Better ceramics through colloid chemistry

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Abstract

In this work, the key role of colloid chemistry in the development of novel processing routes for ceramic manufacture is reported. An overview of the origins of a ceramic processing science is presented, emphasizing the pioneering works and the scientific fundamentals of all processing steps that make use of suspensions. A brief review of the importance of colloid chemistry in the synthesis of nanoparticles with controlled purity, size and shape is given, followed by a description of the suspension properties and their effect in the beneficiation and shaping of ceramics. The main shaping techniques for the production of bulk parts, substrates and coatings and layered ceramics are shown, as well as the multiple possibilities for the design of composites with tailored microstructures and microarchitectures.

Keywords: Processing; Colloids; Suspensions; Rheology; Shaping

Outline

- 1. The origins of a ceramic processing science.**
- 2. Colloidal processing. A historical perspective.**
- 3. A colloidal approach to ceramic processing.**
 - 3.1. Introduction.
 - 3.2. Colloidal routes for powder synthesis.
 - 3.3. Colloidal routes for powder dispersion.
 - 3.3.1. The principles of colloidal stability.
 - 3.3.2. Measuring the stability of suspensions.
 - 3.3.3. Parameters influencing the dispersion.
 - 3.3.4. Heterocoagulation.
 - 3.3.5. Additives for ceramic processing.
- 4. Shaping ceramics using suspensions**
 - 4.1. Taxonomy of shaping processes.
 - 4.2. Direct casting methods.
 - 4.3. Additive manufacturing.
 - 4.3.1. Indirect AM Technologies.
 - 4.3.2. Direct AM Technologies.
 - 4.4. Tailored microarchitectures. Layered ceramics.
- 5. Concluding remarks**

1. The origins of a ceramic processing science

Ceramic processing deals with the different steps involved in the manufacture of a ceramic product. The term *ceramics* comes from the greek “κερασ” (keras), which means *clay*. This word proceeds from a radical of Indo-European languages “*keram*” (keram), which means to burn. Thus, ancient ceramics were clay-based products subjected to burning. Ceramic objects used from the most ancient human civilisations that used hand mixed, hand built and slip decorated earthenware for cooking and storage of foods dated at 20,000 BC. Several thousands of years ago, the potter’s wheel was already used, this

being the first shaping machine. The shaped object was left to dry to achieve a rigid consistency. Later, the use of moulds for pressing the clay and its further hardening by firing in closed kilns were developed. During thousands of years, the technology for the production of ceramic articles continued without substantial changes or innovations. In the subsequent centuries, ceramics were largely used in the household, but artware was also produced. Some figurines were formed in fired clay moulds, and other advances included a specific surface finish used by Greeks and Romans (the so-called “terra sigillata”) or the use of glazes and glasses. In the Christian era, white porcelain appeared in China whose main achievement was its high translucency. In Europe it was in the XVIII century when new developments were registered, such as the duplication of the formula for the white china clay and the invention of specific shaping techniques such as extrusion, slip casting in porous moulds, and tunnel kilns (1). At the end of the XIX century and beginning of the XX century there was some new progress, especially concerning the fabrication of electric furnaces able to operate at higher temperatures and with better atmosphere control. This allowed the production of silicon carbide and fused alumina, among other products. During this period, there was an attempt to increase the knowledge and understanding of the ceramic technology and the treatment of raw materials. This growing interest led to the foundation of the first ceramic societies in the world that also started to publish their corresponding journals (in 1899 the American; in 1901 the British; in 1919 the German). The period between the two World Wars was rich in the creation of a new vision with the integration of other disciplines into the ceramic course. Physical chemistry, thermodynamics, and colloid science were disciplines that started to find strong effect in the development of the crystal structure formation (and therefore the design of many new types of compositions), the design and determination of phase diagrams, with a significant impact in the progress achieved in the field of refractories, and the understanding and control of the slip casting kinetics as a base for the subsequent development of other suspension based forming techniques.

During the second half of the XX century, sciences in general and materials science in particular, experienced a revolution accelerated by the parallel development of technology. In opposition to traditional industrial manufacture, which had a strong dose of empiricism and an engineering sense of the processes, the existing technology focused on the development of new materials, understood as those produced according to well established manufacturing steps, such as: 1) processing and fabrication of the product

following tightly controlled physic-chemistry rules; 2) precise study of the microstructural features; 3) complete characterisation of the properties, either for structural or functional applications, and interrelation of those properties with microstructure and processing strategies. The commercial production during a great part of the past century was conditioned by the lack of the scientific basic concepts operating during the manufacturing process.

In 1968, a committee of the Materials Advisory Board of the National Academy of Sciences carried out a first review of the state of the art on ceramic processing (2). Fig. 1 shows a flow chart described in that report demonstrating the successive interrelationships between ceramic processing, character, processing, and uses. It must be remarked that each category depended on the previous one. The character/properties evaluation constituted the area of physical ceramics and is accepted as a ceramic science. It is clear that the close relationships between character and properties need to be split into different components in order to identify the fundamentals of ceramic processing. Such a breakdown was proposed by Pask (3), who identified the main factors and parameters of processing according to the chart presented in Fig. 2. Processing steps appear divided in starting materials, formation of particulates, formation of assemblies, drying and pre-firing, and firing. Pask considered that ceramic fabrication focuses on the engineering aspects whereas ceramic processing emphasises the scientific aspects of materials behaviour. The properties in the different steps of processing can be integrated into two categories: 1) behavioural properties, such as thermal expansion, mechanical or electrical properties, magnetic susceptibility or transmittance to light; 2) characteristic properties that can be divided into constitutional (related to types and amounts of phases and their composition) or structural (such as shape, size distribution and orientation of phases, either solid particles or liquids or pores).

The main concern is that any defect introduced at any step persists in the following steps thus affecting the final behaviour of the material. This has a dramatic effect on ceramic production since densification is accomplished by a noticeable shrinkage of about 20% so that differential shrinkage must be minimised. For that purpose, the object must be uniform, on one hand, and specific conditions for sintering have to be imposed, on the other hand. The most important parameters to consider are the uniform distribution of temperature, the control of heating/cooling rates to maintain similar temperatures at the

surface and in the interior, and the minimisation of the grain growth after open-pore closure.

The key to understand ceramic processing is to recognise the interdependency of the different steps of the process and to be able to obtain the adequate relations. According to Messer (4), the possible relations are among processing variables, characteristic properties and behavioural properties, which are illustrated in Fig. 3. However, not all are directly related and there are preferred relations. It can be visualised considering that the processing variables determine the characteristic properties and these last determine the behavioural properties. The first are not directly related to the last because it could be possible to obtain a material with identical microstructure using different processing strategies and thus the properties should be the same too.

The homogeneity of the final material will depend on the capability of the starting particles to rearrange during sintering at high temperature. In principle, structural ceramics with the best properties are obtained when the compact sinters to near-to-theoretical density, excepting in the case of porous materials with tailored porosity. Sintering takes place when the consolidated green body is subjected to a thermal treatment during which the surface energy reduces through the formation of polyhedral grains. The control of sintering and densification depends on the characteristics of the powders (5,6). The most important are the particle size distribution, particles shape and distribution, specific surface area, and tendency to agglomeration. In principle, as particles become finer the temperature necessary for sintering would decrease (7). However, in fact, it is very difficult to control the grain growth operating in fine powders densification due to their strong reactivity. With respect to the shape, the most efficient powder should be equiaxed, as it can pack more efficiently than irregular shapes. In most cases, processing involves some stage in the wet state and this requires an adequate dispersion of the powder in the liquid for which some deflocculants are added (8). In general, organic substances are used because inorganics would persist in the final composition and would change the microstructure and properties. However, organic deflocculants can be also a problem since organic salts are used and the cation can remain. This is the case of alkaline salts of polycarboxylates frequently used in ceramics, where the cation can induce the formation of glassy phase in detriment of the material response. This is the reason why ammonium salts are preferred even having lower dispersing power. Moreover, the reduction in size usually means an increase of surface area so that the concentration of deflocculant needed

to attain full coverage also increases. Finally, since any defect will persist in any subsequent step, as established before, it is important to have the best quality of the starting powder but also to control processing to avoid the formation of agglomerates as they cause differential shrinkage during sintering that can lead to cracking, warpage, etc, which negatively affect the properties (9).

Moya et al. (10) demonstrated how the small amount of impurities of silica coming from the glass beaker used to prepare and store the suspensions affected significantly the zeta potential of alumina suspensions, whose isoelectric point changed from pH 8.9 to 5.2 after ageing for 16 days. This example demonstrates that not only the powder characteristics are essential but also the possible contamination derived from other processing steps, such as beneficiation processes or possible reactions with additives, machinery, tools and even beakers and containers.

A clear example of the above statements is shown in Fig. 4, corresponding to the microstructure of an alumina/zirconia multilayer material produced by sequential slip casting with alternating layers of alumina with either monoclinic or metastable tetragonal zirconia. Colloidal processing allows the design of tailored microstructures but the uniformity depends on the suspension homogeneity. When handling suspensions the greatest source of defects arises from the possible presence of remaining bubbles originated during milling/mixing. In the picture it can be seen how big bubbles can distort the geometry of the laminate and produce large defects.

In 1978 a reference book on ceramic processing, entitled “Ceramic processing before firing”, based on a previous conference that was the first that concentrated specifically on topics like raw materials, batch processing, and shaping of ceramics was published (11). The main blocks were devoted to powders, water-particulate systems, green-body formation and microstructure, and processes and applications. There were interesting chapters on rheology of concentrated suspensions, rheology of organic binder suspensions, and tape casting, to mention those focused more on colloidal processing. Another reference book dealing with ceramic fabrication processes was also published in 1978, with specific chapters dedicated to slip casting and tape casting (12). So at the beginning of the 80s there were great expectations on the control of the classical colloidal processes (basically slip casting and tape casting) and the development of new forming processes using suspensions, such as pressure casting and all those processes based in the

gelation and polymerisation of suspensions that concentrated great interest in the 90s, which led nowadays to the emerging additive manufacturing techniques.

However, as mentioned above, when the pioneer ceramists started to apply the fundamentals of colloid-chemistry they came back to the use of clay-based systems, which were used from ancient history and were the first ceramics considered colloidal materials. The origin of colloid science can be dated in the early XIX century, with the theory of Brownian motion and extended later to the dissolution of high molecular polymers and the dispersion of fine particles. It was in the 40s when the first theories of stabilisation of colloids appeared, with the description of the van der Waals forces, the Hamaker constant (13), and the establishment of the electrostatic stabilisation theory due to Derjaguin-Landau (14) and Verwey-Overbeek (15). For the appearance of the first theories of stabilisation of suspensions with polymers it was necessary to wait until the 60s and 70s with the study of the thermodynamics of polymer solutions by Flory and the theory for the steric interaction of Napper (16). A brief history of the application of colloid science to clays can be found in the review of Franks et al. (17). However, in the last decades of the XX century ceramics experienced great advances in many upcoming industrial and technological developments, which was the opportunity of single phase ceramics, mostly oxides, carbides and nitrides. However, colloids are defined as dispersions of two phases with at least one having sizes lower than 1 μm . The problem during the first half of the past century and before was that most commercial powders were much coarser than the desired size for the stabilisation in liquids so that they settled rapidly and impeded the adequate uniformity after wet forming.

The awareness of the enhancement of properties of ceramic products with a well-controlled process in the different processing stages needed a parallel improvement of the quality of the powders to allow not only easy handling but also better packing behaviour and sinterability while maintain the higher purity required for advanced ceramics in opposition to traditional ceramics in which some impurities, such as silica, was not a drawback. Ceramists understood soon that a better control of processing was not enough to produce better ceramics if the raw materials were not adapted to those processing necessities. That is, to obtain better ceramics it was necessary to start from better powders and then to improve their processing. Thus, researchers started to put the focus on the development of new synthesis methods to produce fine powders with the desired characteristics of purity, size, morphology, and absence of agglomerates, capable of

producing dense ceramics with better performance and higher reliability. In 1984 the Materials Research Society (USA) organised a symposium entitled “Better ceramics through chemistry” (18). That symposium was successively repeated in the subsequent years, the seventh edition being celebrated in 1996. The title of the present article and the original lecture in which it is based is an adaptation of the title of this pioneer book and intends to be a small tribute to it.

