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# New Challenges in the Sintering of HA/ZrO<sub>2</sub> Composites

Cristina Vasconcelos\*

*University of Azores/Department of Technological Sciences and Development  
Physics Department of FCT-UNL/ Centre of Physics and Technological Research  
Portugal*

## 1. Introduction

The search for improved the human living standards and longevity in recent decades has led to a strong development of areas related to life sciences. With increasing life expectancy of the population, the constant appeal for the development of materials to be used clinically in the replacement and regeneration of damaged tissues or organs has also allowed the growth of the multidisciplinary field of biomaterials, which is based on the combination of life sciences with materials science and engineering.

Bioceramics, used initially as alternatives to metals in order to increase the biocompatibility of implants, have become a diverse class of biomaterials, presently including three basic types: bioinert high-strength ceramics, bioactive (or surface reactive) and bioresorbable ones. These are the ceramics, which can be used inside the human body without rejection to replace various diseased or damaged parts of the musculoskeletal system. In the last 50 years, several advances in many specialty bioceramics such as alumina, zirconia (ZrO<sub>2</sub>), calcium phosphates and bioactive glasses have made significant contributions to the development of the present health care industry, improving the quality of human life. Recent developments in bioceramics research are, however, focused on bioactive and bioresorbable ceramics, i.e. hydroxyapatite [HA, Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>] and calcium phosphates as they exhibit superior biological properties over other materials. However, the great challenge is the reproduction of structures, properties and functionalities of parts of the human skeleton that result from thousands of years of evolution. The major constituent of bone is HA so it attracts major interest for employing in prosthetic applications due to the similarity of its chemical composition and crystallography to those of mineralized bone of human tissues. In addition the formation of chemical bond with the host tissue offers HA a greater advantage in clinical applications over most other bone substitutes. However, in spite of chemical similarities, mechanical performance of synthetic HA is very poor compared to bone. In fact, its poor mechanical strength makes it unsuitable for load-bearing. In most applications of biomedical materials the mechanical properties are especially important, as well as the chemical reactivity of their surfaces. To overcome these limitations and to meet the requirements for the self-load bearing, HA has been incorporated with other compounds such as mullite (Clifford et al., 2001), ZrO<sub>2</sub> (Y.M. Kong et al., 2005; Sung & D.H.

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\* Corresponding Author

Kim, 2003; W. Li & Gao, 2003), alumina (J. Li et al., 1995), and apatite (Agathopoulos et al., 2003), among others. However, the combination of HA and ZrO<sub>2</sub> have attracted a great attraction for applications to bone tissues exposed under high friction and high impact due to the potential mechanical properties such as high fracture toughness and hardness as well as bioinertness of the ZrO<sub>2</sub> component. A higher strength and fracture toughness can be significantly enhanced either by stress-induced tetragonal (*t*-ZrO<sub>2</sub>) to monoclinic (*m*-ZrO<sub>2</sub>) phase transformation toughening, or by a deflection toughening mechanism. The mechanical behavior is strongly dependent on the structure of the material. Moreover there are basic principles that govern the behavior and properties of a material, which are described as a ratio of its internal structure, processing and their properties. When one aspect of this relationship is changed the others will be affected accordingly.

The processing of materials is another key parameter that will have implications on the final properties of the biomaterial. Many researchers have observed that the mechanical strength and fracture toughness of HA based ceramics can be improved by the use of different sintering techniques which include hot isostatic pressing (HIP), spark plasma sintering (SPS) and microwave sintering. Also a sintering aid based on a low sintering temperature may be helpful if an easy and cost-effective sintering technique has to be used. On the other hand, to minimize the thermal decomposition and improve the densification of the HA/ZrO<sub>2</sub> composites, various atmospheres assisted sintering can be employed. Moreover, the addition of a low melting secondary phase to achieve liquid phase sintering for better densification, incorporation of sintering additives to enhance densification through grain boundary strengthening, and use of nanoscale ceramic powders from sol-gel process for better densification contributed to desirable mechanical and biological properties.

