Issues in nanocomposite ceramic engineering: focus on processing and properties of alumina-based composites

Paola Palmero¹, Frank Kern², Frank Sommer², Mariangela Lombardi¹, Rainer Gadow², Laura Montanaro¹

¹ Department of Applied Science and Technology DISAT, INSTM – R.U. PoliTO – LINCE Lab., Politecnico di Torino, Torino - Italy
² University of Stuttgart, IFKB, Stuttgart - Germany

ABSTRACT
Ceramic nanocomposites, containing at least one phase in the nanometric dimension, have received special interest in recent years. They have, in fact, demonstrated increased performance, reliability and lifetime with respect to monolithic ceramics. However, a successful approach to the production of tailored composite nanostructures requires the development of innovative concepts at each step of manufacturing, from the synthesis of composite nanopowders, to their processing and sintering. This review aims to deepen understanding of some of the critical issues associated with the manufacturing of nanocomposite ceramics, focusing on alumina-based composite systems. Two case studies are presented and briefly discussed. The former illustrates the benefits, in terms of sintered microstructure and related mechanical properties, resulting from the application of an engineering approach to a laboratory-scale protocol for the elaboration of nanocomposites in the system alumina-ZrO₂-YAG (yttrium aluminium garnet). The latter illustrates the manufacturing of alumina-based composites for large-scale applications such as cutting tools, carried out by an injection molding process. The need for an engineering approach to be applied in all processing steps is demonstrated also in this second case study, where a tailored manufacturing process is required to obtain the desired results.

Key words: Alumina-based composites, Ceramic injection molding, Mechanical properties, Processing

Accepted: November 27, 2013

INTRODUCTION: A BRIEF OVERVIEW OF CRITICAL ISSUES FOR CERAMIC NANOCOMPOSITES

Why ceramic nanocomposites?

In recent years, there has been an increasing interest in ceramic nanocomposites consisting of 1 or more fine secondary phases, typically smaller than 100 nm, embedded in a larger grain host matrix (1), in view of the achievement of excellent mechanical properties (such as hardness, fracture strength, fracture toughness, wear and creep resistance). However, improved performance can be reached only through a suitable design of the nanostructure, controlling and optimizing the processing, from nanostructured powders to sintered materials.

With reference to particulate-dispersed alumina-based composites, several examples of reinforcement have been reported in the literature, but most studies have been devoted to Al₂O₃ matrix reinforced by SiC nanograins, mainly thanks to the significant contribution made by the work of Niihara and coworkers (1-4). Al₂O₃–SiC nanocomposites show significant enhancements in fracture strength (up to 30%-50% (5)), at either room or high temperature, as well as in wear and creep resistance, as compared with monolithic alumina with similar grain size. A further increase in strength (up to 30%) was observed after annealing. However, fracture toughness is not significantly improved, in spite of clear evidence of a change from intergranular to transgranular fracture mode (6).

Several models to explain the different mechanisms for strengthening and toughening of these systems have been proposed (7), such as the steep R-curve behavior model (4, 8), the residual stress model (9) and the reduction in processing flaw size model (6, 10).

In general, following Griffith’s equation, the increase in strength in nanocomposites can be attributed to either reduction in critical flaw size or increase in fracture toughness (6). Concerning the first effect, one of the main features in nanocomposites is that the matrix can be significantly refined by very small, well-distributed, second-phase grains, exerting a pinning effect on the matrix grain boundaries during sintering. Abnormal
growth of the matrix grains is always prevented, often leading to a narrower grain size distribution. Additionally, a reduction in the processing flaw size has frequently been observed in nanocomposite ceramics. Again with reference to the alumina–SiC system, hard SiC agglomerates represent the predominant flaw type. During extensive milling of the alumina and SiC powder mixture, SiC particles act as grinding medium and reduce the size of alumina agglomerates, which commonly cause large processing flaws, like pores (6). However, as previously mentioned, the results published to date on alumina–SiC are still very controversial. Ferroni and Pezzotti (11) confirmed the absence of R-curve behavior but found reduced fracture toughness in the alumina–SiC compared with plain alumina. They found that residual stress exerted by thermal mismatch plays a major role, and that only intragranular SiC grains may improve toughness, while SiC located at the grain boundaries will reduce fracture resistance.

As concerns the increase in fracture toughness, the main recognized toughening mechanisms exerted by second-phase particles are crack deflection, crack bowing (6), microcracking and grain bridging (12, 13). In ceramics containing transformable zirconia, toughening occurs due to the transformation of metastable tetragonal ZrO₂ grains to a monoclinic phase. This phase transformation is accompanied by a volume increase (~4%-5%) and a shear distortion (~7%) (12), setting the process zone on both sides of the crack under compressive stress, which counteracts the crack propagation, thereby reducing the stress intensity factor at the crack tip.

Further increases in the mechanical properties of the alumina–SiC composites were achieved by the addition of yttria or YAG, as these oxides act as sintering aids for SiC materials (13). YAG itself is also a reliable reinforcing phase for alumina, for both room and high-temperature applications (14, 15). The two phases show, in fact, mutual insolubility, high chemical and thermal stability and similar thermal expansion coefficients (16). In addition, an early study by Corman (17) indicated that YAG is the most creep-resistant single crystal oxide among several ceramics, as is the polycrystalline sintered material, as shown by Parthasarathy et al (18). It was reported that the bending strength of YAG–Al₂O₃ composites at room temperature – around 400 MPa – can be maintained almost up to the melting point of 2093°C when the displacement speed is high (19, 20).