It was recognised that ceramic processing was one of the most evolving fields in materials science and engineering. Micron- and submicron-sized ceramic powders require high temperatures for sintering whereas the use of fine powders produced by chemical methods leads to materials with higher uniformity and unique properties not attainable by conventional routes that can be sintered at lower heating temperatures. In the subsequent decades chemical processing using solutions received greater attention. Yoshimura classifies those processes into three groups (19): 1) soft chemistry or wet chemistry, 2) biomimetic processing, and 3) soft solution processing. In soft chemistry solute precursors are mixed in solution and transformed into a solid by precipitation or gelation, the most widely used techniques being the precipitation and co-precipitation, the hydrothermal synthesis, the thermo-hydrolysis, and the sol-gel route. Biomimetic processing simulates the processes of bio-systems, which are aqueous solution systems at mild conditions using ambient temperatures and pressures similar to those in biological cells. With these restrictions only limited inorganic materials can be produced. Finally, soft solution processing refers to low-energy fabrication methods employing aqueous solutions in order to obtain shaped materials.

2. Colloidal processing. A historical perspective

The origins of colloidal processing of ceramics are found in the ancient manufacture of earthenware objects taking advantage of the plasticity of clays. Clay particles dispersed in water constituted the first colloidal dispersions prepared and used by humans, but always obeying to experimental practice without a real understanding of the processes involved (20). Clays are formed by silicates having laminar structures that permit the intercalation of water between the layers. This bound water allows the formation of double-layer-like forces between the clay particles which are the responsible for their

plasticity, considered as the capability to deform when applying a shear stress. However, after the creation of the fundamentals of colloid science in the XIX century, its application to other ceramic systems apart from clays was initiated in the XX century. The mixtures of ceramic particles with water to make suspensions were known along the centuries, not only to produce pastes for hand making pottery (with the most sophisticated tool being the potter's wheel) but also to produce slips (name reserved for suspensions of clays in water) for more advanced processes such as slip casting, which is the mother of all slurry forming processes. Slip casting was already used in ancient civilizations for shaping clay products and appeared in Europe toward the end of the XVIII century (21). The first effort to develop plasticity in non-plastic materials was reported in Germany in 1910 by Ruff (22), who described the formation of colloidal particles from ground alumina in acids. Similar acid treatments were used for alumina (23,24) and other refractory oxides such as ZrO_2 , ThO_2 , BeO , etc (25,26) in the 30s, as well as the use of alkaline deflocculants. Slip casting was successfully used for the manufacture of oxide ceramics, the first report being due to Hauth in 1949 (27). The "Crucibles report" of 1953 (28) presented a compilation of "available data on crucibles used for calcining, sintering, melting, and casting", as mentioned in the subtitle of the report. During the 50s the use of suspension based processes was also applied to metal powders and metal-ceramics or cermets (29), although the real development of these systems occurred around three decades later. The basic theoretical and practical principles of slip casting were described by St. Pierre in 1958 (30), and then a number of excellent reports appeared trying to explain the parameters controlling the slip casting performance (31-35). Earth alkaline oxides received great attention for their important implications in the refractories industry and several papers described the dispersion and slip casting of those oxides (CaO , MgO) in water, where the high hygroscopicity caused serious difficulties in their wet processing (36-40).

In slip casting the driving force for the kinetics of wall formation is associated to the capillary forces occurring during the filtration of the suspension in the open porosity of the permeable plaster moulds thus allowing the formation of a cake in contact with the internal walls of the mould and therefore, it is a solid-liquid separation process. Another shaping process that employed suspensions is tape casting, which appeared in 1949. In that case a suspension is spread onto a surface to form a film and the dispersion liquid evaporates.

In the 80s the ceramic community expanded to a greater range of fields than had ever been anticipated and assisted in the popularisation of ceramic materials in new industrial sectors. This was related to the development of pure materials to produce the so-called modern or advanced ceramics, basically consisting of products of pure components with high density obtained from synthesised pure and fine powders. Mixtures of two or more components were conventionally prepared by milling in liquids (preferably alcohols) and subsequent drying and pressing. In that decade the development of hot pressing techniques allowed the densification to theoretical density. Lange compared the microstructure and properties of both pressure-free and pressure assisted techniques in a series of papers that became classic, the 4-part series “Processing-related fracture origins” (41-44). It was noticed that compacts of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ produced by conventional sintering presented irregular, low-density regions on cut surfaces of dense materials, and it was concluded that these low density regions were the origin of flaws responsible for the fracture of the compacts. This was a consequence of the agglomerates of zirconia remaining in the mixture due to inefficient ball milling that experienced a differential shrinkage creating crack-like voids. These agglomerates are inherent to dry forming techniques, but if the van der Waals forces operating among submicronic particles are controlled the formation of defects should be inhibited. This is the ability of colloidal systems, in which the attractive forces can be overcome by stronger repulsive forces so that the particles remain dispersed during the preparation of the suspension and also during the consolidation step. In the absence of agglomerates, the consolidated green body should preserve the dispersion state of the colloidal suspension thus resulting in the desired microstructural uniformity. This was reported in a pioneer work that showed the significantly higher strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ materials produced by slip casting (renamed colloidal filtration to note the capabilities of a proper control of colloidal forces) over those obtained by isostatic pressing (45).

In 1989 Lange published a reference review on ceramic processing demonstrating that the necessity to process advanced ceramics from powders by non-deformation methods together with their brittleness limited the reliable processing of dense ceramics with the desired shape and size and microstructure (46). The colloidal approach offers the opportunity to produce them through an adequate control of the suspension structure not only during the suspension preparation but also during its compaction into a green body leading to uniform microstructures (47). According to Aksay (48), the dispersion stage is

useful for various reasons: 1) in dispersed suspensions agglomerates can be removed by sedimentation or centrifugation; 2) the surface chemistry of the powders can be modified by adsorption of additives; 3) homogeneous dispersion can be obtained even at the nanometer scale. During consolidation there is a transition from a dispersed (the slip) to a consolidated (the cast) structure with a hierarchical clustering and a multimodal void size distribution.

The application of colloidal methods to ceramic processing has received great attention from those pioneering works and the main advantages and the fundamentals of the colloid science applied to ceramic forming methods have been described in some excellent reviews (17,46,49-54) in which the principles of colloid science and their application to ceramics are discussed in detail. Sigmund et al. (49) summarised the technological requirements for an optimum processing control. In order to obtain high reliability and strength the processing method should be able to provide a near-net shaping with a simple processing concept (minimum steps) and high flexibility. In addition, the processing in water should be preferred due to evident cost, environmental and health reasons. That review paper presented the principles of green body formation with the focus on direct casting methods and solid free-form fabrication. Lewis (50) discusses the colloid chemistry and rheology and gives an overview of consolidation via fluid removal, particle flow and gelation. Moreno (51,52) summarises the mechanisms of different methods of consolidation and discusses the tendencies in colloidal forming of ceramics and composites. Pugh and Bergström (53) edited the first book specifically devoted to the colloidal processing of ceramics, with different chapters explaining the basics of colloid chemistry and rheology and their effects in the subsequent shaping steps. Sheppard (54) discusses the problems and limitations existing to select a fabrication suitable to produce large volumes of complex-shaped parts at high rates. Janssen (55) considers two new promising routes for fast and low cost manufacturing of reliable components, reactive-based processing and shaping techniques suitable for CAD/CAM without labour intensive tooling optimisation. Franks et al (17) put the focus on direct shaping by additive manufacturing, direct assembly and ceramic foams. This review presents the principles of green body formation with the focus on direct casting methods and solid free-form fabrication.

3. A colloidal approach to ceramic processing

3.1. Introduction

Fig. 5 shows a general chart of the different steps of ceramic processing. Most ceramic operations include the dispersion of powders in liquids, either for direct consolidation from the suspension (like in slip and pressure slip casting, tape casting, gelcasting, etc) or as an intermediate step for further processing operations, as in the case of milling and mixing, spray drying, filter pressing, etc. For instance, in dry pressing, granulation of primary particles is needed to improve pressing efficiency and to obtain more uniform pressed bodies. Primary particles of non-clay ceramics are highly abrasive and free of plasticity, so that strong friction forces develop during consolidation between the particles and the die walls and between the particles themselves. Hence, the transmission of the applied pressure is poor thus leading to density gradients that can produce cracking. The formation of granules allows reducing pressure and density gradients as they can be plastically deformed during compaction, increasing the contact areas and therefore, the packing density of the pressed compact. This is possible due to the homogeneous distribution of organic additives (deflocculants, binders and plasticizers). Other usual steps are milling and mixing. Milling is required to reduce the particle size of coarse naturally occurring materials or those highly agglomerated during synthesis, but it is very frequent to use the milling step to achieve a better homogenisation of a suspension of a mixture of powders or to homogenise a powder with processing or sintering aids, such as oxides to allow the liquid phase sintering of SiC or the preparation of a complex formulation with binders, plasticisers, wetting agents and other components typically employed in tape casting. Then, the study of dispersion of powders in liquids is extremely important in almost all ceramic forming processes, even those based in dry compaction. The understanding of the suspension parameters has been possible due to the big effort of ceramists to introduce the fundamentals of colloid science in ceramic processing which allows establishing the relationships between the rheological behaviour, the interparticle potentials and the suspension microstructure. Colloidal processing plays a determining role in many ceramic manufacturing steps. Although the colloidal size is typically $<1\text{ }\mu\text{m}$, the same approach may be successfully applied in systems with larger particle size.

Ceramic processing usually consists of 2-phase systems (powder/liquid) or 3-phase systems (powder/liquid/gas). For example, aerosols are widely used for synthesising

special inorganics, as in the case of vapour condensation, freeze drying, and spray pyrolysis, among others. The liquid droplets of the precursors react with vapour phase species in the former, with a cold liquid to freeze the droplets, in the second, and are sprayed into a reactor with a low-temperature chamber where the salts precipitate and a high-temperature chamber for subsequent pyrolysis, in the last. Other synthesis procedures make use of emulsions. Solid dispersions are also frequent in ceramics, being the basis of the glass structure and of solid solutions developed on sintering.

In summary, colloidal suspensions are used and obtained at different levels, including the production of powders with controlled properties, the beneficiation of natural raw materials, the dispersion of powders and mixtures for the production of ceramic/ceramic, ceramic/metal or ceramic/carbon composites, and the manufacture of bulk bodies, substrates and coatings by casting, free-forming, or any other shaping technique that utilises suspensions. The next sections will focus on the following items: 1) the synthesis of powders by chemical routes, such as co-precipitation, sol-gel, freeze drying, and hydrothermal methods; 2) the principles operating in the preparation and stabilisation of the suspensions, including the measurement of colloidal stability through zeta potential and sedimentation tests, and the rheological behaviour of the suspensions as a function of different processing parameters; 3) the forming techniques using suspensions for the manufacture of bulk bodies, substrates, coatings, and other possible shapes.

3.2. Colloidal routes for powder synthesis

Several synthesis routes employ liquid solutions for preparing ceramic powders in the form of colloidal suspensions. In general, a precursor is dissolved in water or in organic solvents and forced to react with the aid of a catalyst. The solvent is then removed and the product is converted into a ceramic powder after a thermal treatment. The most critical step is the solvent removal. The main requirements of a powder for advanced ceramics are the following (6): 1) high purity, 2) small particle size, 3) narrow size distribution, 4) spherical or equiaxial shape, 5) no agglomeration, 6) single phase.

Table 1 summarises the most common methods for synthesising ceramic powders (56-58). There are two main types of synthesis methods in which the particles are formed either by dispersion or fracture of larger units through physical methods, or the

association of molecules proceeding from a solution (59,60). These are referred to as top-down and bottom-up approaches, respectively. The former is based on classical attrition of particles by milling (61) and more recently, mecnosynthesis methods based in the direct mechanochemical activation of the constituent oxides, especially interesting for the development of new phases in multicomponent systems (62). The latter are controlled by nucleation, growth and ageing processes in solution (56-58). The chemical methods can involve reactions at the solid state, liquid solutions or vapour phase. In general, solid state reactions lead to strongly agglomerated powders that require an efficient milling in order to obtain a suitable fine grained powder. There is a variety of liquid solution methods, the most popular being those based on precipitation reactions, on the combustion of a solution, and on the solvent vaporisation.

