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ScienceDirect

Journal of the European Ceramic Society 28 (2008) 1369–1379

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Tailor-made ceramic-based components—Advantages by reactive processing and advanced shaping techniques

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Abstract

Affordable manufacturing of components with complex shapes is still the most essential shortcoming with respect to successful commercial use of advanced ceramics. This holds particularly for components with high demands of geometric precision and mechanical reliability at the same time. Two routes are considered here which offer a high potential for fast and cost-effective manufacturing of reliable components: (I) reactive-based processing exhibiting often low shrinkage and/or advanced shapability (and sometimes savings in raw material and processing costs) and (II) recently developed advanced shaping techniques suitable for CAD/CAM without labor intense tooling optimization. Recent developments in both areas are briefly highlighted.

Keywords: Reactive synthesis; Reaction bonding; Rapid prototyping; Green machining; Slip casting

1. Introduction

Modern structural ceramics and ceramic composites possess a number of unique properties that cannot be achieved by other materials. For example, ceramics combine high hardness, strength, and wear resistance with low density and the ability to withstand high temperatures and corrosive environments. Therefore, they have a potential for saving energy, reducing wear, and increasing the lifetime of components. However, regardless of their excellent properties, structural ceramics are not as widely used in industry as they should and could be. Among the reasons for the reluctance of industry to introduce structural ceramic components are

- high price of ceramic parts,
- insufficient knowledge in "traditional" metal-oriented engineering,
- low toughness,
- redesign components to meet specific ceramic requirements. As ceramic components should be designed in such a manner as to reduce stress concentrations and to avoid tensile stresses, a simple one-to-one substitution of an existing metal part is usually not possible. Other factors that can necessitate design changes are usually the high-elastic modulus and low thermal expansion of ceramics.

There is a number of examples where ceramic components have been designed and tested successfully, but, despite their superior properties, have not been put into production due to their high price. Particularly hard machining, which is usually inevitable for close tolerances in case of conventional manufacturing, plays a key hole here. As it is very time-consuming due to low material removal rates, hard machining increases the manufacturing costs for components drastically. Although the actual cost distribution varies, machining costs contribute a substantial fraction and can in some cases account for 80% of the overall manufacturing costs of a ceramic component.[1] In comparison to hard machining, other cost factors, such as shaping and sintering, are generally of minor importance.

Apart from the high costs associated with hard machining, conventional ceramic production processes have the disadvantage that they are usually suited for mass production, but not for fast and economical manufacturing of prototypes or small-scale series. Since a number of prototypes of the actual component will be required for evaluation in order to introduce a ceramic material into a certain application, the ability to deliver such prototypes in a reasonable time and at an acceptable price can be a decisive factor in a competitive market.

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doi:10.1016/j.jeurceramsoc.2007.12.022

The above remarks should show that it is of vital importance to reduce production costs and to make ceramic manufacturing more flexible. Ideally, a ceramic fabrication process suitable for prototypes or small numbers should make it possible to design a component at the computer, and to directly put the computer-aided design file to the processing line (CAD/CAM).

Challenging approaches are provided by synthesis routes which exhibit low to zero shrinkage, e.g., almost no dimensional change from the precursor to the final product. In this case, reactive processing routes like reaction bonding of silicon nitride or silicon carbide are well known examples, the latter one remerged recently as standard technology for the fabrication of commercial fiber-reinforced ceramic-matrix composite parts (e.g. Cf/C-SiC brake disc rotors). In the past decade, several other techniques have been developed offering low to zero shrinkage capability or – even more important in view of advanced manufacturing – readiness for precise manufacturing of complex shapes.

Shaping techniques like the recently developed rapid prototyping routes as well as advanced slip casting using solid dies, powder injection molding or even the well-known machining in the green state ("green machining") also fulfill the requirements to varying degrees and are therefore highlighted in the second part of the paper.

The present paper gives a brief overview on various approaches in both areas. Although reaction-based processes and shaping techniques are discussed separately, sometimes combinations will give particular advantage. However, all the techniques mentioned in the following offer various advantages and disadvantages in view of raw material costs, versatility, process stability, reproducibility of product performance in case of commercial production lines, etc., which cannot be discussed here in detail.

2. Reaction-based processes

In the following section, some reaction-based processes will be briefly discussed. For more detailed information, there are good general overviews available in the literature.[2–4] Although reaction processes are methods for synthesizing materials rather than shaping techniques for components, they are, in some cases, especially adaptable to certain shaping techniques, e.g., green machining or rapid prototyping, or they can be modified to combine synthesis with growing components directly into a desired shape (e.g. DIMOX), or make plastic forming techniques applicable (e.g. AFCOP). The classic reaction bonding processes (RBSC and RBSN) will be discussed in a very concise manner, as there is a great amount of literature covering these subjects.