With reference to oxide/oxide structural composites, the alumina–zirconia system is currently the most investigated one. The interest in such a system is widely justified by its excellent mechanical properties (hardness, fracture strength, fracture toughness and wear resistance), as alumina provides high strength, and transformable tetragonal zirconia grains exert the above-mentioned toughening effect. Fracture strength and fracture toughness values as high as 1,200 MPa and 8.5 MPa m¹/², respectively, have been reported for alumina–17 vol.% ZrO₂ composites (21). These materials are promising in several industrial applications (cutting tools, grinding media, wear parts etc.). Moreover, these composites are currently employed as orthopedic devices, because they are biocompatible and exhibit a greater crack resistance than pure alumina and a lower sensitivity to aging than pure zirconia.

A different approach to increasing the fracture toughness of brittle ceramics is to incorporate elongated grains with high aspect ratios, such as whiskers, fibers and platelets, which can promote crack deflection and crack bridging (22). However, the incorporation of such second phases can be detrimental for densification, due to the constraints of the network formed by the reinforcing phases. Thus, the concept of an in situ toughening approach, in which elongated second-phase grains are formed during the material processing, first demonstrated for silicon carbide and silicon nitride ceramics, has recently been extended to oxide-based ceramics (22). In alumina-based composites, the elongated second phases are usually aluminate compounds with a layered alumina structure (such as LaAl₁₁O₁₈ (23), SrAl₁₂O₁₉ (24) and CeAl₁₁O₁₈ (25)) or a magnetoplumbite structure (LaMgAl₁₁O₁₉ (26) or CaAl₁₂O₁₉ (27)), commonly referred to as hexaaluminates, characterized by a unique plate-like morphology due to a specific anisotropy in their growth kinetics. By using different hexaaluminates as second phases, Chen and Chen (26) obtained alumina-based composites with toughness values 50% higher than the monolithic alumina. In addition, An and Chan (27) investigated in situ toughening in the alumina–CaAl₁₂O₁₉ system, claiming that an increase in the aspect ratio of the CaAl₁₂O₁₉ second phase resulted in a more pronounced R-curve behavior, and an enhanced toughening was the result of the crack bridging by the elongated grains. The effects are, however, difficult to assign, as doping with rare earth or earth alkaline oxides may also change the grain boundary strength and favor crack deflection. Recent studies have shown that in CeAl₁₁O₁₈–reinforced zirconia-toughened alumina (ZTA), no crack deflection or bridging could be observed; cracks proceeded straight through hexaaluminate precipitates. The improvements in fracture resistance are indirect effects caused by the coarsening of the microstructure and the resulting changes in the state of residual stress and the improved transformability of the zirconia reinforcement (25).

Finally, in recent years, multiphase ceramic composite/nanocomposite materials, made of 3 or more immiscible phases contained in similar volume fractions, were produced. This approach allows the generation of interconnected structures, so that the growth of each phase during sintering is hindered by the others, as the long-order interdiffusion is strongly limited (28, 29). Equivolumetric Al₂O₃–YAG–ZrO₂ composites were produced by
Kim and Kriven (30) as well as by Oelgardt et al (31), with the aim of yielding materials with high strength retention even after prolonged high-temperature annealing. For the same purpose, Kim and Kriven produced alumina-based quadruplex and quintuplex composites (32), to achieve an increased microstructural stability during prolonged high-temperature service, due to longer interdiffusion distances between grains of the same phase.

The main and common feature in all the above-presented alumina-based nanocomposites is keeping a homogeneous microstructure and controlling the size and the distribution of the second phases. For a successful fabrication of the desired composite architecture, it is necessary to apply a rigorous protocol in which all of the steps of the ceramic processing are controlled, starting from the synthesis of the raw composite powders, to their consolidation into dense sintered pieces. In the following, the main issues relating to synthesis, processing and sintering of nanocomposite ceramics are discussed.

**Synthesis of nanocomposite powders**

Most alumina-based composite powders are currently produced by mechanical mixing of the constituent phases. This route involves the selection of raw materials, paying particular attention to the primary particle size, agglomeration degree and purity. Ultra-fine, loosely dispersed powders for both matrix and reinforcing phases guarantee effective mixing and satisfactory dispersion of secondary grains in the final product. In addition, high-purity powders are required to avoid the formation of undesired second phases during sintering. The homogenization of the powder mixtures can be achieved by either wet ball or attrition milling, carried out in aqueous or organic media. Alumina–SiC composites are frequently prepared by this conventional powder mixing route, by using ball-milling as well as ultrasonic dispersion (6).

The most critical step is drying, because of the risk of agglomerate formation. An infrared heat lamp or freeze drying was successfully used to avoid such a drawback (6). Mechanocombinations, implying high-energy milling techniques and frequently carried out under controlled atmospheres, have also been applied when complex compositions or alumina reinforced by intermetallic compounds are envisaged (33). However, these routes present some limitations for the distribution of ultra-fine second-phase particles, due to agglomeration and dispersion problems. To overcome such drawbacks, several wet-chemical methods have been used, presenting the advantages of lower crystallization temperature, higher phase purity and very homogeneous distribution of the second phases in the final composites. Alumina–YAG and alumina–ZrO₂ composite powders have been successfully produced by coprecipitation or sol-gel methods (34, 35); however, the dried products are generally affected by significant agglomeration, and the laboratory-scale characteristics of the powders are often difficult to maintain when large-scale production is concerned. A different approach consists in the in situ formation of second-phase oxide particles by surface sol-gel coating. Gelation occurs during normal mixing, emulsion methods, use of organometallic compounds, and formation of chelated complexes between adsorbed organic additives and inorganic ions (36). Recently, some of the authors of this paper have developed a modified in situ second-phase formation method (37-39), in which a well-dispersed alumina suspension is mixed with the inorganic precursors of second phase, and then spray-dried to avoid second-phase segregation.