Precipitation routes have been largely used for the production of single oxides, either alone or with dopants (Al_2O_3 , TiO_2 , Y_2O_3 doped ZrO_2 , etc.) and for mixed oxides, such as BaTiO_3 , ferrites, etc. (63). The method is based on the dissolution of the precursors in water and the precipitation of insoluble species by pH adjustment. The hydrothermal synthesis allows the production of powders of high purity and controlled composition after thermal treatments of 150-250°C in autoclave for relatively long times (6-8h). A current modification of the method is the use of a microwave oven to activate the reaction in whose case the temperature is lowered (typically <200°C) and times are reduced from several hours to less than 30 min (64,65). Combustion methods have received also great attention in the last years due to the high purity obtained and the simplicity of the process. Combustion solution synthesis consists on the mixing of reactants (usually nitrates or metal-organics such as TEOS) that oxidise by reaction with a reducing agent (the most widely employed being urea) with the help of a combustion aid, often NH_4NO_3 . An external heat supplied by an oven or a hot plate favours the ignition of the mixture provoking a self-sustaining and exothermic redox reaction that results in a fragile foam that can be easily crumbled into powder (66). This is probably the main limitation of this route as some materials are strongly agglomerated and need milling. A variation of the process was the suspension combustion, in which a suspension containing colloidal silica reacted with aluminium nitrate, as a source of Al to produce mullite (67). Whereas the other methods start with a solution that transforms into a suspension here a salt solution is incorporated into a nanoparticulate suspension to form new species that maintain in suspension. In solution drying processes the liquid breaks into small droplets avoiding

segregation during evaporation (68,69) thus allowing to obtain fine powders. The most popular method is freeze drying, in which chlorides, sulphates or nitrates are sprayed in a frozen medium (a mixture of acetone and liquid ice or liquid nitrogen) and then the liquid is removed by sublimation. The obtained powder usually needs a further thermal treatment to promote the transformation of the salts into the corresponding oxides. Some authors mention in this group spray drying, but in general this is a technique employed to form controlled agglomerates (granules) by high speed rotation of a powder in suspension under specific conditions of temperature and pressure. Then, this may be considered as a beneficiation method rather than a synthesis route.

The most popular synthesis methods are probably those based in the gelation from precursors, the most extended being the sol-gel route, which consists on the polymerisation of monomers in a colloidal solution (the sol) that acts as a precursor of an integrated network (the gel) formed by either nanoparticles or reticulated polymers. This is a very versatile technique useful for the production of a very broad variety of compositions with controlled characteristics and large homogeneity (70,71). The main drawbacks refer to the high cost of the precursor solutions and the limitations for obtaining bulk materials and thick films. The sol-gel method consists of the hydrolysis and polycondensation (or peptisation) of metallic precursors, which can be inorganic salts, organic salts such as acetates, oxalates or alcoxides, or organometallics. There are two general types of sol-gel methods, polymeric and colloidal. The former occurs through controlled hydrolysis in an organic medium with a small addition of water in the presence of a catalyst that promotes the slow hydrolysis and the subsequent polycondensation to form structural networks with bonds metal-oxygen-metal. The colloidal sol-gel is performed with aqueous solutions so that uncontrolled hydrolysis takes place spontaneously thus leading to the formation of large agglomerates that are later broken as a consequence of the strong repulsive electrostatic forces generated by the presence of large concentrations of protons. The breakage of the large agglomerates into small particles is known as peptisation process. Polymeric sol-gel is useful for the production of thin glass-like coatings whereas the colloidal process is better suited for the production of nano-sized powders. Fig. 6 illustrates the sequence of reactions in both processes. In the polymeric route the precursors are in solution and evolve to the formation of a gel structure. However, there are important differences in the densification kinetics during gelation depending on the pH conditions of the reaction (72). Under acid catalysis the

hydrolysis reaction is faster than the condensation reaction thus resulting in linear, short polymeric chains with a low fractal index (≤ 2) that produce surface type structures. Conversely, under basic catalysed conditions the condensation rate becomes higher than the hydrolysis rate and larger three-dimensional structures with a high crosslinking are formed which have a high fractal index (≥ 3) and behave as particles. In both cases, the matrix is always a precursor solution and the main application is for thin films but the thickness that can be achieved with basic catalysed sols is much higher. On the other hand, in the colloidal sol-gel route the hydrolysis takes place immediately due to the large excess of water and large precipitates are formed. These precipitates maintain in suspension and the strong electrostatic forces developed by the ion determining ions present in the solution are responsible for their peptisation into small particles. In this case, the system is not a solution but a suspension in fact, in which the particle size reduces progressively until nanoparticles are obtained. Due to the low viscosity it is difficult to establish when the process has finished. In previous works a procedure for the quantification of the peptisation time in colloidal sol-gel was established. This method has demonstrated its suitability for different materials (73-74). The methodology involves the measurement of particle size using dynamic light scattering (DLS) and laser diffraction (LD) techniques and the simultaneous measurement of the transmission and backscattering of light from a suspension contained in a transparent tube over time using the multiple light scattering technique (75,76). The combination of the three optical techniques allows one to determine the evolution of the peptisation process. At the beginning of the process the precipitates are big (tens of microns) and LD measures large particle sizes far away from the detection limit of the DLS technique. The big precipitates impede the transmission of light. There is a time in which transmission sharply increases and backscattering falls down. At this moment, LD measurements are not reliable anymore while DLS measurements provide reliable results. This is the starting of the peptisation process and is called transition time (t_1 in Figure 7) and is not immediate but it needs a certain time to complete the reaction, after which the peptisation is complete, so this can be defined as the true peptisation time (t_2 in Fig. 7). After that, a clear, stable, and translucent suspension is obtained. The values of those peptisation times depend on the parameters of the synthesis, including composition, molar ratios of components, protons concentration, dopants content, temperature and energy imparted during agitation. Figure 7 illustrates the evolution of the optical parameters of a TiO_2 sol produced from Ti-isopropoxide in water with a molar ratio water/ TiO_2 of 100/1 from its

preparation until complete peptisation. The structure of the particles during the different stages of the processes is also schematised.

A process related to sol-gel is the Pechini method (77,78), in which a solution of oxides or salts is mixed with a hydroxycarboxylic acid, such as citric acid. This promotes chelation and after the addition of an alcohol (such as ethylene glycol) and heating to 150-250°C polymerisation occurs. A further heating is needed to remove the organics and to obtain the fine powder. In the citrate gel route complexation of the metallic ions is promoted by citric acid and ammonia in an aqueous solution that is subsequently dried under controlled conditions and thermally treated.

To illustrate the many possibilities of synthesising particles of different composition, particle size, and morphology Fig. 8 shows the microstructure obtained by transmission electron microscopy of some powders obtained by different chemical solution methods, such as freeze drying, colloidal sol-gel, and microwave assisted hydrothermal synthesis. As it can be seen the control of the reactions and the parameters associated with each technique allow one to obtain high purity powders with controlled shape and size and high surface area, as desired for many applications.

3.3. Colloidal routes for powder dispersion

3.3.1. The principles of colloidal stability

A colloid defines a system consisting of one or more dispersed phases into a continuous dispersion phase with at least one of the components having dimensions ranging from 1 nm to 1 μm . Either the dispersed phase or the dispersing medium can be in the solid, liquid, or gas state and thus dispersions have different nature depending on the physical state of the components. In ceramic processing the focus is on dispersions of solids in liquids, referred to as suspensions. The main factors determining the properties of a colloidal system are the particle size and shape, the surface properties, the interparticle interactions and the interactions between particles and the dispersing medium, i.e., the solid-liquid interface. The colloidal approach involves the manipulation and control of those interactions in order to optimise the suspension properties to produce green bodies with reduced number of heterogeneities, better microstructural control and enhanced properties. The description of the basic concerns of colloid chemistry are outside the

scope of this work, but there are many reference books and reviews on colloid and surface science where the reader can find exhaustive information (79-86). The main parameters associated with colloidal suspensions are the following: 1) particle size, it must be small enough to prevent settling, e.g. $< 1\ \mu\text{m}$; 2) Brownian motion that allows the particles to remain dispersed in the liquid, overcoming gravity; 3) the transmission of light depends on the particle size. If it is small enough dispersion occurs and a light beam can be observed (Tyndall effect); 4) hydrodynamic forces; 5) capillary forces; 6) attractive van der Waals forces; 7) electrostatic repulsive forces; 8) polymeric stabilising forces. The adequate control of these interaction forces is the key for obtaining stable suspensions for the manufacture of defect-free ceramics. In brief, a particulate system in suspension tends to destabilise by London-van der Waals attractive forces (87), which are very strong at short distances and are always present, leading to strong agglomeration of particles, or to settle by action of gravity according to the sedimentation law established by Stokes (88). The tendency to sedimentation can be overcome with low particle sizes whereas the agglomeration by London van der Waals forces can be balanced through the action of electrostatic charge associated to the formation of a double layer around the particles or through the adsorption of polymers at the particle surfaces impeding the contact between surfaces by steric hindrance.

Amphoteric oxides dispersed in a polar liquid, such as water, develop charges at the surface of the particles that result in their strong repulsion by Coulombic forces. This is the consequence of the formation of a double layer consisting on a monolayer of ions of opposite sign to that at the surface (counterions) and a diffuse layer with decreasing concentration of these counterions toward the bulk of the suspension. The potential at the shear plane that separates the moving part of the double layer from the stationary part is the so-called zeta potential, whose sign depends on the pH. At acidic pHs, hydroxylated species like MOH_2^+ are formed at the surface whereas at basic pH basic species like MO^- are formed. The pH at which the activity of negative and positive ions are equal defines the zero point of charge (ZPC) where no effective surface charge exists and therefore particles tend to agglomerate by van der Waals forces. The determination of the zero point of charge is essential to know the operating conditions necessary to prepare well-dispersed suspensions far away from the ZPC. The ZPC depends on the own nature of the material and the way it has been obtained, the charge of the cation, the hydration degree, the presence of impurities and the adsorption of electrolytes. In the absence of specific

adsorption the ZPC is also the isoelectric point, which corresponds to the pH where the measured zeta potential is zero. Excellent reviews have been published enumerating the values of ZPC of a wide variety of solid oxides, hydroxides and aqueous hydroxo complex systems (89-92).

The most extended model for studying the stability of suspensions is the DLVO theory, proposed independently by Derjaguin-Landau (14) and Verwey-Overbeck (15), which considers that the total energy of interaction is the sum of the attractive van der Waals potential and the electrostatic potential. The representation of the potential energy with the separation distance typically shows three features: a deep well with negative potential at near to contact distance where particles coagulate and the suspension cannot be redispersed, a maximum energy barrier, with positive potential, which corresponds to the maximum stability at moderate distances, and a possible secondary minimum at longer distance where flocculation occurs and suspensions are redispersable.

At low separations, below a few molecular diameters, the DLVO theory cannot describe particle pair potentials. This theory considers the medium separating the particles as a structural continuum which is useful for large distances, but inadequate when particles are closer than a few nanometers. To explain the interactions at these small distances, the existence of additional non-DLVO forces has been reported. These forces can be attractive, repulsive or oscillatory and can be much stronger than the two previously described DLVO forces at small separations. This is the origin of solvation, structural and hydration forces (80). Short range oscillatory forces appear (93-95) when liquid molecules are confined to a narrow region between two surfaces and consequently, they are induced to order into layers. This is a geometrical effect and is called solvation oscillatory force or structural force. In addition, surface-solvent interaction can induce some ordering in the adjacent liquid and produces a solvation force, which is monotonic and not oscillatory and can be attractive or repulsive. If the liquid is water, then the solvation force is referred to as the hydration force. It appears as a consequence of a strong bonding of water molecules to surfaces containing hydrophilic groups, such as ionic, zwitterionic or H-bonding groups. In the case of water, it has been reported that some clays, surfactant solutions and other colloidal dispersions, remain stable even at very high counterion concentration, where, according to the DLVO theory, they should coagulate in a primary minimum. Velamakanni et al. (93,94) found that when an indifferent electrolyte was added to a highly dispersed aqueous alumina slip (pH 4), short-range

repulsive potentials similar to the hydration forces were developed. Beyond a certain salt concentration (around 0.1M) the repulsive barrier lowers so that particles would coagulate, but an attractive network is formed whose strength increases with salt content and the slip becomes plastic, facilitating particle rearrangements while still maintaining an adhesive interaction. The depth of the resulting potential well and the number of particles per unit volume govern the strength of the network, which has a different strength to that obtained at the isoelectric point. These repulsive hydration forces have important implications in ceramic processing, because slips of technical non-compressible ceramics can be consolidated by plastic deformation behaving like clays.