2.1. Reaction bonded silicon carbide (RBSC)

In this process (also called reaction sintered silicon carbide) that dates back to the 1950s,[5–7] a preform consisting of SiC and C is infiltrated easily in vacuum at 1500–1600 °C by molten Si due to a good wettability,[8] followed by the reaction of C to form SiC:

Fig. 1. RBSiC blower wheel made by milling of two semi-finished C–SiC green parts followed by green state joining and subsequent silicon infiltration (courtesy: Schunk Ceramics, Germany).

$$\mathrm{SiC} + \mathrm{C} + \mathrm{Si} \rightarrow \mathrm{SiC} \qquad (1)$$

The process can be adjusted to yield either pure, but porous SiC, or dense Si/SiC composites as the final product. Normally, the latter one termed silicon-infiltrated silicon carbide (SiSiC) is chosen because of the higher strength. RBSC and SiSiC exhibit small dimensional changes and are suitable for all powder metallurgical (PM) shaping methods. The surface quality after the infiltration/reaction usually necessitates final machining. Fig. 1 shows a blower wheel made by "classical" reaction bonding. In the past decade, the silicon infiltration technique remerged for advanced fiber reinforced structures suitable for space applications and advanced friction systems.[9]

2.2. Reaction bonded silicon nitride (RBSN)

This process was developed in the 1970s.[10,11] Silicon powder compacts are reacted with nitrogen to form silicon nitride bodies at little dimensional change (<0.1%). Reaction bonding takes place at temperatures in the range of 1200–1450 °C:

$$3\mathrm{Si} + 2\mathrm{N}_2 \rightarrow \mathrm{Si}_3\mathrm{N}_4 \qquad (1200\text{–}1450\,^{\circ}\mathrm{C}) \qquad (2)$$

RBSN has normally a considerable residual porosity ($\gg$15%)[12] and, therefore, a relatively low strength. However, a large fraction of residual pores are small (<0.1 μm). The flexural strength of RBSN at a density of 2.55 g/cm^3 (i.e. ~80% T.D.) may reach ~360 MPa.[13]

2.3. Reaction bonded aluminum oxide (RBAO)

The RBAO process[14–23] starts from precursor mixtures consisting of Al and Al_2O_3. In practically all cases, ZrO_2 is added to enhance oxidation and to improve microstructure and mechanical properties of the final product. The precursor mixtures are intensively milled in order to reduce the particle size, mainly that of Al, and to achieve a high degree of homogenization. Green bodies for RBAO contain about 30–45 vol.% of aluminum which bonds the alumina particles so that binder additions are not required. RBAO powder compacts reach substantially high-green strength, i.e., isostatic compaction at pressures as low as 170 MPa is sufficient to obtain green bodies with high strength (∼20 MPa in 4-Pt bending) that can be extensively green machined to complex shapes and down to very low wall thickness values below 50 μm.[23]

After machining, the green compacts are subjected to a two-step heat treatment in air in order to first oxidize Al and then sinter the material. The oxidation of Al is associated with a 28% volume expansion. Together with the high-green densities (typically >60% T.D., up to 75% possible), this leads to a reduced sintering shrinkage of about 10–15%. The newly formed, very fine Al_2O_3 sinters and bonds the originally added Al_2O_3. The sintered material has typical grain sizes of 1–1.5 μm and 0.5 μm for Al_2O_3 and ZrO_2, respectively. RBAO composites tested without any machining, i.e., as fired, using a "Punch-on-Three-Equiaxed-Balls" test configuration exhibit typical strength values of 700 MPa after pressureless sintering and >1 GPa after HIPing.[23]

The process can be modified in various ways, e.g., to form reaction bonded mullite (RBM): in this case, SiC instead of Al_2O_3 is added to the precursor powder.[24–26] The large volume increase (108%) associated with SiC oxidation together with the 28% volume increase from Al oxidation make extremely low (<0.2% linear) sintering shrinkage possible, provided the green density is high (>72% T.D.). RBM may attain strength values of ∼250 MPa.