**Shaping technologies for ceramic nanocomposites**

Structural ceramic materials are commonly shaped by powder-based technologies, which can be roughly subdivided into pressing, plastic forming and casting of dispersions (40). Other special technologies, such as inkjet printing or laser sintering, are currently being researched but are still less relevant from the economic point of view. In all of these shaping technologies, the shift from micron (or submicron) to nano-sized powders, as well as to powder mixtures containing a relevant nanoscale fraction, involves additional complications. The first challenge is the small size of the particles themselves. The increased specific surface area of the nanoparticles leads to lower solid contents of the dispersions, and a fixed interparticle distance has to be maintained to ensure dispersion stability (41, 42). Moreover, the larger the surface area, the greater the amount of surfactant required. The second challenge, specific for nanocomposite ceramics, is the homogeneous dispersion of the nanoparticulate second phase in the matrix. The use of high shear forces during dispersion is necessary to homogeneously distribute the nanoscale second phase. Separation by selective agglomeration or sedimentation during the shaping process has to be completely avoided. This potential drawback of mixing and milling technologies may be completely overcome by fixation of the second phase on the particles of the matrix phase by an in situ second-phase formation, as described in the previous section. In many cases, the use of sophisticated compounding technologies allows the achievement of homogeneous dispersions also by the mixing and milling approach.

In the following section, the specific problems associated with the processing of nanocomposite ceramics by pressing, plastic forming and slip casting are addressed.

Cold pressing is the economically most important shaping technology. Axial pressing, formerly considered inferior due to the inhomogeneous densification, has profited a lot from improved machine concepts which today allow the manufacturing of complex shaped parts.
with high turnover in net-shape quality (43). A key point is pressing granulates with excellent flowability and an exactly defined and reproducible bulk density. These granulates are commonly produced by spray-drying an aqueous dispersion of the ceramic powders. If the composition of a nanocomposite dispersion can be kept homogeneous until the spray-drying process, it can be assumed that the granulate itself will also be homogeneous in composition. A sufficient amount of binder is also required to obtain green specimens with the necessary strength, considering that the binder amount inversely scales up with particle size. The same is true for the plasticizer, added to allow the granules to be crushed and plastically deformed during the pressing process, which is carried out at axial pressures up to 300 MPa. In the green part, no granule artefacts or pressing defects should remain, in order to achieve high mechanical strength in the sintered component (44). Shaping by cold isostatic pressing is commonly performed to obtain blanks of high green strength which are subsequently green machined, but this increases the required amount of binder additives.

On the other hand, the thermoplastic forming process implies the mixing of the ceramic powder with meltable polymers, added to provide sufficient plasticity and green strength, and further additives to improve the wettability and prevent sticking to the mold. The organic additives must cover each individual particle and act as a lubricating film during the plastic deformation. Therefore, the required binder content is scaled for the specific surface area (45). Mixing is normally performed at temperatures of 30 K - 50 K above the melting point of the polymers, whereas higher temperatures lead to thermal decomposition or oxidation of the binders, which will deteriorate the feedstock quality. Double-sigma blade mixers are used for micron-scale powders, but for finer powders, twin-screw extruders or shear roll compactors are necessary to provide higher shear forces. For single component ceramics, even of submicron grain size, the technology is already proven; in contrast, it was recently shown that in the case of nanocomposite ZTA material, the quality of the feedstocks made by this direct mixing technology was inhomogeneous (46, 47). For nanocomposite mixtures, it is therefore necessary to pre-alloy the starting powders. Feedstocks derived from intensively milled aqueous dispersions show the required homogeneity (48).

Slip casting using plaster molds and pressure slip casting/pressure filtration have been successfully tried for shaping ceramics starting from nanoscale dispersions (49, 50). While the processes – in principle – lead to green bodies with high packing density and homogeneity, some technical drawbacks have prevented widespread application. The most frequently applied method of hollow-casting leads to components with a defined outer geometry: the wall thickness is only roughly defined by the soaking time. Components of variable thickness cannot be formed, as the velocity of green body formation is constant. This limits the range of geometries to parts such as plates, tubes or crucibles. The velocity of green body formation strongly depends on the type of porous mold used and even more on the grain size distribution of the ceramic dispersion. Due to the extremely narrow pore channels, green bodies from extremely fine grain dispersions are formed at extremely low speed. Formation of a plate thickness of 10 mm from a dispersion of 300 nm average grain size may take hours, thus involving a lasting stability of the suspension, while the same results are obtained within a few minutes using micron-size starting powders.

Clogging of pores by nanoparticles may almost bring the process to a standstill. In the case of nanocomposite dispersions obtained by mixing and milling, this may lead to selective sedimentation and grain size or concentration gradients across the green body formed (51). Again, the fixation of the dispersion of nanoparticles on the matrix grains can help to prevent segregation effects. Crack-free drying after the shaping process is challenging and time-consuming, as the residual drying stresses increase with decreasing grain sizes (52). Pressure-assisted casting processes can speed up the green body formation, but in principle they face the same difficulties.

Gel casting and direct coagulation casting may also be applied for making nanocomposite green bodies. Both are feasible methods for obtaining highly homogeneous and defect-free green bodies. As the solvent used for dispersion is not removed during shaping, the achievable packing densities are comparable to those of injection molding but always systematically lower than in slip casting or pressing processes (53, 54).

