremely low. The reason is the fact that a silica layer adheres to the surface of each SiC grain. Thus the following decomposition reaction is responsible for this sintering mechanism:[19]

$$SiC(s) + SiO_2(s) \rightleftharpoons 2Si(g) + CO(g) + \tfrac{1}{2}O_2(g) \qquad (2)$$

This complex reaction can be regarded as an evaporation–condensation mechanism, as the left-hand side of the reaction includes only solid compounds, whereas the right-hand side includes only gaseous ones. For kinetic reasons, the decomposition should occur favourably on

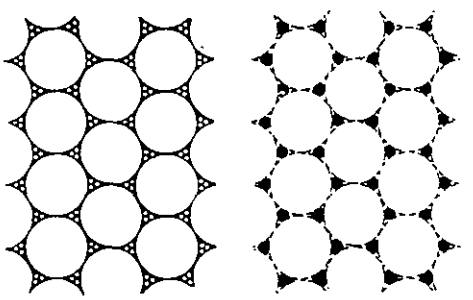

Fig. 16. Idealized green compact (left) and sintered body (right) of a 'recrystallized' advanced ceramic material. Light areas, grains; dark areas, pores.

convex surfaces, i.e. on the fine-grained fraction of the bimodal grain distribution, where the vapour pressure is relatively high. On concave surfaces, especially in the contact regions of the coarse grains, the above reaction runs in reverse, as here the vapour pressure is supposed to be relatively low.

During the firing process particles of the fine-grained fraction all diminish by decomposition ('evaporation'), and thus pores are left. The reverse reaction ('condensation') causes grain growth on the contact points of the coarse grains. As this process is not a recrystallization, the term 'recrystallized silicon carbide' does not describe the firing process of that material properly. Figure 16 (right) shows an idealized microstructure of a 'recrystallized' advanced ceramic. The microstructure of 'recrystallized' silicon carbide (RSiC) shown in Fig. 17 is characterized by interconnected porosity.

Table 9 contains some typical sintering conditions for four 'recrystallized' advanced ceramics. The only important product in Table 9 is RSiC. Naturally, the strength of RSiC, a product with a porosity of about 20%, is much lower than the strength of the dense SiC variants. The interconnected porosity can result in internal oxidation and accelerated surface oxidation at elevated temperatures. On the other hand, it is possible to achieve close tolerances also for large parts because of the shrinkage-free sintering mechanism.

Table 9 also contains Cr_2O_3 for phenomenological reasons. Cr_2O_3 can be 'evaporated' by an oxidation reaction:

$$Cr_2O_3(s) + \tfrac{3}{2}O_2(g) \rightleftharpoons 2CrO_3(g) \qquad (3)$$

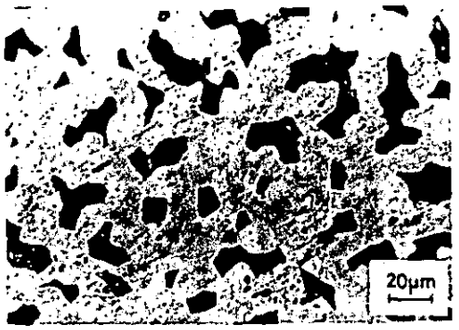

Fig. 17. Optical micrograph of a polished section of 'recrystallized' silicon carbide; firing temperature 2200°C; density: 80% TD.

TABLE 9
Typical Sintering Conditions for some 'Recrystallized' Advanced Ceramics and the Applications for the Corresponding Ceramic Materials

Compound	*Temperature (°C)*	*Atmosphere*	*Application*
SiC	2200	Ar; vacuum	Kiln furniture
B_4C	2200	Ar; vacuum	B_4C/C thermocouples
Si	1100	Vacuum; Ar	Intermediate product for reaction-bonded silicon nitride
Cr_2O_3	1500	Air	Refractory; not recommended, gives toxic CrO_3 vapour

but it should be noted that it can be very dangerous to sinter chromia, as CrO_3 vapour is toxic.

6.2.2 Reaction Bonding (RB)

The term 'reaction bonding' indicates that the strengthening effect during the firing process involves a chemical reaction. The best material strengthened in this way is reaction-bonded silicon nitride (RBSN). The reaction bonding is based on the synthesis reaction

$$3Si + 2N_2 \rightleftharpoons Si_3N_4 \qquad (4)$$

Thus as starting raw material for RBSN, silicon powder is used, as opposed to the other silicon nitride ceramics, which need Si_3N_4 powders. The shaped silicon compact is placed in a furnace under nitrogen or mixed nitrogen–hydrogen atmosphere. The actual strengthening process is very complicated and is not yet fully understood.