2.4. *Sintered alumina aluminide alloys (s-3A)*

As far as powder preparation is concerned, this process is similar to the RBAO process, however, it includes a redox reaction between aluminum and the oxide of another metal.[23,27–35] The basic reaction can be written as

$$\mathrm{Al} + \mathrm{Me}_a\mathrm{O}_b \rightarrow \mathrm{Me}_x\mathrm{Al}_y + \mathrm{Al}_2\mathrm{O}_3 \qquad (3)$$

Sintering has to take place under vacuum or in an inert atmosphere to prevent a reaction between Al and atmospheric oxygen. Examples of oxides that have been used are Cr_2O_3, Fe_2O_3, Nb_2O_5, TiO_2, and ZrO_2. The process can be varied by using a metal such as Cr, Fe, or Mo instead of the metal oxide, and adding only a small amount (≈1 wt.%) of Al to assist sintering. This version of the 3A process has the advantage that the highly exothermic redox reaction takes place only on a very small scale, i.e., between Al and the oxide layer on particles of the other metal, so that higher heating rates can be used. Advantages of the s-3A process are high-green strength allowing green machining, pressureless sintering, and compositional variability.

2.5. *Self-propagating high-temperature synthesis (SHS)*

Modern SHS research began in the late 1960s in the former Soviet Union. The term SHS is used to describe a huge variety of syntheses methods where exothermic reactions are used to form and densify materials.[36–40] It is also often called combustion synthesis. The reactions usually release sufficient energy to yield solid products. Reactants include metals (Ti, Ni, Al, Mg), oxides (TiO_2, MoO_3, Cr_2O_3, Fe_2O_3), and others (N_2, H_2). Products are borides, carbides, carbonitrides, nitrides, silicides, intermetallics, and others. While in other processes-based on exothermic reactions (RBAO, 3A), great care is taken to use slow heating rates and thereby avoid thermal runaway, SHS allows these reactions to proceed in a very short time with velocities in the order of cm/s which normally result in cracking of components. The process is therefore rather suitable for making very small parts, e.g., powders.[38] However, by careful processing also dense parts are possible exhibiting fine microstrcutures.[40]

2.6. *Directed metal oxidation (DIMOX)*

The DIMOX process developed in 1986[41] is based on the reaction of molten Al with oxygen (usually air at ca. 900 °C) to form α-Al_2O_3. If some Mg is alloyed to the Al, the reaction product grows outward from the original Al pool surface either into free space or into a filler compact.[42–46]

The molten aluminum alloy wets the ceramic material and oxidizes so that the growth front moves through the preform away from the melt surface. The reaction is sustained by wicking of liquid Al through tortuous microscopic channels into the reaction product. The filler compact may be prepared by any PM process and may consist of particles (e.g. SiC) or fibers. The filler preform must be coated by a barrier material to prevent alumina–Al growth beyond the surface of the component shape desired.[45] DIMOX is suitable for very large plates (>1 m × 2 m × 3 cm), however, due to its rather slow growth velocity, the process finds presently no application.

2.7. *Volume identical metal oxidation (VIMOX)*

In the VIMOX process, relatively dense (up to 96%) preforms consisting of mixtures of alkaline-earth metals (Mg, Ca, Sr, Ba), non-alkaline earth metals, and oxides are oxidized.[47–52] The resulting materials can be spinel ($MgAl_2O_4$), strontium-doped celsian ((Ba,Sr)Si_2O_8, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), or others.[47,48] The process uses the shrinkage occurring during oxidation of most alkaline-earth metals to compensate for the expansion associated with other reactions, such as aluminum oxidation, spinel or celsian formation, hence dimensional changes are very small.[49,50]. Due to the content of a soft, malleable metal, the precursor compacts can be green-machined using conventional equipment. The process utilizes either intimately mixed alkaline-earth-bearing precursor powders or metal infiltration into a ceramic powder compact.[51] If powders are used, the reactivity of fine alkaline-earth metal powders makes it necessary to handle them in a protective atmosphere. Although the process does not yield typical structural ceramics, it provides an excellent way to synthesize special materials for implant (hydroxyapatite) or radome (celsian) applications.

2.8. *Active-filler controlled pyrolysis (AFCOP)*

Conventional polymer derived ceramics undergo a large shrinkage during polymerization. In order to reduce or even prevent shrinkage, "active" fillers are used that react with decomposition products of the polymer or with the reaction atmosphere, causing a volume increase.[53–57] Starting materials are Si-containing polymers [R1· · ·2, Si(C, N, B, O)0.5· · ·1.5], where R is an organic functional group such as alkyl, etc. Materials such as cross-linked polysilanes, polycarbosilanes, polysiloxanes are suitable. Examples of active fillers are elements (B, Si, Al, Ti, or Mo) or compounds ($CrSi_2$, AlN, B_4C). The final material can vary in composition. Depending on the starting materials, composites such as SiOC/TiC, SiOC/TiN, SiOCN/BN and others can be made. Pyrolysis takes place in inert (Ar) or reactive (N_2, NH_3, CH_4) atmosphere at a temperature of ≈1400 °C.[55] The process has the advantage that plastic shaping technology as for polymers, such as injection molding or extrusion can be used. It also offers compositional variability. Sintered materials exhibit strength values up to 500 MPa.