**Sintering of ceramic nanocomposites**

The sintering of nanocomposite powders to full or nearly full density without appreciable grain growth still presents a significant practical challenge. In ceramic materials, the high temperatures required to fully densify ceramic powders result in large grain sizes when traditional sintering techniques are used. This is particularly true for alumina-based nanocomposites, since Al₃O₃ possesses one of the highest homologous temperatures for full-density sintering (55). For instance, in the case of alumina–SiC composites, the final density of materials fabricated by pressureless sintering does not exceed 98.5% of the theoretical value (6).

To overcome the problem of achieving full densification with limited grain growth, unconventional sintering and densification techniques have been proposed. These include high-pressure densification, spark-plasma sintering and microwave sintering. Hot pressure (HP) sintering is based on the simultaneous application of heat and
pressure, involving particle rearrangement and plastic flow phenomena at the particle contacts. HP, although expensive, has predominantly been used for the consolidation of nanopowders. Generally, it is carried out using a graphite die, with pressure between 20 and 40 MPa, and temperatures between 1550°C and 1800°C (6), under Ar or N₂ atmospheres. In the case of alumina–SiC composites, it was found that the higher the SiC content, the higher the HP temperature (6). Alumina–SiC composites hot pressed at between 1600°C and 1900°C, under 30 MPa of applied pressure, showed a microstructure in which the average grain size was 2-3 μm; the average inclusion diameter was less than 0.2 μm (56). A further advance in sintering techniques is provided by hot isostatic pressing (HIP), in which materials are subjected to both elevated temperature and isostatic gas pressure, in a high-pressure containment vessel. This method is currently applied, as a post-sintering step, for the manufacturing of ZTA femoral heads, being able to increase the final density to the theoretical value, and retaining a fine grain size, thus improving the mechanical properties and reliability of the ceramic implants (57). Spark plasma sintering (SPS) is a further emerging technology, which combines pulsed electric currents and uniaxial compaction. SPS offers considerable advantages over HP since its combination of high heating rate, low sintering temperatures and short sintering time allows us to maintain submicron or ultra-fine microstructures, as already demonstrated for a wide range of composites such as alumina–SiC (58), alumina–YAG (59, 60), alumina–ZrO₂ (61, 62) and alumina–Nd₂Ti₂O₇ (63). Finally, the microwave (MW) processing (64) of monolith and composite ceramic materials has been recognized to offer a number of advantages over conventional sintering approaches. The interaction of high-frequency electromagnetic fields with polycrystalline dielectric materials leads to volumetric, selective and rapid heating. The increase in densification rates, at relatively low sintering temperatures, makes the MW fabricating technique significantly faster than the conventional process, with consequent shorter firing time and less energy consumption. In the case of ZTA composite, this process was successful in yielding fully dense materials, with uniform and finer microstructures when compared with conventionally fabricated ceramics.

This review is devoted to deepening some of the aforementioned crucial aspects of processing and sintering of alumina-based nanocomposite powders. To better discuss such key aspects, 2 case studies are presented here and discussed. The former deals with the assessment of a lab-scale protocol for the processing of alumina-based composite powders, in which an innovative approach is applied, allowing the in situ formation of oxide second phases. We show here that the successful tailoring of the micro/nano architecture of the sintered materials can be achieved only through a careful control of all of the several steps involved in the process. The manufacturing of composite ceramics at a technical or industrial scale is even more challenging, as the process has to be reliable, cost-effective and not time-consuming. This is shown in the second case study, where we illustrate the manufacturing of alumina-based composites for cutting tools by ceramic injection molding (CIM). This technology allows, in fact, the mass production of simple and complex near-net-shape ceramic parts, with high precision and narrow dimensional tolerances. The need for an engineered approach applied to all of the processing steps is demonstrated also in this case, where a tailored manufacturing process, including compounding of feedstocks, design of the mold and thermal processing technology, is required to obtain the desired result.

**CASE STUDY 1: DEVELOPMENT OF ALUMINA-BASED COMPOSITES BY A LAB-SCALE SMART PROTOCOL**

We discuss first an innovative but reliable procedure to develop alumina-based bi- or multi-phase composites. This process consists of the surface modification of commercial alumina powders by inorganic precursors of the desired second phases. Upon calcination, precursors can react with the matrix material to produce the secondary phases by a solid state reaction mechanism (in the case of miscible phases, such as alumina-YAG, here referred to as AY) or directly crystallize as second-phase oxides on the matrix particles surface (in the case of immiscible systems, such as alumina-ZrO₂, [AZ]). The authors demonstrated also the feasibility of this process for miscible-immiscible systems, as in the case of alumina-ZrO₂-YAG (AZY) composites (65).

The whole process, from synthesis to sintering, consists of a few simple steps, each of them to be carefully controlled to achieve the desired final properties. For the sake of clarity, a flow chart of the elaboration process is presented in Figure 1, listing the most critical steps of the process, namely: (i) selection of suitable raw powders; (ii) drying step; (iii) calcination pre-treatment; (iv) green body formation and (v) sintering. In the following sections, their role in the microstructural development and properties of nanocomposite ceramics is reported and briefly discussed.