## **2. Constrained sintering by rigid inclusions: Solid-state sintering of ceramic-composites**

In nature the combination of various materials is a constant search for an optimization of properties and functions. By analyzing the different tissues and organs that constitute the human body is possible to verify that they typically result from a combination of different types of biological materials. As an example, natural bone is an ideal nanocomposite, which consists of approximately 30% of matrix material and 70% of nanosized mineral (matrix material- collagen fibers (polymer) plus mineral - HA crystals (ceramic)).

In the development of biomaterials that strategy is also widely used. A variety of materials that result from the combination of two (or more) materials, with composition and structure and different properties that display the higher end of its individual components are composites. One of the most important characteristics of composites is the possibility of modifying the properties with the change of only one of several processing variables such as size, shape, distribution and orientation of the constituents, among others. The principal material of a composite that involves the "reinforcement" is called matrix, with regard to the extent in the body, and the second component (e.g. SiC particles or fibers, ZrO<sub>2</sub> particles, etc.) is usually referred as the filler (or inclusion).

When attempting to join different materials, several factors need to be considered to ensure the integrity of the resulting structure. These include the physical and chemical properties of each component (reactivity, coefficient of thermal expansion, tensile and compression strength, etc.) and the processing conditions (temperature and atmosphere).

One of the most popular paths to the formation of polycrystalline ceramic composites involves powder compaction into a porous body which would receive sintering treating rather than melting or other methods. The reasons for that are two: First, ceramics usually melt at high temperatures, which makes melting difficult and inefficient. Second, ceramics are brittle which is not suitable for processing by thermo-mechanical forming. Sintering commonly refers to the process by which a system of powder particles in contact is consolidated to form dense polycrystalline aggregates through physical and chemical changes when subjected to appropriate temperatures. Almost all aspects of the sintering process have been addressed in many books and publications (Exner, 1980; Exner & Arzt, 1996; German, 1996; Kingery et al., 1976; Kingery & Berg, 1955; Coble & Gupta, 1967).

Sinterization is one of the most important manufacturing and delicate steps that a ceramic body is subject. The most important because it determines, in large part, the final properties of the ceramic, such as microstructure, mechanical properties and final crystalline phases and in the case of bioceramics, their behavior in service. Is one of the more delicate because the achievement of the desired final properties is dependent of the processing parameters such as material properties (e.g. melting temperature,  $T_m$ ), impurities, temperature and time, initial compact density, initial particle size distribution, and applied pressure. Usually a self-supporting compact is obtained from powders that are compacted uniaxially or isostatically to form a "green body", followed by a densification stage involving sintering at appropriate temperatures. So, temperature, time, initial particle size of the material and sintering atmosphere, nature of additives, etc. are the most important factors which can influence the sintering process and the resulting microstructure.

The heat-assisted treatment of sintering usually improves the mechanical strength of the material through the formation of a solid bond between the particles. This process is generally accompanied with densification (i.e. elimination of the pores) and strengthening of the compact, a process driven by interfacial energy ( $\gamma$ ). From a macroscopic point of view, during sintering not only dimensional changes of the products occurs, i.e. the compacts usually contract as the material densifies, but also their shape may vary as a consequence of anisotropic sintering contraction, phase transformations, etc. Moreover, anisotropic shrinkage behavior of composite powders can cause formation of coalesced pores and other microstructural changes in sintered compacts. Hence, based on the application and the expected properties of the final product, there are different techniques to control the mechanism and stages of the sintering process.

The driving force to bond individual particles together, during sintering, is the reduction of free energy of surfaces of powder compacts. This can be achieved by the elimination of pores and reduction of grain boundaries via grain growth. Since  $\gamma_{sv}$  (surface free energy of the solid-vapor interface) is normally greater than  $\gamma_{ss}$  (surface free energy of the solid-solid interface), the solid-vapor interfaces tend to be replaced by solid-solid interface when enough energy is provided. Through the driving force, the neck growth between adjacent particles results in a bonded network polycrystalline microstructure with the pores trapped inside, as shown in Fig.1a.