Finally, another type of stabilisation can arise from the use of polymers, which can remain free in the dispersing medium leading to a volume restriction phenomenon or the adsorption of polymer molecules at the surface, which is the so-called steric stabilization, for which the main issue is the strong anchoring of the polymer to the surface, and the length of the adsorbed polymer chains must be long enough to provide the desired hindrance effect. The main concerns of the polymeric stabilisation have been described elsewhere (16,96,97). Polymeric stabilisation is more suited to organic solvents, but in many processes the use of water is preferred for health, environmental, and cost considerations. For water systems, it is customary to use polyelectrolytes, which are polymer chains formed by charged monomers, the most usual being poly(acrylates), poly(carbonates), etc. In this case the adsorption of the polymer prevents the contact among particles while the presence of charges provides electrostatic repulsion at longer distances, combining both mechanisms and this is why this stability mechanism is referred to as electrosteric.

3.3.2. Measuring the stability of suspensions

As stated before, the stability of suspensions depends on a number of factors, including specific parameters related to the powder characteristics, such as composition, particle size distribution, surface area, phases, particles shape, etc., or related to the suspension, such as its pH, nature and concentration of deflocculants, presence of electrolytes (impurities, etc.), effect of different types of additives (binders, plasticizers, thickeners, gelling agents, etc.), milling/mixing conditions, temperature, ageing time, and so on. All these parameters affect significantly the stability of the suspension and determine the

properties of the green and sintered bodies. Therefore, it is essential to make a good characterisation of the suspensions optimising the different parameters in play.

Fig. 9 presents a brief summary of the most important properties to be controlled to achieve the best stability and the main techniques employed for its determination. On one hand, a first group of properties includes the colloidal stability, which is studied through zeta potential measurements, the possible formation of agglomerates, which is controlled measuring the particle size distribution, and the integrity of the material in solution to avoid solubility, for which a series of suspensions are usually maintained at different pH values and after a certain equilibrium time they are centrifuged and the supernatant is analysed by chemical techniques in order to determine the concentration of ions of the material present in the liquid as a result of the solubilisation at any pH. All these tests are usually carried out with optical techniques employing diluted or very diluted suspensions. Some examples of the relations between solubility and pH stability with zeta potentials are described elsewhere (98-100).

There are many techniques for the characterisation of particle size distribution, such as those based in X-ray sedimentation, centrifugation, particle counters, etc., but the most popular currently are the laser diffraction equipments (87,101-103). In the case of nanoparticles, the most employed technique is dynamic light scattering, where the size is determined from the Brownian motion of particles in suspension that produce time dependent fluctuations in the intensity of the dispersed light.

The colloidal stability parameter is zeta potential, which can be measured attending to various electrokinetic phenomena, the most frequent being electrophoresis in which particles migrate toward an electrode with opposite sign to that of the particles surfaces as a consequence of an applied electric field. Recent instruments employ the laser Doppler velocimetry technique to determine the mobility of particles in the fluid (104). These laser equipments make also use of very diluted suspensions, normally containing solid concentrations of 0.1 g.L^{-1} or less. Other types of equipment make use of an acoustic signal, in which the parameter measured is the electrokinetic sonic amplitude (ESA) that correlates the amplitude of the applied electric field and the pressure amplitude of the generated sound wave (105,106). This technique allows one to measure concentrated suspensions with solids loadings of up to 30-40 vol.%, which are characteristic of some shape forming techniques, but the major limitation refers to the fact that this technique does not give a direct measurement of the electrophoretic mobility as the other techniques

do but gives an indirect estimation through the ESA signal that must be converted into mobility with mathematical approximations.

The stability against sedimentation is a critical parameter to assure the uniformity of the suspension during a period of time sufficient for handling and shaping until a green body is formed. The tendency to sedimentation can be evaluated by visual inspection filling graduated tubes with suspensions prepared at different conditions and measuring the sedimentation front. There exists, however, a specific instrument to evaluate any changes in the stability of a suspension contained in a tube based in the multiple light scattering (MLS) of a laser beam that moves along the height of the tube periodically during the desired time (75,76,107,108). Variations in the transmitted and backscattered light at the top and the bottom of the tube indicate changes of stability, including sedimentation, creaming, bubbling etc. Sedimentation tests can be done with dilute or concentrated suspensions, although in concentrated ones the transmission may be too low to detect changes. Figure 10 illustrates the measuring principle of the sedimentation analyser (a), the sedimentation front along time by visual inspection (b), and the experimental curves (c) determined for a suspension of coarse particles of bioactive glass measured every 5 min up to 1h (109). As the particles settle the amount of light backscattered becomes higher on vessel's middle and bottom, whereas at the top of the cell the suspension clarifies and the backscattering decreases.

In practice, most processes need the preparation and characterisation of concentrated suspensions and thus, the rheological properties are the most important indicators of the stability. In principle, the viscosity must be as low as possible for the highest possible solids loading in order to reduce the amount of water to be removed during drying. This is essential in shaping to reduce shrinkage and to achieve the maximum green density. In general, the suspensions must be slightly shear thinning so that the viscosity at rest remains high to retard sedimentation. Shear thickening has to be avoided because the increase of viscosity on shearing difficults or impedes mixing and milling, on one hand, and the wet body has too low viscosity and consistency leading to deformation during drying. Shear thickening is less common than shear thinning and is usually associated to the presence of irregular, non-equiaxed particles and high solids concentrations. This is frequent in the case of traditional ceramics, with characteristic plate-like particles, or suspensions of fibres or elongated particles. As an example, Figure 11 shows the effect of attrition milling of rod-like particles of on the rheological behaviour of mullite

suspensions. In that case the average size changes from 1.8 to 0.7 μm and the aspect ratio decreases from 0.6 to 0.3 and the strong shear thickening of suspensions prepared with starting powder practically disappears when they are attrition milled (110).

Except in the case in which high pressure is applied for shaping, suspensions without yield point or a yield as minimum as possible are preferred. Similarly, time dependent rheological behaviour reduces the control of the composition and the reliability of the process, for example in slip and pressure slip casting, where suspensions with higher viscosity, yield stress or thixotropy promotes an increased casting rate with a loose of control kinetics and a reduction of the green density (111,112).

The basic concepts and practical implications of rheology are described in many books and reviews so that the reader is referred to them for more information (113-117). The present work will focus on the implications of rheology in the preparation and optimization of the suspensions and the correlation between processing parameters and rheological behaviour assuming that the reader is familiarised with the basic concepts of rheology.

The suspension stability can be evaluated using different techniques that provide complementary information, the most important being the particle size, zeta potential, sedimentation and rheological behaviour. Figure 12 shows the strong relations among particle size, zeta potential and viscosity for alumina suspensions prepared to 75 wt% solids and different concentrations of a poly(acrylic) acid based polyelectrolyte (0.5, 0.8, 1.0, and 1.5 wt%). As it can be seen there is a perfect match among the values (118). For insufficient concentration of deflocculant the zeta potential is low and the viscosity is high due to the presence of agglomerates, which are evident from the large particle size measured. For the optimum deflocculant content the viscosity reaches a minimum that corresponds with a maximum of zeta potential. Particle size also decreases as they are well dispersed. An excess of deflocculant may lead to a small reduction of zeta potential and a small increase of viscosity.

However, it must be noted that particle size and zeta potential are measured generally with dilute suspensions. However, in most ceramic operations concentrated suspensions are desired. As the solids loading increases the interactions among particles also increase and in some cases this may mean that the concentration of deflocculant necessary to provide a good dispersion is higher than predicted from zeta potentials. It is worth noting

that zeta potential provides only information about the electrostatic contribution to the stability, but polyelectrolytes have also associated a steric contribution due to the adsorption to the particle surface and this contribution becomes increasingly important as particles approach each other. This explains why sometimes diluted suspensions dispersed with polyelectrolytes have moderate values of zeta potential whereas the corresponding concentrated suspensions have good rheological behaviour.

3.3.3. Parameters influencing the dispersion

As it can be observed in the flow chart of Fig. 5 the first step of ceramic processing is the modification of the starting powders for improved processing and shaping, which can be achieved by the so-called beneficiation processes. Most of these are carried out using suspensions and have a key role not only in their stability but also in the shaping performance. Beneficiation processes include the operations described in the following.

Milling. During milling the particle size distribution becomes narrower and the average size decreases either as a consequence of an effective size reduction or due to the breaking down of agglomerates. Therefore, the tendency to settle is lower so that the stability against sedimentation is larger. At the same time the size reduction produces also an increase of the specific surface area, i.e. of the surface activity of these new fresh surfaces and particles tend to reaggregate and therefore the viscosity increases (61,119). Then, there is a critical time at which measured particle size reaches a minimum and above which it tends to slightly increase again. The selection of the suitable milling time must be a compromise between milling efficiency and the possible contamination from balls and mill walls. In general, for technical ceramics, with particles sizes in the submicrometer size range ball milling does not provide the energy required to fracture particles but only to disperse agglomerates with a relatively low effect on the surface area, thus usually leading to less viscous suspensions.

Mixing. Mixing is a basic operation when more than two components are present, which are most of the practical situations. To assure the uniformity of multicomponent systems mixing is critical (120). In technical ceramics, it is customary to use submicron-sized particles and different kinds of mills with different power and dispersion efficiency can be employed to achieve the maximum dispersion of the components. However, in that case, the mills can break down agglomerates to more or less extent but there is not true

milling due to the small initial particle size. This has, however, a strong effect in the rheology. Figure 13 shows the flow curves of submicron-sized Si_3N_4 aqueous suspensions with Al_2O_3 and Y_2O_3 as sintering aids prepared to a solids loading of 65 wt% using different dispersing methods, i.e. agitation with helices, ball mill, centrifugal mill, and attrition mill. The last produces the lowest viscosity but the added cost of milling, the cleaning requirements and the greater contamination make this route less adequate than ball milling, in spite of its slightly higher viscosity (121).

Sonication. Another aspect is that the concentration of deflocculant required to provide stability increases with surface area. In the case of nanoparticles the ratio surface/volume significantly increases and the solids loading that can be prepared maintaining good flowing properties is much lower. Deflocculant contents required to disperse submicron sized particles is typically lower than 1 wt% on a dry solids basis, whereas in the case of nanoparticles the maximum solids loading while maintaining flowability seriously reduces and the required concentration of deflocculant increases. For example, concentrated suspensions of nanosized titania with up to 30 vol.% solids could be prepared with 4 wt% deflocculant (122).

In recent years, the use of sonicators has become increasingly popular. In fact, sonicators not only have a strong dispersing power but also the contamination is much lower because there are no shearing parts of mixers and tools. However, sonication produces local overheating that can promote aggregation. When the viscosity is low sonication improves the dispersion and reduces the viscosity even more. However, if the viscosity is high or time-dependent, or the particles are not fully dispersed, sonication has a deleterious effect and the slurry becomes a paste. In addition to the suspension properties the operation mode can also help to achieve better dispersion. One example of this can be seen in Figure 14, in which the aspect of two green tapes of Al_2O_3 prepared with the same aqueous suspension (53 vol.% solids dispersed with a polyacrylic emulsion) using continuous (a) and pulsed sonication (b) is compared (123). The use of ice baths or temperature controllers is highly recommended for sonication in order to avoid overheating. For suspensions with moderate or low viscosity the dispersion is highly effective allowing the homogeneous dispersion in a few minutes of suspensions that with a ball mill could require several hours milling. These great advantages justify the increasing application of ultrasound in the suspension preparation.