**Selection of raw alumina powders**

The selection of the starting raw alumina powder was done according to the nanocomposite structure and composition to be developed. Both transition alumina (such as γ-Al₂O₃) and α-Al₂O₃ can be used as matrix raw material. The main advantages of the γ-phase are its loosely packed...
In the case of AZ materials, only commercial \( \alpha - \text{Al}_2\text{O}_3 \) powders were used, whereas in the more complex case of AY, which involves a solid state reaction between the yttrium-rich phase and alumina during calcination and/or sintering to yield the YAG phase, both transition and \( \alpha \)-alumina nanopowders were compared. The following 3 raw materials were selected: a nanocrystalline; \( \gamma/\delta-\text{Al}_2\text{O}_3 \) alumina powder (Nanotek\textsuperscript{®}; Nanophase Technologies Corporation, Darien, IL, USA), highly pure (99.95%), characterized by an average crystallite size of 45 nm and a specific surface area of 35 m\(^2\) g\(^{-1}\); the latter (CR1; Baikowski, France), is characterized by an average particle size of 600 nm and a specific surface area of 3 m\(^2\) g\(^{-1}\). All of the powders showed a certain degree of agglomeration, with a starting agglomerate size of about 5.5, 5 and 2.5 \( \mu \text{m} \) for Nanotek, TM-DAR and CR1 powders, respectively. To disperse them, aqueous suspensions, with a solid loading of 33 \( \text{wt}\% \), were ball-milled for a maximum of 10 hours, by using both alumina or zirconia spheres (powder to spheres weight ratio of 1:5) as milling media. In all cases, a significant reduction of the starting agglomerate size was reached, leading to fine agglomerates of about 0.4-0.6 \( \mu \text{m} \) in size. The 3 powders were then doped with \( \text{YCl}_3\cdot6\text{H}_2\text{O} \) (Aldrich, 99.99\% purity) aqueous solution to produce \( \text{Al}_2\text{O}_3-5\text{vol.\% YAG} \), according to the process shown in Figure 1. Samples are hereafter referred to as N-AY, T-AY and C-AY, for Nanotek, TM-DAR and CR1 composite powders, respectively. Figure 2 shows the dilatometric and derivative curves of N-AY (Fig. 2a) and T-AY (Fig. 2b) powders. In the first case, we can observe a 2-step sintering behavior, typical of a transition alumina, the former step being imputable to the phase transformation from \( \gamma \) to \( \alpha \)-phase, the latter to the \( \alpha \)-phase sintering (65). The peak on the derivative curve, at about 1200\(^\circ\)C, corresponds to the temperature of the maximum rate of transformation phenomena, in which volume reduction and change of grain morphology occur. As stated in a previous paper (67), a very slow heating rate (1\(^\circ\)/\text{C/min}), applied in the temperature range in which such transformation takes place (700\(^\circ\)-1500\(^\circ\)C), was necessary to counteract the formation of the vermicular structure and to allow a homogeneous particle rearrangement during the subsequent sintering step. In this way, in fact, a close-packed microstructure developed and a homogeneous, final sintered microstructure was obtained. In fact, the sintered materials showed a homogeneous distribution of the YAG grains (about 300 nm in size) inside a submicronic alumina matrix (68). However, only a moderate final density (of about 95\% of the theoretical value) was achieved. A very different behavior was observed in the case of T-AY, where a fired density close to theoretical value (99.7\%) was achieved (60), besides the formation of a very homogeneous microstructure. According to these results, \( \alpha \)-alumina powders were shown to be preferable as raw materials; however, further investigations on the role of the starting \( \alpha \)-alumina particle sizes on the composite microstructure and properties were carried out. As described in (60), T-AY and C-AY sintered materials were processed in a similar way, so that the only difference between them was in the mean grain size of the starting alumina powder. The 2 sintered materials showed significant differences in final density and microstructural development. In fact, a full densification was reached by T-AY material (99.7\%), characterized by a ultra-fine morphology, finer particle size and higher specific surface area. On the other hand, its main drawback is represented by the high-temperature \( \gamma \) to \( \alpha \)-phase transformation, which can give rise to the formation of a vermicular structure (66), enclosing a network of large pores, which is detrimental for densification. As a consequence, the final sintering stage requires a very high temperature to achieve full densification, thus leading to significant grain growth and consequent loss of the nanostructure.
Two drying procedures were tested: in one case, the suspension was slowly dried in an oven, at 105°C, overnight. In the second case, the suspension was diluted to 4 wt% and spray-dried (Mini Spray Dried Büchi B-290), that is, submitted to a “flash” drying process, as the liquid medium was converted into fine droplets, and instantaneously evaporated. Both dried powders were calcined at 600°C, for 30 minutes, then die pressed at about 300 MPa and pressureless sintered at 1500°C for 3 hours. Some micrographs of the sintered samples are presented in Figure 4. In the case of the oven-dried product (Fig. 4a), a poor distribution of the zirconia particles inside the alumina matrix can be easily observed, imputable to the powder sedimentation and subsequent segregation between powder and doping solution during the slow drying process. A further consequence of the inhomogeneous distribution of zirconia is the bimodal size distribution of the alumina grains. In fact, in the zirconia-rich areas, a fine and homogeneous matrix can be observed, whereas larger alumina particles were detected in the zirconia-free regions, due to a reduced pinning efficiency of the second phase. In contrast, we can see a completely homogeneous distribution of the zirconia particles in the spray-dried material (Fig. 4b), giving rise to a narrow grain size distribution of very fine alumina grains.

Drying step of the doped suspension

A key aspect of the elaboration process shown in Figure 1 is the drying step, as demonstrated for both AZ and AY materials (65). In the case of the AZ composite powder, a well-dispersed alumina suspension was mixed with a zirconium chloride aqueous solution, and then homogenized under magnetic stirring for about 2 hours.