2.9. Reactive metal penetration (RMP)

The process is based on the reaction and displacement of a dense silica-containing part by molten Al.[58–64] Thus, silica,[58] glasses or mullite[59] can be used as reactant phase. The process requires wetting of the oxide by molten Al. When mullite or mullite glasses are used, the reaction can be described by the following equation:

$$3Al_6Si_2O_{13} + (8 + x)Al \rightarrow 13Al_2O_3 + 6Si + (x)Al$$

As most of the Si diffuses out into the surrounding Al melt, the final material is a composite of Al_2O_3 and Al alloyed with some Si. Depending on whether mullite or mullite-glass is used as the starting material, volume changes of +0.3% and −1.4%, respectively, are observed. Hence, glassy preforms are converted at nearly no dimensional changes into composite parts. The four-point bending strength of the resulting composites are 250–370 MPa,[58,59] and the toughness 6.6 MPa$\sqrt{m}$.[61] Kinetics of bulk penetration show a $t^{1/2}$ dependence. After 2 h, a penetration depth of 6 mm has been reported.[59] Other metal oxides, such as TiO_2 or NiO have also been reduced by molten Al in this process.[62] A problem arises in this process from the steadily increasing amount of Si in the liquid Al pool.

2.10. Chemical vapor infiltration (CVI) and chemical vapor deposition (CVD)

While CVD is a technology for depositing surface layers on a substrate, CVI works by infiltrating gaseous reactants into a porous preform. Both processes are conducted at elevated temperatures. Originally developed for densifying porous graphite bodies, CVI has the advantage that it can be used for a variety of materials including silicides, borides, carbides, nitrides, and oxides.[63] Much work has been done on SiC composites. Disadvantages of CVI include toxic and corrosive reactants and long reaction times.[65–67] CVI is mainly used for the making of fiber-reinforced materials.

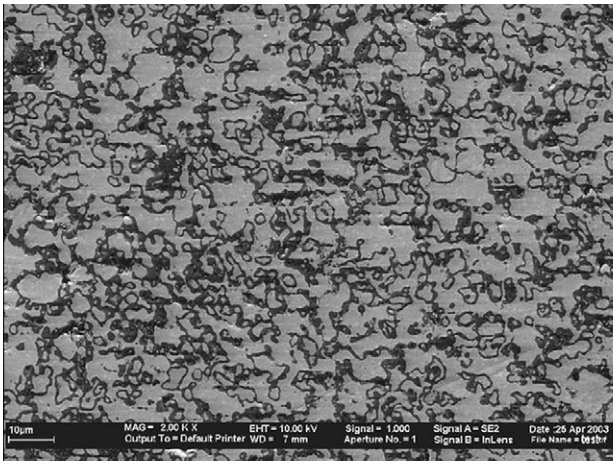

Fig. 2. Microstructure of reactive cast FeCrAl alloy (white) reinforced with in situ formed alumina (dark). Due to the ceramic reinforcement an advanced creep and corrosion resistance can be achieved compared to conventional cast monolithic alloys.

2.11. Reactive casting of ceramic composites

The reactive casting concept[68–74] also utilizes the exothermic reactions between Al and oxide components as does the s-3A technology except that liquid Al is infiltrated into a porous oxide preform. For example, molten Al or an Al-rich alloy is pressure infiltrated into, and reacted with, a porous TiO_2 preform to yield dense $Al_2O_3/TiAl_3$ composites.[68–70] By tailoring the reactivity of the preform, i.e., by controlling the temperature and preform particle size, the extent of reaction during infiltration can be designed as required. Typically, the dimensional change from perform to the final body is <0.5%. By varying the precursor composition, also Al_2O_3 composites comprised of multicomponent metal alloys can be made, i.e., heat resistant Ni-Fe-Cr.[73,74] A typical microstructure of these composites is represented in Fig. 2.

In a process modification, Al is incorporated as solid phase in the starting preform (as opposed to infiltrating the Al from outside). Subsequent heating above the Al melting point under a modestly applied pressure results in spreading ("in situ infiltration" or short-distance infiltration) and reaction of liquid Al with oxide reactants.[71,72] This process also yields interpenetrating phase composites with high-solidus temperatures.

3. Shaping techniques

In this section, we focus on advanced shaping techniques suitable for high-precision manufacturing of complex components with particular emphasis on routes which can be even combined with reactive processing. Other widely used ceramic shaping technologies that are more adapted for delivering preforms of simple geometry such as dry pressing, tape casting, or extrusion, will not be discussed here. Nonetheless, optimization of these classic shape-forming processes can drastically reduce the amount of machining required and is therefore of great importance.[75,76] The two most versatile shape-forming technologies for complex components are rapid prototyping and green machining. However, casting and molding techniques which allows the use of dense dies offer also a potential for fast fabrication of complex shaped parts. This holds particularly when precise dies can be made easily by rapid prototyping or conventional machining. Therefore, also powder injection molding and recently developed advanced casting techniques are addressed briefly.