Order of addition of the components. Another practical aspect to be considered in the preparation of suspensions with several components is their order of addition. In many previous works it has been demonstrated that this can lead to important differences in the rheology that persist after sintering, resulting in inhomogeneous compacts (124). Better uniformity is generally achieved when the minor component is first added and once it is dispersed the major phase must be incorporated. In any case, the deflocculant needed for each component must be added prior to the corresponding powder (125). Otherwise, a flocculated suspension will be obtained that will be hardly redispersed.

Similarly, when different additives are necessary in the suspension, the order of addition of the components is critical. The dispersing agent should be added before the particles and before any other organic compounds to prevent competitive adsorption among them onto the particles surfaces. This was a well-known problem in tape casting technology, in which suspensions with different types of additives (solvents, deflocculants, binders, plasticizers, surface modifiers, defoamers, etc) are used (126-129). Several works demonstrated that when deflocculant was added first the viscosity was lower than when there was simultaneous addition of deflocculants and binders (130-132).

Solids loading. It is well known that the viscosity of concentrated suspensions increases exponentially with the increase of volume fraction of solids (133-138). There are several models for predicting the variation of viscosity with the volume fraction of solids. One of the most frequently employed in ceramic suspensions is the Krieger model and the modified model by Krieger-Dougherty. These models include the maximum packing fraction, which is the maximum content of particles that can be prepared in practice and above which viscosity sharply increases toward infinite. These models are very useful since they allow to predict the viscosity of a suspension at any solids content. The equation proposed in the Krieger-Dougherty model is

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-2.5\phi_m}$$

which relates the relative viscosity (that of the sample with regards to that of the solvent) with the volume fraction ϕ of solids in the suspension and the maximum packing factor ϕ_m , that is, the volume fraction value where viscosity increases toward infinity. The coefficient 2.5 accounts for the sphericity coefficient included in the pioneering Einstein equation. In the modified Krieger-Dougherty model the exponent becomes n and the values can be different to 2.5, corresponding to deviations from sphericity.

Particle size and shape. Particle size and shape of the starting materials are modified during milling and mixing, which tend not only to reduce the particle size but also the shape factor, as shown above. In general, coarse particle sizes have a great effect on the stability of the slurry, which tends to settle in short processing times. In addition, coarse particles are usually irregular in shape favouring their interaction and accelerating sedimentation. After milling, the lower particle size facilitates the stability over longer times, although this usually needs the deflocculant content to be readjusted as the surface area tends to increase. In addition, comminution can modify significantly the shape of the particles, leading to increased sphericity, which has a strong effect in the rheology of the suspensions. Clarke (139) studied the rheological behaviour of concentrated suspensions and observed that viscosity significantly increased and the maximum packing fraction decreased as the particles shape deviated from sphericity so that the preparation of concentrated suspensions became more difficult. Figure 15 illustrates a typical variation of viscosity with fraction of solids for suspensions prepared with particles of different shapes, from nearly spherical to grains, platelets and rods. Spherical particles allow the preparation of suspensions with above 40 vol.% solids whereas the maximum content achievable for rod like particles is about 20 vol.%. This is an important factor to take into account in practice.

Granulation. Granulation processes consist of the controlled formation of agglomerates of desired characteristics with better compressibility and deformability than the isolated particles, which are essential to achieve a uniform compaction during pressing operations. The main processes are pelletisation, freeze drying and spray drying. Pelletisation is the physical process from which a raw material is intentionally agglomerated into pellets by rotation in the presence of some humidity and/or a binder. The last technique is the most frequently used in ceramics, for example for the preparation of granules with excellent flow properties as desired for filling moulds in pressing operations. In spray drying, a suspension is fed into the drying chamber and atomised by pumping it at high pressure through a multi-nozzle array, after that the upward spiralling droplets encounter hot air and are fed through a diffuser into the chamber (140). The uniformity of the granules is a function of the dispersion properties of the suspension and the physical parameters applied during spraying (141-143). Another technique for the granulation of powders is freeze drying, but the obtained granules have larger pores size and concentration, so that very light granules can be produced (144-146). Sometimes the preparation of

concentrated suspensions of mixtures may be complex due to the differences in shape or size, the hydrophobic character of one of the components, etc., or simply when a homogeneous mixture is required for pressing. In the last years, the densification with fast sintering techniques such as SPS, flash sintering, or microwave sintering has received great attention mainly due to the lower temperature/time cycles used in the process that make it possible to obtain dense parts without exaggerated grain growth and to sinter materials that could decompose by conventional techniques, such as ceramic composites containing graphene or graphene oxide. In such cases, colloidal processing allows the possibility of preparing less concentrated suspensions with optimized rheological behaviour that are subsequently freeze dried leading to mixtures of powders with better uniformity than those obtained by dry mixing (147-149).

Bimodal and nanostructured suspensions. Another aspect is the multimodality. Very few studies concerning the modelling of rheological behaviour of suspensions with multimodal size distributions have been proposed. Farris established a model that related the viscosity-concentration behaviour of multimodal suspensions of rigid particles to the behaviour of the unimodal components (150). Contrarily to the lack of modelling studies for multi or bimodality, there are many experimental works reporting the use of bimodal distributions to improve the packing efficiency and thus, the density of shaped parts. The starting point is the Furnas model (151-153) for the packing of particles with different size, in which the smaller particles could fill the voids left among the larger particles during feeding and mould filling, especially when it is accompanied of vibration to improve particles flow. The requirement for small particles to enter into the voids left by the coarse ones is that there should be a significant difference of sizes, typically by 60-80%. Tari et al (154) prepared alumina suspensions, mixing powders with two different average sizes demonstrating that the mixtures allowed the preparation of suspensions with solids loadings as high as 70 vol.% and obtained slip cast bodies with very high relative density (78%). Similar observations have been done for mixtures of Al_2O_3 -Ni prepared by slip casting, with maximum green densities of 70 vol.% (155).

Bimodal suspensions with one phase in the nanometer size have received increased attention in the last years. Nanostructured ceramics and composites are being used in many different domains, such as chemistry, electronics, magnetic materials, biotechnology, etc. The new properties associated to the small size can strongly differ from those of the bulk conventional material. However, its processing becomes more

difficult due to the worse dispersibility of smaller particles as a consequence of their higher surface area. In some technologies the final user buys stable suspensions containing the nanoparticles but in most cases they have low solids contents and the packing density of the obtained materials is poor. This is the case, for example, of most commercial suspensions of nanoparticles supplied as feedstocks for the production of thermal barrier coatings or other thick coatings by plasma spraying techniques (156). One possibility to increase the solids content of available suspensions is to disperse solid nanoparticles in those colloidal suspensions. In this way Benavente et al (157) prepared bimodal suspensions dispersing fine zirconia powders (by 100 nm) in a colloidal suspension of nanosized ZrO_2 of around 15 nm with up to 30 vol.% solids for slip casting obtaining green densities of up to 57% of theoretical. The same processing strategy was followed by Vicent et al (158) to increase the concentration of TiO_2 suspensions by dispersing commercial nanoparticles in a colloidal suspension of the same titania to obtain free-flowing micrometre-sized nanostructured granules by spray drying, which had much higher uniformity than those obtained with the diluted commercial colloidal suspension. Mixtures of nanosized titania with submicron-sized zirconia also demonstrated to give better uniformity and better mechanical properties of the final coatings produced by atmospheric plasma spraying (159). Santacruz et al. (160) achieved concentrated suspensions of nanoparticles by heating the suspensions in a bath at 50°C for between 1 and 4 days depending on the desired final solids content. The higher packing density reached with bimodal size distribution makes easier the sintering process and usually leads to denser bodies or similar densities at lower sintering temperatures. In the case of bimodal feedstocks for thermal spray the obtained granules were also more homogeneous and without the donut type particles appearing in the diluted suspensions, leading to homogeneous microstructures, although the final density in this case was not significantly higher.

3.3.4. Heterocoagulation

When two or more components coexist in the suspension, each one will have a different electrokinetic behaviour and thus, they may display different isoelectric points. In that case there will be also a region of pH between the isoelectric points of the different components where they have an opposite charge sign and consequently, they will tend to

attract electrostatically leading to the phenomenon referred to as heterocoagulation. When particles have similar size and shape this leads to undesired agglomeration that should be avoided. However, when preparing mixtures, the isoelectric points of the components may be very different. As a general rule the isoelectric point decreases when the charge of the metal increases. Typical values of isoelectric pH are above 11 for MO oxides, 8-9 for M_2O_3 , 6-8 for M_3O_4 , and 2-5 for MO_2 . Hence, for mixtures of Al_2O_3/ZrO_2 the isoelectric points are typically 9 and 4-6, respectively, which implies that within that at intermediate pHs there will be heterocoagulation. Stable suspensions would then require to be prepared at $pH < 3$ or $pH > 10$, which are extreme conditions not assumable in practice. However, when particles are dissimilar in size or shape, heterocoagulation can be used to promote controlled clustering or to produce core-shell structures. One common example is the preparation of mixtures of alumina with silica using nanosized silica or even precursors that promote the reaction and formation of silica at the surface of alumina particles (161-163). During thermal treatment at high temperature the shell layer of silica promotes the formation of mullite by reaction sintering with the alumina core. The same methodology has been also used combining submicron-sized alumina with nanosized titania, which react to produce aluminium titanate. In this case sintering rate determines the final microstructure of the composite. It has been shown that conventional sintering leads to a biphasic microstructure but formed aluminium titanate grows above the nano range as a consequence of the long-time associated with sintering (164). However, when fast sintering techniques are used, such as SPS, the process is very fast and the reacted aluminum titanate has no time to grow, remaining with very small grain size (165). The same approach has been used to promote the formation of nanoparticles of zirconium titanate in mixtures of zirconia and titania (166).

These examples illustrate the possibilities of heterocoagulation between particles of different size. Another application is the use of particles with very different shape. One such example is the coating of carbon nanotubes with zirconia nanoparticles. Garmendia et al. (167) synthesised zirconia by a hydrothermal route onto carbon nanotubes and the composite powders were later mixed with submicronic zirconia and subsequently slip cast in plaster moulds. The zirconia-coated nanotubes were dispersed with polyethyleneimine and the isoelectric point shifted up to $pH \geq 9$ whereas the zirconia particles constituting the matrix was dispersed with a polyacrylate and the isoelectric point shifted down to pH 3, so that heterocoagulation was possible in a broad pH range from 3 to 9. Dusak et al (168)

prepared silica-coated maghemite composite powders demonstrating that it is possible to produce nanoclusters assembling nanoparticles with controlled size.

The calculations of the interparticle interactions can be done in the light of the DLVO theory. Uschauer et al (169) developed software (called Hamaker-2) showing the benefit of this predictive approach applied to mullite production by heterocoagulation and its suitability compared with the experimental results. The software Hamaker-2 was developed at EPFL (Lausanne, Switzerland) and is freely available (it can be downloaded at <http://hamaker.epfl.ch>).