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Calcination pre-treatment

An extensive investigation of AZ powders (69), carried out by in situ high-temperature X-ray diffraction (XRD) and transmission electron microscopy (TEM), highlighted the key role of the calcination pre-treatment on the ZrO$_2$ crystallization kinetics and crystallite size. By doping an alumina powder with a zirconium chloride aqueous solution, a zirconium-rich amorphous layer is yielded, homogeneously covering the alumina particles. By TEM observation, zirconia starts to crystallize from the amorphous film at about 500°C, by homogeneous nucleation. The calcination temperature plays a significant role in this mechanism, since at low temperature (i.e., at 600°C) a fast nucleation occurs, but the crystal growth is still negligible. At higher temperature (i.e., at 1000°C), the nucleation rate decreases, diffusion becomes more effective and the growth of the existing nuclei is predominant. Also the calcination time significantly affects the microstructural development of the doped powders. In particular, a prolonged treatment at low temperature (for instance, at 600°C for 10 hours) induces the amorphous layer to drain into discrete pockets among the alumina grains, dragging the zirconia crystals. Such gathering of zirconia nanocrystals could promote their coalescence and growth during the subsequent thermal treatments, hindering a successful control of the nanostructure. Obversely, a treatment at higher temperature for a short time promotes a fast disappearance of the amorphous phase layer and the crystallization of larger zirconia grains. This demonstrates that thermal treatment is a powerful tool for tailoring the nanocomposite powder features and, consequently, the sintered microstructures.

A different approach for the set-up of the thermal pre-treatment was used in the case of AY powders. The crystallization of YAG on the alumina particle surface occurs at high temperature and, in most cases, transient second phases (such as the orthorhombic perovskite YAO$_3$ or the monoclinic Y$_4$Al$_2$O$_9$) crystallize prior to YAG. As an example (70), Figure 5 (curve a) shows the XRD patterns of AY calcined at 1200°C for 30 minutes, showing the crystallization of YAG, besides traces of monoclinic and perovskite phases. However, such high-temperature treatment induced the formation of alumina agglomerates, hard to break even after 6 days of ball-milling. So the calcination temperature was decreased to 1050°C – i.e., to the lowest temperature at which yttrium-aluminates have been detected by XRD. In addition, to limit agglomeration, a “fast” calcination was carried out, by plunging the powder for a short time (5 minutes) in a tubular furnace, kept at the above temperature.

In Figure 5 (curve b), the XRD pattern of this powder is reported, showing the appearance of the perovskite phase, beside $\alpha$-alumina. This treatment was successful in yielding a less agglomerated powder, easy to disperse after 24 hours of ball-milling. Finally, it was found that the “fast” calcination allowed the retention of a lower size of the second-phase crystallites than in the conventional processes (71): in fact, ZrO$_2$ crystallites of about 16 and 30 nm were measured for AZY powders calcined at...
1050°C for 5 minutes by “fast” and conventional treatments, respectively.

**Forming method**

A further key aspect of the elaboration process here presented is the forming method. In a study by the authors (70), the preparation and mechanical characterization of the 3-phase AZY (Al$_2$O$_3$–5 vol% YAG–5 vol% ZrO$_2$) composite were compared with those of the reference bi-phasic AZ (Al$_2$O$_3$–10 vol% ZrO$_2$) and AY (Al$_2$O$_3$–10 vol% YAG) materials. In all cases, aqueous suspensions at 65 wt% solid loading were prepared and ball-milled with zirconia milling spheres for 48-96 hours. A part of the suspension was cast into porous moulds, and drying was performed in a humidity-controlled chamber for about 1 week. The remaining aliquots were slowly dried under magnetic stirring, and then uniaxially pressed at 300 MPa. The green densities of the slip cast samples were 5%-10% higher than the pressed materials, confirming the hypothesis of a more effective particle packing induced by the wet forming method. Full densification was reached by all of the slip cast samples, whereas slightly lower density values (<99%) were determined for the pressed ones. Such differences can easily be explained by comparing the microstructure of the slip cast and pressed samples. For instance, in Figure 6, the microstructures of pressed and slip cast AZY materials are shown. In spite of the very homogeneous distribution of YAG and ZrO$_2$ grains in both microstructures, the former sample presents some large flaws, as shown in the inset of Figure 6a, probably induced by the cold, uniaxial pressing. In contrast, an almost defect-free microstructure was obtained in the case of slip cast materials (Fig. 6b).

The presence of large flaws has an expected, negative impact on the mechanical properties. The Vickers hardness values of AZ, AY and AZY pressed bodies were in the range 1,550-1,700 HV, significantly lower than those of the denser, slip cast samples (in the range 1,900-1,950 HV), thus highlighting the key role of a suitable forming technique for improving the performance of ceramics.

**Sintering**

The role of dopants and second phases (such as zirconia, yttria and YAG) in delaying the densification behavior of alumina is well-known (72). This is shown in Figure 7, depicting the dilatometric curves of pure Al$_2$O$_3$ and of AZ and AY composites sintered at 1550°C at 5°C/min (72). While the onset sintering temperature of pure alumina was about 1000°C, sintering of composites was delayed to 1100°C for AZ and to 1150°C for AY (AY-5). In addition, second phases also raise the temperature of the maximum sintering rate in comparison with the pure alumina, as shown by the derivative curves in Figure 7b. We can observe a very flat sintering curve for the pure Al$_2$O$_3$, with a maximum densification rate at 1250°C, while the very steep curves of AZ and AY are very similar, showing maximum densification rates at 1350°C and 1375°C, respectively.

To decrease the maximum sintering temperature, with the aim of retaining a fine microstructure as much as possible, the role of the heating rate was investigated. It was found that the lower the heating rate, the lower the onset and the maximum sintering rate temperatures. However, such a displacement was very limited, since the above temperatures were lowered by about 20°C-30°C passing from heating rates of 10°C/min, to 5°C/min and finally to 2°C/min.