Through further heating of the compact, the residual pores become smaller in size and number, and isolated from each other (Fig.1b). These isolated pores could completely disappear in the final stages of sintering depending on processing parameters.

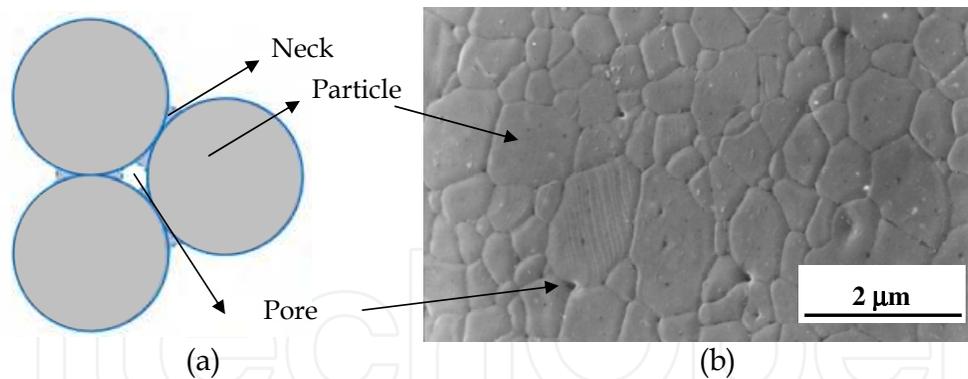


Fig. 1. (a) Sintering model geometry of sphere particles. (b) SEM microstructure of a HA compact, sintered at 1100 °C for 1 h.

During sintering, material moves through mechanisms of viscous flow or diffusion (or both) in order to eliminate porosity and reduce the  $\gamma_{sv}$ . Diffusion is among the most important phenomena observed in sintering of ceramic materials. Diffusive mass transport takes place when there is a gradient in the chemical potential and when the species in question has sufficient mobility. There are a number of competing paths for mass transport during ceramic sintering (Garay, 2010), such as grain boundary diffusion, volume diffusion and surface diffusion. Usually surface diffusion, leads to coarsening, which is the growth of the neck between particles leading to the reduction of the specific surface area. The other transport mechanisms, normally volume diffusion and grain boundary diffusion lead to densification.

Most of ceramic particles, including oxides, need elevated temperatures to be sintered to high levels of densification. Densification of covalent-ionic ceramics without additives is extremely difficult due to the low diffusivity in the solid state following from the nature of bonding in such materials. The sinter temperature is usually at  $T > 0.5T_m$  [K]. Hence, the high temperature ensures that the atoms have sufficient mobility to diffuse to the pores and densify ceramic powders. On the other hand, abnormal grains grow due to Ostwald ripening (German, 1996) when traditional sintering techniques are used, can also occur. Temperature, however, is not the only factor that affects the densification process. A high “green density”, uniform packing, small particle size, spherical particles and narrow size distribution, for narrow-pore size distribution (Yeh & Sacks, 1990) are also important. In the formation of polycrystalline matrix composites, the presence of second-phase inclusions (e.g. particles) leads to a drastic reduction in the matrix densification rate. Thus considerable difficulties are often encountered in the formation of polycrystalline matrix ceramic composites by conventional, pressure less sintering.

Recent developments in bioceramic composites produced a new set of challenges for sintering theory, particularly when differential densification occurs due to constrained sinterization, i.e parts of a structure densify at different rates and temperatures than other parts (Green et al., 2008) because matrix densifies around rigid inclusions. Inclusions and heterogeneities not only reduce the rate of densification, but also cause differential sintering which generates defects that reduce the strength of the final composite due to differential shrinkage. It was shown that the large inclusions can effectively retard the matrix densification and affect the composite microstructure characteristics (Sudre & Lange, 1997).