3.3.5. Additives for ceramic processing

All ceramic processing steps involve the use of substances capable of maintaining the structure of the suspension and the green body, the so-called processing additives (8,11,21,84). There is a complex nomenclature to refer the multiple functions and composition of the additives. Fig. 16 shows the main processing additives used in ceramics. In the simplest approach processing additives can have two basic functions: 1) to separate the particles from each other, or 2) to approach particles, i.e., dispersion or agglomeration that are accomplished by a reduction or an increase of viscosity, respectively. The first additive is the liquid medium in which particles are dispersed. Some processes have preferentially employed organic solvents, either in comminution (e.g. attrition milling) or shaping, as in tape casting or electrophoretic deposition. However, in the 90s there was a growing interest in developing aqueous processing methods, because of the obvious environmental, economic and health advantages of water (126,170-172). Moreover, aqueous suspensions with low viscosity can be prepared to very high solids loadings. In opposition, water has some inherent problems, such as the low evaporation rate, which creates drying gradients that can lead to differential shrinkage and eventually the cracking of the material, the ability to form hydrogen bonds that favour the surface oxidation, easier warpage and lower consistency in the absence of organic binders. An additional problem relates to the much lower amount of available additives for aqueous processing, since there are much more organic compounds and polymers soluble in organic solvents than in water. In addition to these points, the user has also a lack of information and expertise because some processes have been traditionally performed in organic solvents, especially for advanced ceramics, such as in tape casting, electrophoretic deposition, low-pressure injection moulding, and the few additives and

auxiliary elements available are protected by the suppliers, which give a very restricted information (tradenames, general type of molecule, etc, without specifying the specific molecules, molecular weight, etc.). All these parameters make difficult the complete transference to water systems in technologies like those mentioned above, Some studies have compared the performance of aqueous and non-aqueous tape casting for the same system, such as Nahas et al. (173) who achieved alumina tapes with similar properties of those obtained by non-aqueous tape casting, while more recently Michálek et al. (174) stated that for the production of multilayer systems ethanol-based slurries led to higher density and performance. When immersed in a liquid, particles are subjected to multiple body interactions and the stability depends on the tendency to settling due to gravitational forces and the tendency to agglomeration arising from attractive London-van der Waals forces. To overcome these destabilisation effects deflocculants are added to maintain particles far apart by action of charged surfaces (electrostatic mechanism), by adsorption of polymers that promote steric hindrance or by an electrosteric mechanism resulting from the adsorption of charged polymers (polyelectrolytes). Depletion occurs adding non-adsorbing polymers that promote the volume exclusion of particles and can be attractive at very small separation distances, or repulsive, for longer separations.

Another big group of additives include all the additives that promote flocculation or coagulation, in which the suspension destabilises by the formation of a physical gel, associated to the loose of stability of the particles, or by chemical gelation occurring either through the cross-linking of monomers with a catalyst or by thermal gelation, in which cases a polymer network is formed that retain the particles inside. Binders are additives that contribute to viscosity acting as thickeners or forming polymeric bridges that provide adhesion among particles and strength to the green body. Plasticizers are small chains that decrease the glass transition temperature of the binder and provide flexibility, necessary for handling cast tapes. In all cases, suspensions must be firstly dispersed prior to the addition of other additives required for the formation of structures in order to prevent competitive adsorption between the additives (132).

4. Shaping ceramics using suspensions

4.1. Taxonomy of shaping processes

In an exciting review published in 2008, Evans (175) demonstrated the relevance of an integrated approach to processing of materials and claimed the existence of at least 70 ways to make ceramics. The broad variety of manufacturing processes and the multiple variations of those processes, together with the long list of specific terms and abbreviations make their classification difficult and confusing. This ambiguity helps to defend proprietorship, as it also happens with other specific topics, for example the large number of terms associated to processing additives discussed before. Evans claims that the use of a taxonomy serves to integrate all materials, not only ceramics. From the textbooks on materials processing (176,177), the forming processes have been traditionally divided into four categories: casting processes, forming processes, machining processes and joining processes. Evans maintains in general those classes of processes and separates the free forming processes but pointing out that they could be loaded individually into one of those four classes. The classification of Evans aims to identify similarities and includes new forming methods, grouping them into the following classes of processing methods: 1) casting/solidification processing, whose basic principle is the casting or pouring of a slurry or paste onto a surface that determines the shape; 2) deformation, based on the change of shape by plastic deformation, as in superplastic forming, or the processing using preceramic polymers, as in fibre spinning; 3) machining/material removal, involving any operation of cutting, ablation, abrasion, etc.; 4) joining, which implies the assembly of pieces shaped separately; 5) solid free forming, in which the body is shaped without moulds. In the last case, many processes could be included in the first group as most of them employ a slurry.

Table 2 illustrates the most popular shaping processes making use of suspensions and representative references of pioneering works are given. There are two main groups of techniques, those based on the *direct casting* of slurries upon a mould and those produced without moulds (*additive manufacturing*). The manufacture of a ceramic body involves two complementary steps, the shaping method and the consolidation mechanism, which can take place simultaneously or not. There are different shaping methods using the same consolidation mechanism; for example, a suspension containing a gel-former can consolidate into a green body by pouring or casting in a mould or by injection moulding. A brief summary of the different processes is given below.

4.2. Direct casting methods

Direct casting shaping methods can be classified according to the consolidation mechanism into three general groups:

1) Fluid removal. The liquid can be removed by filtration through a mould or be lost without mould contact. The oldest and most widely used process is slip casting (31-35), which is based in the filtration of water from a slurry through a permeable mould by capillary forces that form a cake of the particles attached to the mould. The main limitation of slip casting is that wall thickness formation follows a parabolic law with time so that the packing efficiency decreases along the growing cake. The casting rate can increase with the help of external forces, such as centrifugation (178,179), the application of vacuum, microwave heating (180,181) or most frequently, by applying an external pressure, as in filter pressing and pressure casting (182-187). During filtration, water passes through the pores of the permeable mould and a cake of particles develops. Hence, shaping and consolidation take place simultaneously.

Fluid removal can be achieved also by free loss of the liquid without contact with a mould by evaporation or sublimation. Electrophoretic deposition (EPD) involves the solid/liquid separation as in filtration but in this case the particles move by action of an electric field (i.e. electrophoresis) and the liquid is stationary (188-191). After migration particles coagulate in the substrate, which is subsequently withdrawn and the liquid retained in the wet deposit evaporates.

Evaporation of the liquid after casting is also the basis of the tape casting process, which is a low-cost massive manufacturing process for making laminated materials with controlled thickness, usually from a few tens to a few hundreds of micrometres, for applications in the electronic industry, multilayer capacitors, etc. (192-195). A well-dispersed suspension is prepared containing binders and plasticizers to provide the desired consistency and flexibility. The suspension is spread onto a substrate and left to dry. Tape casting was traditionally employed for the manufacture of planar sheets using non aqueous suspensions, but during the 90s the use of water was preferred (126,170-172). However, water evaporates very slowly as compared with organic tapes so that the top side of the tape dries whereas the bottom is still wet. This creates a drying gradient that could provoke the cracking of the tape (196).

Other processes in which the material is deposited onto a substrate and left to dry are dip coating (197,198) and spin coating (199,200), normally used for the preparation of thin coatings in sol-gel technology or layers of few microns in ceramic technologies like capacitors or solid oxide fuel cells. Similarly, screen printing consists on the spreading of a slurry onto a substrate, which makes this technique very useful for application of enamels in tiles or to apply electrode layers in SOFCs (201). This kind of coatings can be also produced by spraying with a gun or with aerograph (202). Another group of techniques that could be considered in this category are thermal spraying techniques that are coating processes in which melted (or heated) materials are sprayed onto a surface. Among the different thermal projection techniques, the plasma spraying is the most directly related with the use of suspensions and precursor solutions since the feedstock can be in the form of powders (preferably spray dried, as in atmospheric plasma spraying, APS) or as a suspension (suspension plasma spraying, SPS) or even a precursor solution (solution precursor plasma spraying, SPPS). The feedstock is heated by electrical (plasma or arc) or chemical means (combustion flame) and fed into a plasma torch, where it vaporises and is propelled to the substrate, in which the splats (condensed drops) consolidate forming a thick coating (203-207).

Another way to remove the liquid is by sublimation, which is the case of freeze casting, where a slurry is frozen and subsequently lyophilised to promote sublimation of ice (208-211). This technique has experienced a fast growth in the last decade for the production of materials with directional porosity.

2) Formation of a physical gel by coalescence of the particles inside the suspension via a percolating network of particles by flocculation or coagulation due to changes of pH and/or electrolyte (deflocculant) content. According to the theory of dispersion of lyophilic colloids the stability between particles can be represented by the potential energy interaction (interparticle potentials) as a function of separation distance. At very short distances particles approach until they enter into contact and fall into a deep well that is known as primary minimum. When this happens there are not repulsive forces to overcome the always present van der Waals forces and a strong agglomeration occurs. This interaction in the primary minimum is referred to as coagulation. The energy versus distance can show another minimum at longer separation. In this case agglomerates can be also formed but the particle surfaces do not touch each other but are separated by some intermediate molecules (of the solvent, deflocculant, etc.). At this point a less deep well

appears called secondary minimum. Particles attracting in a secondary minimum experience the so-called flocculation, which is reversible since there is not direct contact so that flocculated suspensions can be redispersed.

After shaping the consolidated body retains the suspension liquid, which is removed on drying and is accomplished by a variable shrinkage depending basically on the solids content of the starting suspension and the concentration of additives. The most common processes leading to physical gelling are based on the flocculation of the slurry by addition of counterions, like in the vibraforming process (212,213), or the coagulation of the suspension in a primary minimum by shifting the slurry pH toward the isoelectric point as in the coagulation casting methods (214-217). A different method was proposed by Lange using isostatic pressure on a concentrated slurry inside a mould, the so-called isopressing method (218). Other group of techniques is based in the physical gel formed because of a change of temperature in a slurry containing polymeric binders. This mechanism is the basis of temperature induced forming and temperature induced gelation (219-223). Another process based on the coagulation is the hydrolysis assisted solidification HAS process, where the consolidation takes place due to the hydrolysis of aluminium-nitride powder, which causes dramatic increases in the viscosity of the ceramic suspension (224,225).

3) Formation of a chemical gel by polymerisation of monomers or thermogelation of polysaccharides with a percolating network of additives. In this case, the structure is a consequence of polymerisation (i.e., a chemical gel) and particles collapse inside that network. As in the case of physical gelation, the as-shaped body retains the liquid that must be subsequently removed producing a drying shrinkage. The pioneering research on novel near-net shaping methods started with the in-situ polymerisation methods, which started with the development of the gelcasting process in the early 90s by Janney and Omatete (226,227). The pioneering works used organic solvents and toxic monomers, but they evolved soon towards less toxic systems and aqueous media and different shaping approaches (228-231). The process was later extended to polysaccharide gelation, based on the formation of a gel due to the cross-linking of polymer chains and their association into double helix aggregates on cooling below its glass transition temperature (232-237). The most widely used polymers for gelcasting include seaweeds (agar, agarose, carrageenan), gelatin and gums (locust bean gum, xanthan gum, etc). There are also polysaccharides that gel on heating, the most popular being the methylcellulose

derivatives, but their gel strength is much lower. Other polysaccharides, such as alginates, form a gel by chemical bonds by action of multivalent ions, such as Ca^{2+} . The Ca–alginate junction zones join two chains of polymer forming the so-called egg-box structure (238-240). Starches have been widely used for the shaping of porous ceramics in the so-called starch consolidation (241-244). Starch granules are insoluble in water below the gelling temperature but there is water absorption resulting in a slight swelling. After burn-out and sintering a porous body is obtained. Other additives used for the consolidation of ceramics are pectins (that are also polysaccharides) and proteins, with egg ovalbumin as the most representative. This is the basis of the protein forming processes (245,246).

The origin of all these techniques can be found in the injection moulding process (247-249), where a ceramic powder is dispersed in a polymer carrier and injected at high pressure into a mould in which the blend consolidates on cooling if a thermostable polymer is used or on heating when using thermosetting polymers. Typical temperatures are of 80-120°C and pressures are about 40-60 MPa. The use of waxes allows reduction of the viscosity and the pressure, this being the origin of low pressure injection moulding, (LPIM) (250-253). After that, the LPIM process was adapted to water systems, making use of the thermogelling additives used for aqueous gelcasting. The pressure employed in that case is typically well below 1 MPa. There are other related shaping techniques such as chemorheology, based in the flow and gelation of reactive polymers (254,255), or self-hardening, in which a slip containing a small quantity (2-3 wt%) of epoxy resin and hardener, is self-hardened on heating at 70-80 °C (256).

In general, these shaping methods are originally intended for the manufacture of dense bodies except freeze drying, whose main interest is in the production of materials with aligned porosity. However, all these methods can be adapted for the production of porous ceramics by introducing sacrificial templates, or by impregnation of a polymeric sponge or introducing a surfactant and a gel former able to retain the bubbles during consolidation, etc. The main methods for the manufacture and performance of porous ceramics has been extensively reported by Studart et al. (257) and Hammel et al (258).