3.1. Rapid prototyping

The term "rapid prototyping" (RP) is used for several technologies for making accurate 3D models directly from CAD files without having to manufacture tools or dies. Originally designed for making models, RP technology can be applied to make ready products, in which case it is also referred to as rapid manufacturing. Often also the term "solid freeform fabrication" (SFF) is used which highlights that tools are unnecessary. All RP technologies have in common that 3D objects are obtained by successively building layers upon one another and, therefore, suitable for automated manufacturing without having to make molds or dies, so that even the term "desktop manufacturing" has been used. One problem of RP for manufacturing ceramic components is an insufficient surface quality that necessitates sometimes further machining. The main disadvantage of all RP processes is the relatively long manufacturing time it takes to build a component, typically in the order of hours/piece. In spite of this drawback for manufacturing larger numbers of components, RP technology is of great benefit for delivering prototypes in a short time and at an economical price.

3.1.1. Stereolithography

In this process, a laser is used to polymerize layers in a suspension of ceramic powders in a photoreactive resin.[77–79] Stereolithography is the first RP process reported and has been available for polymers since 1988. This technology has reached a high degree of maturity. Potential problems include delamination and mechanical properties that stay below those of conventionally sintered parts.[78]

3.1.2. Direct photo shaping (DPS) and laser curing of polymers

This process is based on layer-by-layer photocuring polymerizable compositions curable by visible light. Light projection via a digital micromirror device is then used for selectively photoimaging each layer. DPS has been successfully used to fabricate high-strength silicon nitride.[80] A somehow similar approach is used when preceramic polymers are used and cross linked by a laser resulting in complex 3D structures.[81]

3.1.3. Indirect and direct ink-jet printing

In indirect printing, a glue droplet is deposited locally in order to bind ceramic powder layers spread homogeneously on substrates.[82–84] 3D structure are formed then layer by layer with a modified ink jet system thereby using the advantage of an existing highly developed technology. This advantage holds also for direct ink jet printing.[85–88] However, here difficulties with formulating a ceramic ink in such a manner as to achieve an acceptable compromise of solid loading, viscosity, drying properties, and stability, is still an obstacle to manufacturing defect free parts and require respective techniques for deposition.[89] Alternatively to printing a ceramic-containing suspension, also dry printing of powders using ultrasonic vibration of capillaries is recently developed offering easy raster printing of multi-material patterns (Fig. 3).

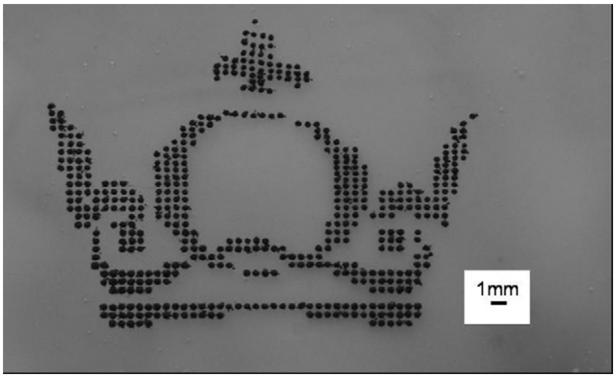

Fig. 3. Dry printing of WC pattern with 42DPI (0.6 mm pitch) on paper by ultrasonic vibrating a microfeeding system. By controlling nozzle diameter, voltage amplitude and oscillation duration multiphase-material deposition and/or 3D graded materials can be assembled directly from a computer file (courtesy: Julian Evans, University College London, England).

3.1.4. Selective gelation

This RP technique works by localized gelation of a slurry layer by impact of droplets of a salt solution. Selective gelation has been used to make alumina gear wheels. Strength testing of alumina formed by this process has shown strengths similar to conventionally processed alumina.[90] Like direct ink jet printing, it has the advantage that it makes use of existing ink jet technology. Selective gelating is possible also by laser exposure causing evaporation of water.[91]

3.1.5. Fused deposition of ceramics (FDC)

In the original version of this process, a polymer filament is extruded through a nozzle. For ceramic materials, this process works by extrusion of a ceramic-loaded filament to build parts layer by layer in a continuous deposition.[92–94] After shaping, the polymer fraction can be removed using the well-known process of binder-burn-out developed for injection-molded samples. Samples of FDC parts are shown in Fig. 4. For discontinuous deposition, also highly filled hot-melt suspension particulates can be formed by acoustic waves in a droplet generating chamber.[95] A commercial ink-jet printer can then be used for the deposition of ceramic objects.