A different approach involves the use of nonconventional sintering techniques, such as HP and SPS. In a study by the authors (60), the role of such advanced sintering methods on AY microstructural development and mechanical properties was compared with conventional pressureless sintering (PS). A poor final density (94.4%) was achieved by the PS material, whereas higher values were obtained by the 2 innovative methods, especially in the case of SPS, which enabled a full densification. Comparable microstructures were obtained by the 3 sintering methods, since well-distributed YAG grains (of
about 450-500 nm in size) were located in the alumina matrix, whose average size was about 1 μm for PS and HP materials, and slightly larger (1.3 μm) for the SPS sample.

Such differences in microstructural features are shown in Figure 8. The final density and microstructural features played a major role in determining the mechanical properties. The hardest material was the HP one, due to its final density and relatively fine microstructure. However, the most relevant difference was found in the creep rate of the materials, with the values of the denser HP and SPS samples at least one order of magnitude lower than that of the PS material.

**CASE STUDY 2: INJECTION MOLDING TECHNOLOGY APPLIED TO CERAMIC NANOCOMPOSITES**

Cutting tools for wood and wood-based materials, such as medium density fiberboard (MDF) or particle boards, require a very sharp cutting edge (tip radius <10 μm) and a cutting angle of ~55°, to be able to cut the wood fibers and produce a smooth surface. The most common tool geometries are rectangular reversible cutting inserts of ~30x12x1.5 mm³ with a trapezoidal transverse section having 2 blade edges along the long sides.

The tools are mounted on peripheral milling cutters using either a bolted or clamping assembly. State-of-the-art tools are made from cemented carbide (WC-Co) because they can offer a good ratio of price and performance (73, 74). However, due to the rising cost of tungsten and cobalt materials, cutting tools made by alumina- or silicon nitride–based composite ceramics have attracted increasing interest (75-77). Whereas today’s machine technology allows high-speed cutting, the speed of peripheral milling cutters with mounted cemented carbide tools is limited due to the high specific gravity and resulting high centrifugal forces of the WC-Co tools. Advanced technical ceramics could overcome this drawback due to their lower tool weight.

During operation, the tools are progressively blunted by abrasive wear which is mainly caused by mineral constituents of the workpieces. As soon as the blunting has proceeded, the tools must be exchanged to maintain the desired machining result. High tribochemical wear and oxidation resistance must thus be one of most important features of the tool material. Studies by Gogolewski et al and by some of the authors (75, 78) have shown that high hardness alone does not guarantee wear resistance. Wear should proceed on an atomic scale, therefore extremely fine-grained materials with strong grain boundaries are beneficial to avoid breakout of whole grains.
associated with rapid blunting during operation. Requirements for fracture resistance and bending strength seem to be moderate.

The materials tried for the applications were magnesium-doped fine-grained alumina and alumina-based composites like ZTA (containing 7.5-10 vol% ZrO₂), alumina–SiC (with 5 vol% SiC) and alumina-chromia-yttria (ACY) composites having a micro-nano architecture.

Manufacturing the desired tool geometries using the classical axial pressing route in net-shape quality is not possible, because blade geometries cannot be shaped during the pressing operation. The blade edges must be either roughly premachined in the green state – which is difficult due to the delicate component geometry – and subsequently hard machined, or completely made by hard machining using a final high-precision fine grinding step. Due to the high hardness and abrasion resistance desired for the final application, the hard machining becomes costly and time-consuming. These considerations finally led to the concept of producing net-shape quality tools by the injection molding technique. The aim was either to completely abstain from machining (“real” net shape, the ideal case) or to limit the machining to the final sharpening operation associated with very low material removal (near-net shape). As already stated, this strategy included an integrated processing chain from the selection and compounding of raw materials to the shaping operation and the final heat treatment processes. Because it has been shown by Gogolewski et al (75) that final grain sizes in the sintered components should be of submicron size, the alumina powders chosen were submicron α-aluminas (average particle size of 300-400 nm) and the second phases (SiC, ZrO₂, and YCrO₃) were nanopowders. The injection molding feedstocks were prepared in a 3-stage process starting with intensive milling of the starting powders in an aqueous dispersion, then kneading the thermoplastic binder with dispersion at 140°C in a sigma-blade mixer, thereby first removing the solvent and premixing the feedstock. In the third stage, the premixed feedstocks were homogenized at high torque in either a twin-screw extruder or a shear-roll compactor. In feedstocks based on a 300-nm alumina containing 10 vol% of 20-nm zirconia, the premilling and high energy mixing is the key to obtain a feedstock with sufficient homogeneity and dispersion of the second phase. While the premilling stage mainly affects the distribution of the phases in the microstructures, which is essential especially in the case of ZTA (Fig. 9), the posthomogenizing affects the distribution of the binder and solids, which becomes important during molding at high shear rates where insufficiently homogenized or overplastified feedstocks tend to segregate the binder and thus lead to detrimental flaws in the final components.

The shaping process requires a specially designed mold allowing for excellent surface quality, and hydrodynamic boundary conditions must be respected to obtain a homogeneous form filling especially in the significant areas (blade edges). Gate location and geometry are crucial. A central positioned pin gate at the flat side of the plate resulted in poor mold filling and shear cracks progressing along the edge. In contrast, a film gate at the short side of the cavity resulted in a good fountain flow–like mold filling resulting in high-quality green parts with sharp edges (Fig. 10). The mold was evacuated prior to filling to ensure good edge quality and avoid air traps. Injection molding of the parts requires high demands on the machine to ensure complete and mold filling but no overfilling, which would create a burr at the blade edge.