Also, differences in rates of sinterization between inclusions and matrix may develop stresses which cause sintering defects such as cracks and isolated pores. In fact, the matrix sintering is inhibited when it tries to densify and contract around the inclusions. In this situation, the mean stress will be compressive on the inclusion and tensile on the matrix, thereby opposing densification. The internal stress field will also depend on the shape of the second phase and its volume fraction. It was also reported that the densification rate decreases with increasing volume fraction of inclusions and that densification apparently stops before the theoretical density is reached. It was shown (Brinker & Scherer, 1990) that when inclusions inhibit densification, coarsening mechanisms such as surface diffusion are favored over sintering. Although several improvements in the mechanical properties (e.g. toughness) of ceramic matrices can be achieved by introducing certain reinforcing particles, they tend to inhibit shrinkage so that the full density of the compact may never be achieved, unless a pressurized process, such as hot-pressing or other approaches is applied.

The success in powder consolidation is intimately related to the control of the competition between densification and coarsening. The growth of larger particles, as shown in Fig.2, and shrinkage of small ones (coarsening) is observed often during sintering of crystalline materials. Control of grain growth is thus an essential aspect of controlling the densification-coarsening competition, and producing ceramics with desirable microstructures.

The volume fraction of a particulate second phase present in a composite is an important factor in sintering and resultant shrinkage, and the shape and size of the reinforcing phase may also influence the sintering behavior of the matrix material. The effect of heterogeneities, especially, rigid inclusions, on the matrix densification has been a subject of several studies (Bordia & Scherer, 1988; Scherer, 1987). It was shown that at the first stage of densification, the volume fraction, shape, and distribution of the inclusions affects the morphology of the network formed by the differential densification of the matrix. The matrix properties determine whether, in later stages of densification, the interstitial porous regions can reach full density or not. It was concluded that grain growth in the dense regions of the matrix limits the final densification of the composite.

Many properties of composites are predicted on the basis of the rule of mixtures, which is a method based on an assumption that a composite property is the volume weighed average of the phases (matrix and dispersed phase) properties.

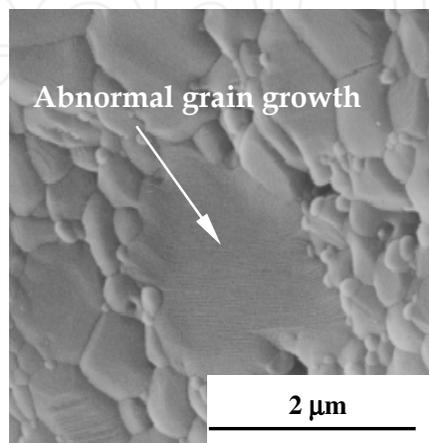


Fig. 2. SEM microstructure of a HA compact after sintering at 1300 °C for 2 h.

Description of sintering of particle-reinforced composites, for a large extent of densification and if no interfacial reaction occurs between the matrix and reinforcement, can be made in terms of a simple rule of mixtures approach (Edrees et al., 1998), as shown by equation (1):

$$\left(\frac{\Delta V}{V_0}\right)_c = \left(\frac{\Delta V}{V_0}\right)_m (1-p) \quad (1)$$

where the subscripts  $c$  and  $m$  refer to composite and matrix, respectively, and where  $p$  is the volume fraction of the filler; therefore, the shrinkage of the composite after sintering is equal to the shrinkage that would be found in the isolated matrix times the matrix volume fraction of the composite.