3.1.6. Selective laser sintering (SLS)

In SLS, a laser is used to heat and bond powder particles in a layer-by-layer process through the motion of the laser beam. Bonding phases with lower melting temperatures can be used to avoid the necessity for very high temperatures.[96] This technology is still at a developmental stage for ceramic materials due to the difficulties arising from constraint sintering. How-

Fig. 4. Parts are made by fused deposition of ceramics (FDC) using a 55 vol.% Si_3N_4 powder loaded polymer filament of 1.78 mm diameter. The port plate (on the left) was built by FDC with minimal surface smoothing of the top face before sintering. The blade (middle) is a turbine blade that was green machined by hand after building by FDC and then sintered. The nozzle (right) is a generic nozzle shape for a rocket engine application that was built by FDC without any further machining at the green or sintered state (courtesy: S.C. Danforth, Rutgers Univ., USA, see also ref. [94]).

ever, glass-based structures can be densified completely due to the easy liquid phase sintering taking place.[97,98]

3.1.7. Laminated object manufacturing (LOM)

In the original version of this process, sheets of paper laminated with heat-activated glue are stacked and cut to the desired shape with a laser. The process can be modified by using ceramic sheets as a feedstock and spraying them with a solvent prior to lamination.[99,100] LOM is faster than other RP processes because the laser has to scan only the outline of each layer instead of the whole surface area.

3.2. Green machining

Green machining of ceramic powder compacts allows drastically higher material removal rates when compared to hard machining. Machining of fired components usually requires diamond tools due to the high hardness of ceramics, and it is limited to abrasive operations such as grinding. Cutting or chipping techniques such as turning, drilling, or end milling, which are widely used for shaping metals, though cannot be used for hard machining due to the brittle nature of ceramics. In contrast, green machining generally allows the use of these techniques, provided the strength of the green bodies is sufficiently high. Wherever substantial amounts of material need to be removed for shaping, green machining is therefore preferable to hard machining. Green machining is also suited for automated manufacturing directly from CAD/CAM files and has the advantage that it relies on standard equipment long established in metal-shaping industry. However, for conventional ceramics, green machining is restricted to relatively simple geometries and thick walls by the low strength of the powder compacts, even if binders are added in order to increase green strength. Although a variety of binders is available, most of them organic, such as polyvinyl alcohol (PVA), waxes, thermoplastic resins, or starch,[101] their use does not improve green strength sufficiently to allow green machining of complex parts with thin walls. In addition, low-green strength limits possible machining operations to grinding and cutting, and does not permit drilling, turning, or milling. Use of acrylic binder has led to a green strength of 6.5 MPa that allows better green machining than conventional binder systems.[102] Higher green strengths can be achieved for precursors containing ductile metals, i.e., as mentioned in chapter 2.3 for RBAO. Standard equipment as applied for metal parts can then be used. For example, tools made from high-speed steel or cemented carbide are suitable for use with common techniques such as drilling, turning, or end-milling. Furthermore, these bodies can be positioned in standard fixtures. High-cutting speeds give the best results, the speed being limited by the centrifugal forces acting on the green body. Fig. 5 shows a number of RBAO components shaped entirely by green machining.

Fig. 5. RBAO “green” parts shaped by high-speed milling and turning. The high strength of the isopressed Al/Al_2O_3 powder compacts allows damage free machining using conventional grips and tools.

3.3. Powder injection molding

Injection molding is a standard procedure for shaping complex-shaped components made from polymers. Injection molding can also be applied to metals and ceramics if the powders are mixed with a suitable binder. This is referred to as powder injection molding (PIM). PIM can be divided into a high-pressure (HPIM) and a low-pressure (LPIM) variant. While the first usually works with polymeric (thermoplastic) binders, the latter makes use of wax-based systems and can be performed at low temperatures and pressure, i.e., 60–80 °C and 0.2–0.6 MPa. However, combinations of both can be used as well as water-based systems, and solvents or lubricants may be added. The PIM process consists of the basic steps mixing, granulation, injection, debinding, and sintering. Requirements for the powder include a wide particle size distribution, high-packing density, and fine, equiaxed particles.[103–105] Debinding is a critical step in the process. It is usually done either by wicking (e.g. in a powder bed), thermal decomposition, use of a solvent, or catalytically. Problems that can occur are cracking and warpage of the component. The formation of cracks and voids can occur during injection molding or during debinding.[106]

Fig. 6. Lance nozzels with central transfer channel and feedtrough formed by powder injection molding using inserts (courtesy: Kläger Spritzguß GmbH, Germany).