The furnace is heated initially to about 1250°C. The nitrogen permeates the porous silicon compacts and starts to react with the silicon to form Si_3N_4. Initially, Si_3N_4 whiskers grow from the surface of the original silicon particle into the pores. The newly formed silicon nitride is the low-temperature modification α-Si_3N_4. The temperature is gradually raised to about 1400°C, near the melting point of silicon. The reaction rate increases with increasing temperature. At elevated temperatures the formation of the high-temperature modification, β-Si_3N_4, is favoured.

Great care should be taken in the control of the nitrogen flow and temperature increase. As the reaction is exothermic, it may easily proceed too fast. This will cause the silicon to melt and to exude from the surface of the compact. A nitriding cycle may take more than a week, depending on the atmosphere, the volumes of the compacts, the quantity of material in the furnace, and the green density of the silicon compacts.

The porosity of the green bodies must not be too low, or nitrogen may not permeate into the interior of the silicon compact. Thorough nitridation is difficult if the thickness of a compact exceeds 3 cm.

During the reaction bonding process about 60% weight gain occurs. However, it is more important that the volume of the newly formed Si_3N_4 exceeds the volume of the original silicon by more than 22%. As the compacts do not shrink or grow at all, the porosity of the compacts decreases during the nitridation process. For this reason, higher relative densities (85% TD) can be achieved for reaction-bonded silicon nitride than for recrystallized silicon carbide. The better densification of RBSN is one but not the only reason for better strength. Figure 18 shows the microstructure of injection moulded RBSN. To guarantee good quality, both high densification and a narrow band width of pore size distribution are demanded.

It is even possible to achieve higher densifications through a combination of reaction bonding and pressureless sintering (SRBSN). The powder mixtures contain silicon, the same as for RBSN, and the same additives as are usually taken for SSN (pressureless sintered silicon nitride), such as magnesia or combinations of yttria and alumina (see

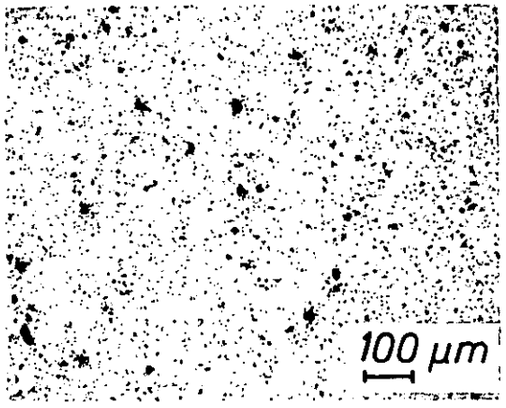

Fig. 18. Optical micrograph of a polished section of reaction bonded silicon nitride.

Table 6). Initially, the compacts are reaction bonded as usual at relatively low temperatures (up to 1400°C). After nitridation is completed the temperature is raised to the level required for pressureless sintering (1800°C). The density and properties of the corresponding SRBSN can be compared with SSN, but shrinkage for SRBSN amounts to only 6%, whereas that for SSN exceeds 16%. Thus SRBSN seems to be a good alternative for SSN provided that the wall thickness is low.

There is also a reaction bonded silicon carbide (RBSiC); however, this has a higher porosity than RBSN. RBSiC (not to be mistaken for SiSiC; see below) is much less important than RBSN and is therefore only mentioned but not discussed here.

6.2.3 Infiltration

It is impossible for mainly single-phase ceramics to combine both of the discussed purposes of firing — the achievement of high densification and the retaining of low shrinkage. However, two-phase ceramics can be densified completely without shrinkage by an infiltration technique. The best-known of these infiltrated ceramic materials is silicon infiltrated silicon carbide (SiSiC). This can be mistaken for RBSiC, because in earlier publications SiSiC was also called reaction bonded or reaction sintered silicon carbide.

The raw material mixture used for SiSiC consists of commercial SiC powders (α) and carbon-containing compounds (graphite and/or

carbon black and/or hydrocarbons). The shaped compact is exposed to liquid or vaporous silicon at temperatures above the melting point of silicon (1410°C). The silicon infiltrates into the pores of the compact and partially reacts with the carbon to form *in situ* SiC (β):

$$Si + C \rightleftharpoons SiC\,(\text{cubic}, \beta) \tag{5}$$

The remaining pores are filled with the excess silicon. The resulting optimized material is a non-porous composite. Figure 19 shows the microstructure of SiSiC. The dark areas represent silicon carbide and the white areas represent the excess silicon.

It should be mentioned with regard to application that silicon tends to exude from the surface at temperatures above 1200°C, which limits the application temperature for this material.