### 3. Drawbacks in conventional sinterization of HA/ZrO<sub>2</sub> composites

The inherent low strength and fracture toughness of synthetic HA have restricted its use to high load resistant implants (bones) due to its inferior mechanical properties (especially fracture toughness) compared to cortical bone (LeGeros et al., 1993). For example, its fracture toughness ( $K_{Ic}$ ) is 1 MPa.m<sup>1/2</sup>, below the minimum of the range of values for human bones: 2–12 MPa.m<sup>1/2</sup>. Moreover, the Weibull modulus ( $n$ ) is low in wet environments ( $n = 5-12$ ) (DeWith et al., 1981) which indicates a weak structure of the HA implants. On the other hand, synthetic HA is more isotropic with a larger grain size than the biological HA (Cao & Hench, 1996). Further, bone is a complex composite of an organic (collagen) and an inorganic (biological apatite) component. Therefore, the synthesis of composites made of HA have been put forward, in which the addition of second phase into HA for improving its fracture toughness was widely used and investigated (Kong et al., 1999; H.W. Kim et al., 2003; Shen et al., 2001; Adolfsson et al., 2005; Kumar et al., 2005; Rao et al., 2002; Wu et al., 1998). For example, both the fracture toughness and flexural strength of HA can be improved substantially by the addition of ZrO<sub>2</sub> (Yu et al., 2003). It was widely reported that that HA/ZrO<sub>2</sub> composites show significantly higher mechanical properties, in particular bending strength, micro-hardness and Young's modules have proved to be bigger than those of pure HA (Miao et al., 2004). The incorporation of ZrO<sub>2</sub> into HA enhances its mechanical properties and will not affect its biocompatibility. On the other hand, implants made of the HA/ZrO<sub>2</sub> composites are highly biocompatible with no adverse reactions when used in rabbit mandibles (Vaidhyanathan et al., 1997). Further, the Y<sub>2</sub>O<sub>3</sub> addition into ZrO<sub>2</sub> can stabilize the tetragonal phase at room temperature (YSZ), and the tetragonal phase plays a major role in the fracture toughness increase. The toughening mechanisms include transformation and crack deflection toughening. Transformation toughening mechanism is an important mechanism in ceramic composites (Garvie et al., 1975). A great deal of energy is absorbed due to the volume expansion during the transformation of t-ZrO<sub>2</sub> to m-ZrO<sub>2</sub> so that the fracture toughness is enhanced. On the other hand, the ZrO<sub>2</sub> particles dispersed in matrix would disturb the crack tip stress field and make the crack deflect and/or curve, then the driving force of crack propagation decreased and newborn surface area of crack increased, therefore the toughness was enhanced (Faber & Evans, 1983). The change of crack propagation mode, the increase of crack length and the formation of newborn surface area of crack at crack tip will consume energy. The main factor causing crack deflection is the

internal stress caused by the interface effect, especially the interaction between internal stress/interface and cracks. The reason for the improvement of fracture toughness by this mechanism is the growth of surface area of crack and the change of the stress field distribution due to the crack propagating by deflection.

In general, the mechanical properties decrease significantly with increasing content of porosity and grain size, while a high crystallinity, a low porosity and small grain size tend to give a higher stiffness, a higher compressive and tensile strength and a greater fracture toughness. Recently it were obtained HA/YSZ composites with improved mechanical properties, flexural strength of ~155 MPa and fracture toughness of ~2.1 MP m<sup>1/2</sup>, due to the contribution of 25 wt% YSZ component (Sung et al., 2007). The increased fracture toughness would result from the stress-induced tetragonal to monoclinic phase transformation in the YSZ component of HA/YSZ composites. In spite of a better mechanical behaviour, HA/YSZ composites must display uniform microstructures with a high degree of dispersion and without decomposition of the HA, during the sintering process. There are, however, some problems concerning the ceramic processing of HA/ZrO<sub>2</sub> composite that should be solved. These problems are related to the influence synthesis and sintering conditions on phase stability of HA and *t*-ZrO<sub>2</sub>. The conventional mechanical mixing of HA and YSZ powders has been reported for the preparation of HA/YSZ composites through sintering (H.W. Kim et al., 2005; Kumar et al., 2005; Rapacz-Kmita et al., 2006). However, this mechanical mixing would cause low sintering density and/or non-uniform YSZ phase distribution in the sintered HA matrix due to the large particle size and/or segregation of YSZ particles, as shown in both micrographs of Fig.3.