Recently, also partially soluble binders are available easing the debinding procedure.[107]

PIM is most suited for small components[108] due to the time needed for the debinding process which increases with component size. The main advantage of the process is its excellent suitability for economic processing. Whereas, HPIM is typical used for mass production of components of complex shape and normally not applicable for manufacturing prototypes or small-scale series due to high-tooling costs, LPIM offers essential advantage for tailor-made parts due to the usability of low-cost tooling materials like aluminum, braze or even polymers (Fig. 6).

3.4. Slip casting and other casting techniques

As slip casting is one of the most widely used shape-forming processes in ceramic industry, in particular for sanitaryware and kitchenware, a great amount of work has been put into its development. In the original version, slip casting works by casting aqueous suspensions of ceramic particles into porous plaster molds. Many variations of the process are possible, from the use of non-aqueous suspensions to casting assisted by pressure or centrifugal forces. Although most widely used for relatively simple shapes with low demands as to precision, advanced slip casting with fugitive mold techniques can also be employed for complex shapes such as gas-turbine rotors.[99] In order to achieve good particle dispersion, slip casting requires thorough control of characteristics such as pH, viscosity, and addition of steric stabilizers. As it is necessary to manufacture optimized molds, slip casting is of limited value for prototyping.

A number of advanced derivatives of slip casting have been developed in which solidification of the green body after pouring slurry into a dense mold takes place by sublimation or chemical reactions instead of removing liquid by capillary forces. Among these are freeze casting [109–110], gel casting [111–113], direct coagulation casting (DCC) [114–116], hydrolysis assisted solidification (HAS) [117], and temperature induced formation (TIF) [118–120].

In freeze casting, an aqueous slurry is cast, frozen, and subsequently dried in the frozen state to obtain a green body.[109–110]

In the gelcasting process, a ceramic powder slurry containing organic monomers is cast into a mold. The monomer is then polymerized in situ to form gelled parts.[111] Alternatively, an existing polymeric species can be cross-linked. Gelcast green bodies are sufficiently strong to allow some green machining, and undergo a linear sintering shrinkage of ∼16%.[112] A binder burnout step is necessary prior to sintering. Possible defects in gelcast bodies are knit lines and air bubbles. Gelcasting has also been used for solid freeform fabrication of components with a computer-controlled extrusion apparatus by depositing droplets of a ceramic suspension containing a freshly admixed cross-linking agent.[113]

While gelcasting makes use of a polymerization or cross-linking reaction, direct coagulation casting is based on the coagulation of a castable aqueous ceramic suspension by an enzymatic reaction. In DCC, a colloidal suspension (e.g. of alumina) containing urea is cast into a mold. The addition of a urease breaks down urea, thereby releasing ammonia, which turns the initially acidic suspension alkaline, causing it to coagulate.[114,115] The process has also been applied to silicon nitride.[116] After coagulation, the green body can be removed from the mold, dried, and sintered. Hydrolysis-assisted solidification (HAS) is similar to DCC in that it is based on setting

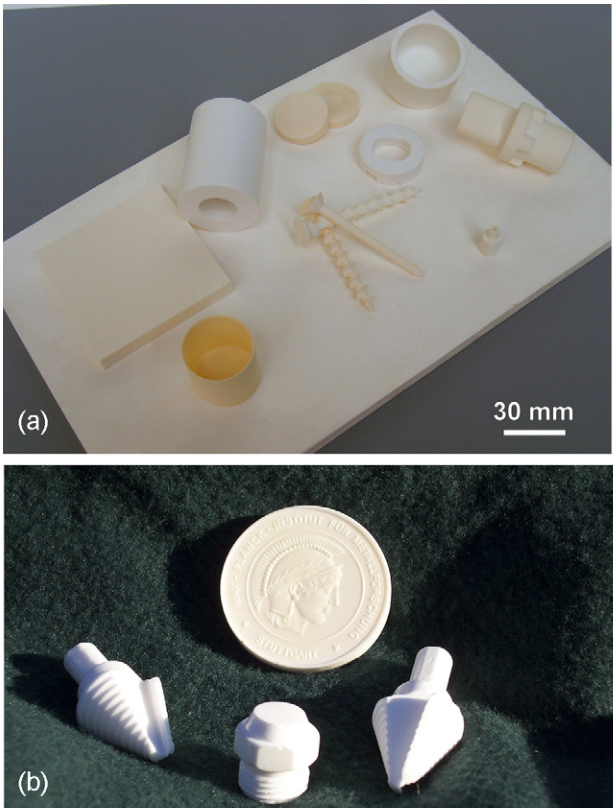

Fig. 7. Fired parts shaped by slip casting using impermeable dies. (a) In situ reaction of AlN particles in aqueous suspension – *hydrolysis assisted solidification* (*HAS*) – shifts pH and increase solid loading thereby enhancing drastically the viscosity (courtesy: T. Kosmac, IJS, Slovenia). (b) Increasing the temperature slightly – *temperature induced forming* (*TIF*) – favors the gelation of alumina suspensions when polyacrylic acids are added adequately (courtesy: W. Sigmund, UFL, USA).