6.3 Concluding Remarks on Firing

It has been shown that there are many different techniques to densify or at least to strengthen the shaped compacts to achieve advanced ceramic bodies. As these techniques are so important for the characteristics of the ceramic materials, advanced ceramics can be classified not only by the base material but also by the strengthening technique, although this

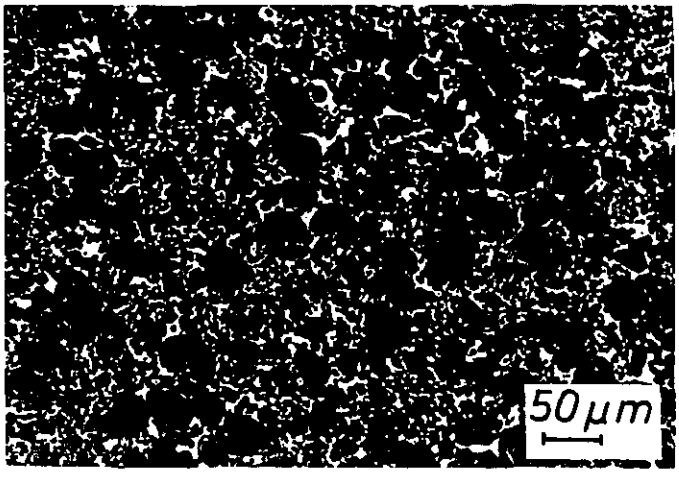

Fig. 19. Optical micrograph of a polished section of silicon infiltrated silicon carbide.

TABLE 10
Porosities and Room Temperature Flexural Strength for some Silicon Carbide and Silicon Nitride Materials

Material	*Porosity (%)*	*Room temperature bending strength (MPa)*	*Comment*
SSiC	3	450	+
HPSiC	0	650	+
HIPSiC	0	700	
HIPSSiC	0	500	+
RSiC	20	130	+
SiSiC	0	500	
SSN	3	800	
HPSN	0	900	
HIPSN	0	1000	
HIPSSN	0	900	
RBSN	15	350	+
SRBSN	3	800	

+, Material does not show any decrease in strength up to 1400°C.

subclassification by base material has been performed only for some non-oxide ceramics. Table 10 contains this subclassification for silicon carbide and silicon nitride; also, the porosities and the available flexural strengths of these materials are summarized.

7 FINAL MACHINING

It has already been pointed out that advanced ceramics are difficult and expensive to machine because of their extreme hardness and brittleness. Although final machining should be minimized, it cannot often be omitted, as machining of some surfaces is generally required, to achieve improved surface finish, to meet dimensional tolerances and to remove surface flaws.

Most ceramics cannot be successfully machined with the sort of cutting tools used for metals, as these tools are not hard enough. The tools must have a higher hardness than the ceramic being machined and must be able to remove surface stock without overstressing the ceramic body.

With regard to the costs, the importance of final machining is very high; however, it is not considered in detail here, because there are too

TABLE 11
Final Machining Processes[6]

Type	*Action*	*Principle*
Mounted abrasive machining	Mechanical	Immersion of hard particles in a softer matrix; tool moves in relation to the ceramic workpiece
Free abrasive machining: (1) lapping (2) trepanning	Mechanical	Loose hard particles; tool moves in relation to the ceramic workpiece; particles and coolant between workpiece and tool (hollow cylinder)
Impact machining (1) sandblasting (2) ultrasonic machining	Mechanical	Removal of stock by high-velocity impact against the workpiece by moved air; tool vibration gives acceleration to particles striking workpiece
Chemical machining	Chemical	Immersion of surface to be machined in a liquid in which ceramic is soluble
Electrical discharge machining (only possible with conductive *materials*)	Electrical	Dielectric liquid between shaped tool and workpiece; sparks produced by electrical discharge result in combination of vaporization, cavitation and thermal shock
Laser machining	Thermal	(1) Scoring of substrates for fracture to desired size (2) Removal by evaporation

many individual problems to be solved. Ceramic material can be removed by mechanical, thermal, electrical or thermal action. The principles of the most important final machining methods are summarized in Table 11.

8 CONCLUSIONS

The processing of advanced bulk ceramics is determined by two apparently controversial principles — quality and costs. This has been

discussed here for both the shape-forming and the firing processes. The multiplicity of ceramic techniques demonstrates this duality in advanced ceramic processing. The key for future developments will be to produce advanced ceramic materials of high quality for a good price. This will reduce the number of different processing techniques. This can be explained in the following way: if dense pressureless sintered silicon carbide could be produced with excellent quality, with close tolerances for large parts and for a good price, production of recrystallized, hot pressed and hot isostatically pressed silicon carbide materials would no longer be necessary.

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