Regarding the process performance and the final green densities, the conventional shaping processes can use either water, which is preferred in slip casting and derived processes (pressure casting, centrifugal casting, gelcasting, DCC, short-repulsive forces, and freeze casting) or organic solvents, which are often used in tape casting, temperature induced flocculation, electrophoretic deposition, and low-pressure injection moulding.

All the methods require a low content of deflocculant, just to cover the particles surface, typically 0.3-1.0 wt% for submicronic powders, and 1-4 wt% for nanoparticles. The green densities are also variable, the highest always being for slip casting, due to the low draining rate associated to the filtration process that allows the rearrangement of particles toward the moulds wall during casting. Typical densities for slip casting are in the range of 60% TD or above. In pressure casting, the much faster kinetics leads to somewhat lower densities, normally 1-2% lower than in slip casting. The processes based on pouring use solids contents as large as possible but in most of them there is a larger concentration of additives (gelling, coagulating, etc.) so that the green densities tend to be lower than 60% and there is also a significant drying shrinkage, which can be of up to 5% or even more. In tape casting, the solids loading must be very high in water to reduce drying gradients, but in organics the solids loading is less important as there is a fast drying just after casting. The densities are lower than in previous processes and the content of additives is higher (may be 10-15 wt%) so that careful drying and debinding are needed. Due to the lower green densities and the needing of debinding in some cases the sintered densities are also lower 96-98% whereas in slip casting it is easy to reach 99% of theoretical density.

4.3. Additive manufacturing

Additive manufacturing (AM) is an addition type technology in which bulk objects are produced layer by layer from 3D model data through a computer-aided design (CAD). It is also known as rapid prototyping (RP), solid free form (SFF) or 3D printing. These technologies have experienced a fast development from its initial conception in the 80s due to their ability to design very complex geometries with very high precision and maximum material savings. A great variety of materials have been produced by AM techniques, including metals, ceramics, polymers along with combinations in the form of composites, hybrid structures and laminates and FGMs (259-264). Moreover, these technologies not only have a great impact on manufacturing performance but also in business and management, which have a deep effect on society (265,266). The most common applications in metals are related to advanced metals and alloys for aerospace industry, whereas in the field of ceramics is the manufacture of 3D scaffolds. AM allows dense or porous objects to be obtained through three types of techniques (267): 1) those not capable of producing dense structures, 2) techniques producing fully dense monolithic

ceramic bodies with restriction in dimension, and 3) techniques that can produce fully dense monolithic ceramic bodies without restriction in dimension. Many AM technologies are mainly used for the production of porous structures for several reasons, the most important being: 1) the possibility of reproducing the desired structure with a precise control of dimensions, shape and number and characteristics of pores, 2) the superior capacity to reproduce fine filigree structures, and 3) the availability of other simplest and more economical techniques for the manufacture of dense parts.

AM technologies can be divided into two categories (267): *direct*, where the material is directly deposited only in the position giving the desired shape of the final object, and *indirect*, in which a layer of material is first deposited, subsequently the cross section (slice) of the part is inscribed in the layer and, after completing all layers to complete the process, excess material surrounding the part is removed to release the final object.

4.3.1. Indirect AM Technologies

Indirect technologies are based in the AM of the object and the subsequent thermal treatment to obtain the final properties. These technologies are faster and are suited for the manufacture of parts with large overhangs since the excess material forms a support to the successive layers. The major drawbacks are the restrictions in shape due to the necessity to remove the excess material and the limitations using multimaterial systems. A first group of indirect AM techniques make use of powders, the so-called Powder-Based 3D Printing (P-3DP) methods, in which the structure is obtained by the successive deposition of layers of a flowable powder. The most common methods of this group are; “Three-dimensional printing” (3DP) (268,269) and “Powder-Based Selective Laser sintering” (PSLS) (270-272): The P-SLS process works similarly to the P-3DP one, with the difference that the cross sections of the part to be built are inscribed by means of a laser beam. In 3DP an organic binder solution is sprayed through printheads onto selected regions of a powder bed surface producing solidification. Subsequent layers are deposited and spread on the previous layers until the object is formed. The main advantages refer to the high flexibility of geometrical design without the addition of supports. It is better suited for porous designs. In SLS different layers of powder are spread and the part is obtained after different runs of heating and joining with the laser source.

AM technologies can use also liquid feedstocks (slurries). The slurry content can be 3D printed by either photopolymerisation, inkjet printing or extrusion. The main methods

are: “Slurry-Based 3DP” (S-3DP) or “Layer-wise Slurry Deposition” ((LSD) (273,274), in which a doctor blade deposition is combined with the binder jetting technology, and “Slurry-Based SLS” (S-SLS), where a ceramic slurry is used to increase the powder packing density in the powder bed; “Stereolithography” (SL), based on the photopolymerisation of a liquid resin filled with ceramic particles, in a layer-by-layer fashion (275-278). The major advantage of SL process is the possibility to obtain very complex shapes with smooth surfaces, although the needing of supports is a limiting factor.

Finally, another group of techniques make use of bulk solids, which includes the “Laminated Object Manufacturing” (LOM), in which 3D building parts are obtained by the lamination of paper, tapes, or similar shapes at low-medium temperature and pressure (279-281). Thin sheets of materials are cut into cross sections according to sliced digital CAD models and the object is obtained by layer-wise adhesion of several sheets pre-coated with adhesive agents. The main advantages are the possibility to produce large scale pieces in a fast and accurate way due to the low deformation induced during the process. The main drawbacks are the possibility of delamination, the anisotropy along the planar directions and the building direction and restrictions in shape, since laminated sheets are used.

4.3.2. Direct AM Technologies

In direct AM technologies the properties of the object are obtained during shaping without further treatments. The advantages of direct AM over indirect AM are that no removal of excess material is needed and thus there are much lower geometrical limitations and this allows the production of complex structures of composites of different types of materials. The main drawbacks of direct AM are that they require support structures for overhangs above a certain dimension, these processes are slower and can have shape restrictions since the material is deposited in specific positions in a sequential fashion. The most popular technologies of this group are “Direct Inkjet Printing” (DIP), based on the successive deposition of individual drops of a slurry by a printing head (282-284), and the group of techniques based on the extrusion of a viscous ceramic paste through a nozzle forming a filament, namely “Filament Extrusion 3D Printing”, “Robocasting” (285-287) or “Direct Ink Writing” (DIW) (288-290), and “Fused Deposition Modeling” (FDM) (291-293). In DIW the designed shape is obtained by direct writing of a wax or a thermoplastic filament filled with ceramic particles with moving nozzles layer by layer

until the part is complete. In DIW the extruder is not heated. Debinding and sintering then follow so that the part is free of organics. DIW is very versatile as freestanding structures with high-aspect-ratio walls or spanning parts can be produced without supports. FSD makes use of thermoplastic polymers in the form of filament, which is continuously extruded within a moving nozzle at a temperature just above its melting point. The extruder is heated to melt the material, which solidifies immediately over the previously printed layer.

Figures 17 and 18 show some pictures demonstrating the great capabilities of these AM technologies in the production of porous and dense materials with very complex shapes and filigree structures that cannot be produced by conventional direct casting techniques. On one hand, Figure 17 shows several parts produced by indirect AM technologies, including (a) ceramic heat exchangers obtained by lithography-based ceramic manufacturing (294), (b) some pieces of alumina built up by indirect selective laser sintering and post processing (295), (c) porcelain pieces by layerwise slurry deposition (273), (d) open cell SiOC multicomponents obtained by stereolithography (296), and (e) in-situ synthesized MAX-phase composites realised by laminated object manufacturing (297). On the other hand, some examples of the capabilities of direct AM technologies can be seen in Figure 18, such as: (a) 3D fine scale ceramic components formed by ink-jet prototyping process (298), (b,c) three dimensional structures formed by direct ink writing (299), (d,e) calcium phosphate scaffolds fabricated by robocasting (300), (f-i) and advanced electroceramic components by fused deposition technique (301). All these pictures demonstrate the great feasibility of AM technologies in the production of very complex shapes and porous objects that could not be obtained by conventional shaping techniques.

4.4. Tailored microarchitectures. Layered ceramics

Modern engineering applications require the use of new materials with tailored designs and properties not attainable by conventional single materials. In this context, the development of simple and reliable methods for the manufacture of composites has gained interest for the preparation of complex-shaped parts that can satisfy a specific functional property associated with the main application while the complex structure provides other capabilities and properties, either structural or functional. As stated throughout this review, one of the major drawbacks of ceramics is their difficult

processing and lack of reproducibility because of defects (pores, agglomerates, etc.) present in the microstructure. These defects can lead to low and variable values of fracture strength of the sintered specimens and lower reliability. The most popular way to produce better ceramics has been the careful control of processing and the development of colloidal processing routes (302). In the last years, another approach has been the design of “flaw-tolerant” ceramics, mainly based in “bio-inspired” layered architectures (303).

A simple classification of ceramic-matrix composites (CMCs) can be seen in Figure 19. CMCs can be formed by a bulk structure with multiphase composition with secondary dispersed phases into a matrix, or can be arranged into tailored architectures built up from layers. This is the case of laminates, which in the simplest case can be a coating onto a substrate, or there can be layers of alternating composition (ABABAB...) or a continuous variation of composition to produce the so-called functionally graded materials (FGMs). In addition, these changes can include different ceramic phases, different families of materials (ceramic reinforced with carbon derivatives, metals, polymers, etc) or different porosity. In general, classification of these ceramic-ceramic composites is done according to the geometry of the second phase, this giving place to ceramics reinforced with particles, platelets or fibres, and whiskers. These materials will have an intrinsic reinforcement associated to the effect of the second phase, that is, the materials properties and the microstructural uniformity. The second group of materials is characterised by the presence of interfaces between the layers that produce an extrinsic reinforcement mechanism.

Multilayer ceramics exhibit enhanced toughness and, higher energy absorption capability and/or non-catastrophic failure (303,304). There are two possible designs of laminates, depending on the fracture energy of the interfaces, which can be weak or strong. Laminates with weak interfaces display higher fracture toughness and much higher work of fracture than the monolithic counterparts due to interface delamination, in which the fracture of the first layer leads to crack propagation along the interface (305-307). This behaviour is referred to as graceful failure (304). The matrix layer is usually thicker and denser and provides mechanical strength, whereas the weak interfaces are carbonaceous phases, boron nitride, titanium carbides and borides, etc., and determine the toughness and the work of fracture. Laminates with strong interfaces exhibit crack growth resistance (R-curve) behaviour due to the microstructural design and/or the presence of compressive residual stresses, acting as a barrier to crack propagation (308-310). The reinforcement is

achieved by energy dissipation mechanisms such as crack deflection, crack branching and/or crack bifurcation. The most widely studied layered composite with strong interfaces is based in the system $\text{Al}_2\text{O}_3\text{-ZrO}_2$, which is composed by compatible phases that can develop residual stresses by two different ways, the mismatch of thermal expansion coefficients and the phase transformation of zirconia. In the first approach partially stabilized zirconia is used (311-313), whereas in the second one pure monoclinic zirconia without stabilisers is used (314-316).

A seminal paper by Claussen employed hot pressing to prepare sandwiches of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ and studied their toughness when the notch was inserted in the component under tensile stresses or under compressive stresses (317). However, most of the work performed on multilayer ceramics has been performed through colloidal processing techniques, due to the limitations of superposing the layers with a good dimensional precision at the interface by simply pressing. The most common procedures for the manufacture of multilayers for structural applications are the following:

1) ***Tape casting and lamination*** (318-320). In tape casting sheets of controlled thickness and composition have been mainly obtained using non-aqueous suspensions, with the incorporation of several additives, including deflocculants, defoamers, binders and plasticizers.

2) ***Sequential slip casting*** (321-323). In this case, a first layer is cast onto a permeable plaster mould and any subsequent layer is cast on the previous as-cast layer giving place to a perfect adhesion and a sharp interface with the advantage that no binders are used and thus, no debinding is required. The control of the casting kinetics allows obtaining layers in the desired positions and with a very high thickness precision.

3) ***Centrifugation***. Centrifugal methods were developed by Lange (324,325) using suspensions coagulated through the addition of salts so that no segregation occurred during centrifugation.