a green body by increasing the pH of the suspension. However, while DCC employs an enzymatic reaction, HAS works by hydrolysis of aluminum nitride.[117] Temperature-induced formation (TIF) achieves solidification of the slurry by an increase in temperature.[118–120] Some examples of parts made by the HAS and TIF technique are shown in Fig. 7. It requires only small amounts of binder and has been applied to rapid prototyping, e.g., stereolithography, for making the mold. TIF has been demonstrated to deliver green bodies of high density. All casting methods do not eliminate sintering shrinkage or the need for manufacturing molds, but they are eminently suitable for complex shapes.

4. Conclusions

Various advanced techniques are available today for the manufacturing of ceramic-based components. Particularly, reactive synthesis routes exhibiting net-shaping capabilities (RBSC, DIMOX, VIMOX, AFCOP, RMP, RCC) or advanced machinability of precursors (RBAO; s-3A) offer essential advantages for fast and versatile fabrication of components with complex geometries. Also not addressed here, these techniques achieve often-superior mechanical and functional performances. Beside negligible shrinkage or advanced machinability, however, the shaping process should allow the direct use of CAD files (as for green machining or rapid prototyping) or the suitability of easy and fast producible, low cost dies (i.e. cast-polymers or machined-braze dies as for LPIM, HAS; DCC, or TIF). Most favorable is the combination of an advanced shaping technique with reaction synthesis as demonstrated by the examples in Figs. 8 and 9. Such combinations allow manufacturing of precisely shaped, high-performance parts with complex geometry according to the specific requirements of the customer in a short period of time.

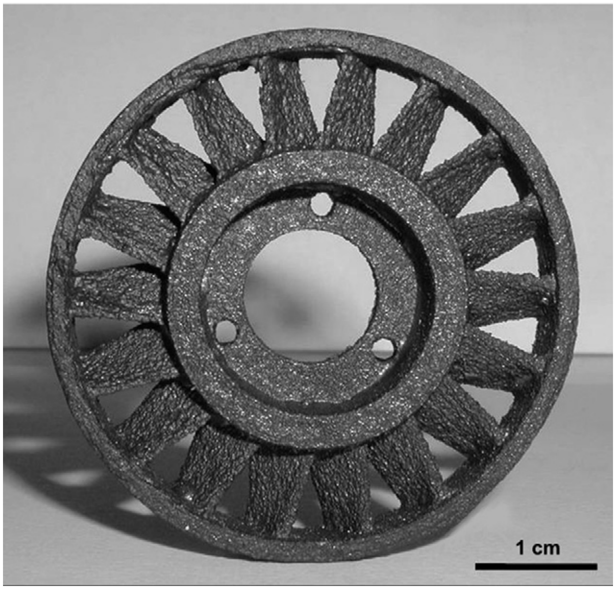

Fig. 8. SiSiC turbine wheel fabricated by selective laser curing (SLC) of polymer-derived precursor followed by silicon infiltration (courtesy: N. Travitzky, University Erlangen, Germany).

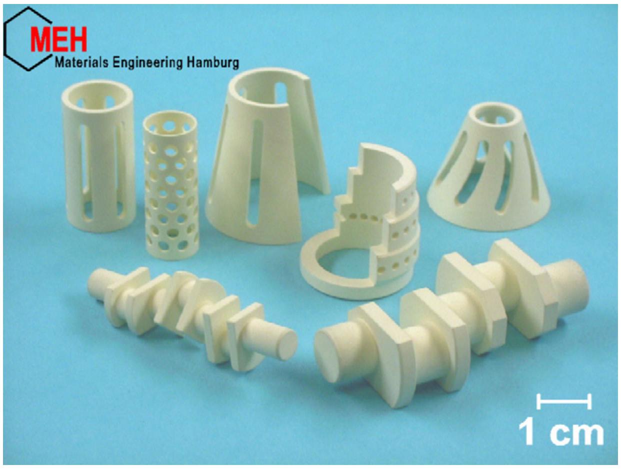

Fig. 9. Fired RBAO parts shaped by turning and milling in green state offering smooth surfaces (ra < 0.5 μm) with almost no defects. Dimensional tolerances <20 μm are achieved due to homogeneous isotropic shrinkage during reaction bonding. [121].

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