The following thermal treatment steps (i.e., debinding and sintering) must be executed with care to avoid bloating, especially the debinding of the fine-grained green bodies. In sintering, a full densification should be achieved at the lowest possible temperatures to obtain fine-grain microstructures and thereby high hardness and abrasion resistance. Figure 11 shows that, with the chosen manufacturing route, blades of high sharpness can be obtained without the need for final machining. The density at the functional regions is very high; some structural defects apart from these regions may be formed but are of no importance for the specific application. The image also shows that the microstructures from injection molding are
The cross-section shows the “hydrodynamic halo” of the molding process. Due to the transient conditions of the mold-filling process, temperature and viscosity of the paste change during the injection process. Because cooling proceeds from the mold surface to the hotter core of the fluid flow, the material in contact with the wall rapidly freezes. This so-called fountain flow behavior means that the core flow overruns the material at the wall, and ceramic grains embedded in the polymer follow the fluid flow forming textures (80). As the shape of noncubic grains is anisotropic, a crystallographical misorientation results, which is amplified during sintering.

It was shown that in pure alumina the orientation in the core is random, while the grains at the surface or at weld lines are oriented with the c-axis orthogonal to the surface. In the transition region, an orientation gradient is formed. In the case of multiphase composites, this effect is less pronounced. The green bodies were subsequently debindered in water to remove the water-soluble part of the thermoplastic binder system, dried and then thermally treated at 800°C. Sintering of the materials was then carried out to obtain the best possible densification and avoid coarsening by oversintering. Good results with full densification were obtained for ACY (alumina(chromia)/YAG) and alumina in hydrogen. Almost fully dense alumina-SiC was obtained in argon. The ZTA materials required higher sintering temperatures than the expected ones. Best mechanical properties were achieved at a sintering temperature of 1575°C and 2 hours of dwell. Alumina and zirconia grain sizes, evaluated through the linear intercept method of 100 grains each, were \( \approx 1 \) μm and \( \approx 400 \) nm, respectively.

In application tests, the alumina-based nanocomposites revealed different wear behavior and thus performance. The alumina and ACY showed the best results: low wear and limited edge recession. ZTA materials turned out to be too soft, resulting in high wear. However, the materials exhibited a wear mechanism at the atomic scale. Grain materials were abraded, and grain breakouts were only observed in the vicinity of manufacturing-related small defects. The alumina–SiC material with the coarsest matrix of all tested materials showed intolerable grain pullout. Moreover, here the sintering additives form a very thin but glassy sintering skin which has to be removed, contradicting the idea of net-shape manufacturing (Fig. 12).

The results of the research project on injection molded alumina-based nanocomposites for wood machining showed clearly that nanocomposite materials can possess the necessary properties for the desired application. A tailored manufacturing process including the compounding of feedstocks, proper design of the mold and choice of molding parameters as well as thermal processing technology are required to obtain the desired result. The feasibility of producing performing ceramic blades was clearly proven.

**CONCLUSIONS**

Nano-sized particle-reinforced ceramics represent a new class of materials with improved mechanical properties, even at high temperatures, compared with monolithic ceramics. A system of particular interest has been alumina–SiC, because here the most greatly
improved mechanical properties, in terms of fracture strength, hardness, wear and creep resistance were reported. Such exceptional results have stimulated research into designing other engineering nanocomposite ceramics, and a variety of particulate-reinforced alumina composites are currently under investigation. The less widely investigated oxide-oxide systems may become economically even more interesting as they can be sintered in nonprotective atmosphere and without application of pressure.

However, before the novel properties can be fully realized in a macroscopic nanocomposite, considerable basic research is necessary. In fact, similar to all nanostructured materials, the properties of nanocomposites are structure- and size-dependent, so that a basic understanding of their structure–property relations is the key to enable the nanoscale design of multifunctional materials for engineering applications.

The change in the reinforcement scale, from micro to nano, poses new challenges in the development of suitable processing techniques for these composites. On the one hand, important factors such as powder raw material, processing route, shaping technology and sintering route, which govern the evolution of desired properties, must be well understood. On the other hand, an engineering approach to manufacturing must be applied, in which all of the above processing steps should be carefully controlled to produce the desired micro/nano architectural features in the sintered composites. This is illustrated in the first case study of this review, dealing with a smart protocol for the laboratory-scale elaboration of alumina-based oxide composites. Through the proper selection of the raw powders and their controlled processing, homogeneous and tailored bi-phase and even 3-phase micro/nano structures can be obtained, showing appropriate mechanical properties.

Large-scale application of nanocomposites requires the scaling up of the manufacturing process, involving further challenges related to reliability and cost of the process itself. In fact, the same high-performance features which make the nanocomposite ceramics so interesting in their properties are detrimental to their production. Due to the extreme hardness and abrasion resistance of such nanocomposites, final machining becomes very costly and time-consuming. From a manufacturing point of view, net-shape or at least near-net-shape manufacturing is mandatory to accomplish reasonable cost targets. This is the topic of the second case study, which illustrates the manufacturing of oxide-based cutting tools by CIM technology. This technology allows, in fact, the mass production of simple and complex near-net-shape ceramic parts, with high precision and narrow dimensional tolerances. The need for an engineered approach applied to all of the processing steps is demonstrated also in this case, where a tailored manufacturing process, including compounding of feedstocks, design of the mold, choice of molding parameters and thermal processing technology is required to reach the desired result.

Financial support: The authors would like to thank the ALF (Industriegemeinschaft industrielle Forschung) for financing parts of this study under grant no. 16611N/2.

Conflict of interest: The authors declare they have no conflicts of interest.

Address for correspondence: Paola Palmero DISAT Politecnico di Torino Corso Duca degli Abruzzi 24 IT-10129 Torino, Italy paola.palmero@polito.it
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