4) ***Dip coating of tapes*** (326,327). A simple method to combine thin and thick layers is by simply dipping the green tapes in a dip coating slurry of the desired composition. Layers as thin as 1-2 μm can be obtained by proper control of the slurry solids loading, immersion time and withdrawal rate.

5) ***Electrophoretic deposition*** (328-330). Thin layers can be formed by application of an electric field between two electrodes contained inside a diluted suspension that can be

also in water or in an organic medium. The main parameters controlling the thickness of the layers are the stability of the suspension (conductivity and zeta potential), the applied current density or voltage and the deposition time.

Figure 20 illustrates some of the main methods for the production of layered ceramics, as well as some possible microstructures attainable by those methods. On one hand, the figure shows the formation of different layers from the slurries by sequential slip casting. Suspensions with alternating composition ABABAB can be sequentially cast to produce a laminate. If the composition changes from one layer to another a FGM is formed. On the other hand, the most popular method for manufacturing laminates is tape casting. The lamination of different tapes leads to layered ceramics with similar thicknesses. However, there is the possibility to coat some of the tapes (or all) by dipping, so that thin layers alternate among thick layers. Some characteristic microstructures of the laminates produced by each method are shown in the figure. These pictures correspond from top to down to a multilayer alternating thick $\text{Al}_2\text{O}_3/\text{t-ZrO}_2$ with $\text{Al}_2\text{O}_3/\text{m-ZrO}_2$ (314), a FGM with gradual composition from pure Al_2O_3 to Y-TZP (331), a laminate composed of layers of Al_2O_3 , $\text{Al}_2\text{O}_3/\text{YTZP}$ and $\text{Al}_2\text{O}_3/\text{YTZP}/\text{Graphene oxide}$ (332), a laminate combining thick Al_2O_3 layers with very thin layers of YTZP (326) and finally, a laminate composed by YSZ layers comprising thin layers of YSZ and graphene oxide (327).

5. Concluding remarks

In summary, colloidal processing has experienced a continuously growing role in ceramic processing from its massive study and implementation from the early 80s. Figure 21 summarises the many aspects of the use and capabilities of colloidal processing of ceramics. Colloid science operates in most of the process stages, from the synthesis of pure powders with controlled size and shape, to the different methods for the transformation of raw materials through beneficiation processes and the shape forming into components, either bulk 3D parts, 2D substrates and coatings or specific microarchitectures built up by lamination of individual sheets. The most important issue in colloidal processing is the possibility to handle and control the interparticle forces during the successive processing steps thus allowing the reduction of the number and size of agglomerates in order to obtain more uniform microstructures. Moreover, there is a

great variety of materials that can be processed through a colloidal approach, including ceramics, metals, cements, carbon derivatives, etc. Colloidal routes are especially suited for mixtures, dispersions and composite materials, and have been successfully used for most ceramic matrix composites. It is of particular interest in the case of nanotechnologies and nanocomposites, where some components have sizes in the same range of colloidal forces, so that the colloid chemistry becomes a fundamental tool for the control of the stability. Regarding the composition of the materials, the models explaining the colloidal stability of suspensions refer to the formation of a double layer and in practice most ceramic suspensions are deflocculated with electrolytes or polyelectrolytes, the last having also a steric contribution to the stability. Although in principle this should be applied for oxidic surfaces, metals and non oxidic compounds actually oxidise at the surface and therefore they can be treated as oxides too. Further advantages of colloidal routes are the feasibility to produce either dense bodies or porous materials with different ways to introduce the porosity and resulting in different porosity features (random, directional, hierarchical, etc.). Finally, the fast growth of fast sintering techniques (spark plasma sintering, cold sintering, flash sintering, microwave sintering, etc.) makes essential the use of uniform powders and hence, the dispersion of different phases in mixtures and composites is much more efficient when using controlled colloidal processing routes. Consequently, it is possible to conclude that colloidal processing has reached a prominent position in ceramic science and technology from the pioneering works appearing 40 years ago so that currently all ceramists recognise the basic statement of this review: better ceramics can be obtained through colloid chemistry.

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RODRIGO MORENO

Captions to figures

Fig. 1. Flow chart demonstrating the successive interrelationships between ceramic processing, character, processing, and uses as stated by Pask (Adapted from ref. 3, with permission).

Fig. 2. Main factors and parameters of processing according to Pask. Processing steps appear divided in starting materials, formation of particulates, formation of assemblies, drying and pre-firing, and firing. Ceramic fabrication focuses on the engineering aspects whereas ceramic processing emphasizes the scientific aspects of materials behaviour. (Adapted from ref. 3, with permission).

Fig. 3. Possible and preferred relations among processing variables, microstructure and properties, according to Messer (ref. 4).

Fig. 4. Effect of a big bubble introduced during slip casting in a layered ceramic. The bubble produces a big pore with a distortion in the layer interface affecting the macroscopic properties.

Fig. 5. Sequence of steps of ceramic processing showing the important role of suspensions in the different stages, including dry shaping methods (die pressing) where the suspension has a key role on the formation of spray dried granules for a more efficient packing behaviour.

Fig. 6. Stages of the two types of sol-gel processes (i.e. the colloidal route and the polymeric route) from the hydrolysis to the peptisation or polycondensation to obtain a nanoparticulate sol or a polymeric gel, respectively.

Fig. 7. Evolution of mean particle size and optical transmission and backscattering measured for a colloidal sol-gel solution of Ti-isopropoxide. Particle sizes are measured by laser diffraction (LD) and dynamic light scattering (DLS), and transmission and backscattering are measured by near-infrared light scattering. There are two characteristic times corresponding to the start of the peptisation and the time in which it is completely finished.

Fig. 8. Examples of microstructures obtained by transmission electron microscopy of nanopowders produced by different chemical techniques: TiO₂ obtained by colloidal sol-gel and subsequent heating at 300°C (a), Al₂O₃ obtained by freeze drying from aluminium nitrate and heated at 800°C (b), hollow TiO₂ spheres obtained from TiCl₅ (c), ZrO₂ obtained by microwave assisted hydrothermal reaction at 180°C from zirconium oxychloride (d), MnO₂ nanowires obtained by microwaves using MnSO₄ and a ionic liquid (e), Sr-doped lanthanum manganite obtained by Pechini method and calcined at 800°C (f).

Fig. 9. Properties controlling the stability of diluted and concentrated suspensions and the corresponding measuring techniques.

Fig. 10. Scheme of the measuring principle of the sedimentation analyser (a), photos showing the sedimentation front along time (b), and experimental optical curves (c) determined for a suspension of coarse particles of bioactive glass measured every 5 min up to 1h (109). As the solid settles the amount of light backscattered becomes higher on vessel's middle and bottom, whereas at the top of the cell the suspension clarifies and the backscattering decreases.

Fig. 11. Effect of particle size and aspect ratio on the rheological behaviour of concentrated suspensions. The example shows SEM pictures of a commercial mullite powder, as-received (a) and after attrition milling for 7 h (b) with a size reduction from 1.8 to 0.7 µm and a change of aspect ratio from 0.5 to 0.3, and flow curves of suspensions of the as-recived mullite prepared at 60 and 65 wt% solids and of milled powder prepared at 65 wt% solids.

Fig. 12. Relations among particle size, zeta potential and viscosity for alumina suspensions prepared to 75 wt% solids and different concentrations of a poly(acrylic) acid based polyelectrolyte (0.5, 0.8, 1.0, and 1.5 wt%). As it can be seen there is a perfect match among the values (118).

Fig. 13. Flow curves of a suspension of Si_3N_4 with 65 wt% solids prepared by different milling/mixing routes, i.e. agitation with helices, ball mill, centrifugal mill and attrition mill.

Fig. 14. Pictures of green tapes of Al_2O_3 -YTZP homogenized with continuous and pulsed sonication showing the defects originated with continuous sonication.

Fig. 15. Evolution of viscosity with volume fraction of solids for suspensions prepared with particles with different shapes, spherical particles, grains, platelets and rods.

Fig. 16. Schematic representation of the different types of processing additives and their actuation mechanism.

Fig. 17. 3D parts produced by indirect AM technologies, including (a) ceramic heat exchangers obtained by Lithography-Based Ceramic Manufacturing (294), (b) some pieces of alumina built up by indirect selective laser sintering and post processing (295), (c) porcelain pieces by layerwise slurry deposition (273), (d) open cell SiOC multicomponents obtained by stereolithography (296), and (e) in-situ synthesized MAX-phase composites realised by Laminated Object Manufacturing (297). [Pictures reproduced with permission].

Fig. 18. 3D parts produced by direct AM technologies (a) 3D fine scale ceramic components formed by ink-jet prototyping process (298), (b,c) three dimensional structures formed by direct ink writing (299), (d,e) calcium phosphate scaffolds fabricated by robocasting (300), (f-i) and advanced electroceramic components by fused deposition technique (301). [Pictures reproduced with permission].

Fig. 19. Classification of ceramic-matrix composites (CMCs) as monolithic materials or materials with interfaces and characteristic microstructures of the different types of composites.

Fig. 20. Main methods for the production of layered ceramics, sequential slip casting, tape casting and lamination and dipping of cast tapes and characteristic microstructures attainable by those methods.

Fig. 21. Summary of the ubiquitous presence of colloid chemistry in all ceramic processes including beneficiation and shaping and versatility regarding the wide variety of materials, monophasic or composites, range of porosities, and design of microstructures and microarchitectures.

Tables

Table 1. Classification of synthesis routes with the basic principles, main methods and most important techniques.

Type	Principle	Method	Technique
Mechanical	Comminution		
	Mechanochemical synthesis		
Chemical	Solid-state reaction	Reaction between solids	High temperature reaction Reaction sintering Self-propagating high-temperature synthesis (SHS)
		Thermal decomposition	
	Liquid solution	Precipitation-filtration	Co-precipitation Hydrothermal synthesis Microwave synthesis Sonochemical synthesis Microemulsion
		Solution combustion	Alcohol solutions Organometallics Chlorides Suspension combustion
		Solvent vaporisation	Direct evaporation
			Solution drying Freeze-drying Emulsion drying Codecomposition
			Gelation-evaporation Pechini Citrate gel Glycine nitrate Sol-gel Polymeric route Colloidal route
	Vapor phase reaction	Gas-solid reaction	Spray pyrolysis
		Gas-liquid reaction	
		Gas-gas reaction	

Table 2. Classification of the shaping methods, with their consolidation mechanisms and description of the most characteristic processes.

METHOD	MECHANISM		PROCESS	REF.
Direct Casting	Fluid removal	Filtration	Slip casting	31-35
			Centrifugal casting	178,179
			Microwave casting	180,181
			Filter pressing	182,183
			Pressure casting	184-187
		Fluid loss	Electrophoretic deposition (EPD)	188-191
			Tape casting	192-196
			Freeze Casting	197-200
			Immersion (Dip coating)	201,202
			Spin coating	203,204
			Screen Printing	205
			Spray coating and aerosol deposition	206
			Thermal Projection	207-211
	Physical Gel formation		Vibration forming (Claylike / Vibraforming)	212,213
			Direct coagulation casting (DCC)	214-217
			Colloidal isopressing	218
			Temperature Induced Forming (TIF)	219,220
			Temperature Induced Gelation (TIG)	221,222
			Temperature Induced Coagulation Casting (TICC)	223
	Chemical gel formation		Hydrolysis Assisted Consolidation (HAS)	224,225
			Gelcasting (polymerisation of monomers)	226-231
			Thermal gelation (polysaccharides)	232-237
			Chemical gelation (polysaccharides)	238-240
			Starch consolidation (SC)	241-244
			Protein Forming	245,246
			Injection Moulding	247-249
			Low Pressure Injection Moulding (LPIM)	250-253
			Chemorheology	254,255
Additive manufacturing (AM)	Indirect AM		Self Hardening Suspension Casting (SSC)	256
			Three Dimensional Printing (3 DP)	268,269
			Selective Laser Sintering (SLS)	270-272
			Layerwise slurry deposition (LSD)	273,274
			Stereolithography (SL)	275-278
	Direct AM		Laminated Object Manufacturing (LOM)	279-281
			Direct Inkjet Printing (DIP)	282-284
			Robocasting/Direct Ink Writting (DIW)	285-290
			Fused Deposition Modelling (FDM)	291-293

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