Non-uniform distribution of the YSZ phase in the HA matrix, as shown in Fig.3, would seriously deteriorate the mechanical properties of HA/YSZ composites. Rather, the addition of ZrO<sub>2</sub> particles reduces the size of HA grains, ZrO<sub>2</sub> can thus act as an effective grain growth inhibitor to the HA grains. However, such composites cannot be sintered at temperatures same as the sintering of pure HA, while the sintering temperature for pure HA does not exceed the 1000 °C, the specimens made of HA-20 vol.% YSZ must be necessarily heated up to 1100 °C to obtain near full dense compacts (Khalil et al., 2007). Furthermore, the higher sintering temperature of HA/ZrO<sub>2</sub> composite, frequently, causes an extreme grain coarsening, also illustrated in Fig.2, and HA phase decomposition, leading to a considerable deterioration of mechanical properties. Also, at high temperature the calcium, which is the main component of the HA, diffuses into YSZ and changes its tetragonal structure into the stable cubic phase, hindering the transformation toughening mechanism (Wu & Yeh, 1988). Furthermore, calcium diffusion also favours the decomposition of HA, leading to the formation of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) and calcium zirconate (CZ, CaZrO<sub>3</sub>). The presence of such phases in the composite drastically reduces its mechanical behaviour (LeGeros, 1993). The formation of other phases among HA also interferes with the sinterability of the composites due to differential shrinkage, leading to overall reduced density as compared to that of pure HA. For instance, the sinterability of a HA-20wt.%ZrO<sub>2</sub> (PSZ; 3 mol% Y<sub>2</sub>O<sub>3</sub>-doped) composite was affected by the differential shrinkage due to HA thermal decomposition (Wu & Yeh, 1988). Therefore, if there is no reaction between HA and ZrO<sub>2</sub>, the strength and toughness of HA are indeed improved significantly. HA and ZrO<sub>2</sub> readily react with each other above 1000 °C (Shen et al., 2001). However, reducing the temperature, the densification is

usually difficult unless very special processes, such as HIP, SPS, or other approaches are employed. Hence, another disadvantage of such materials is related to its processing. It is difficult to densify the HA/ZrO<sub>2</sub> by pressureless sintering. However, despite the use of a cold isostatic pressing, a poor densification (apparent porosity ~30%) have been obtained in HA-20-vol%-ZrO<sub>2</sub> composites, after sintering in air at 1350°C for 1 h, (H. W. Kim et al., 2002a) (Fig. 4).

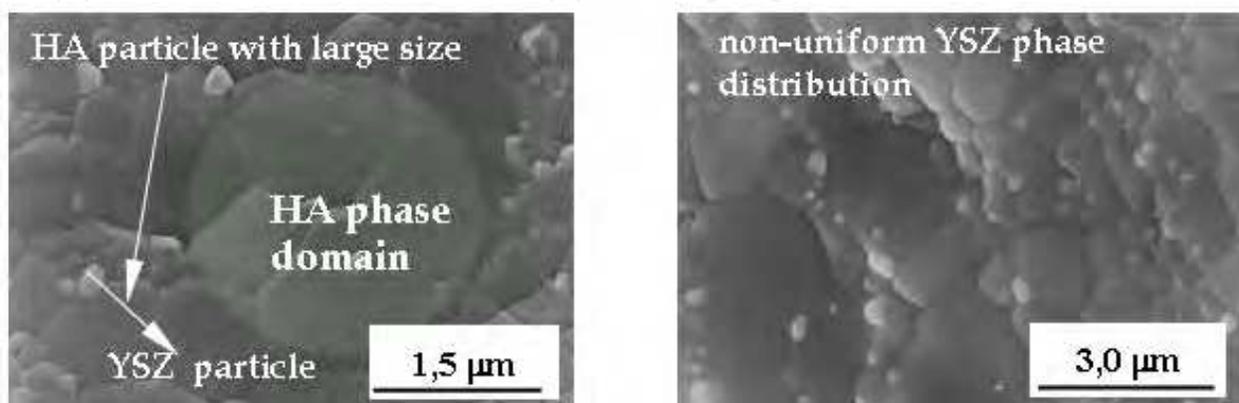


Fig. 3. SEM microstructures of HA-15 vol.% YSZ, sintered at 1300°C, 1h.

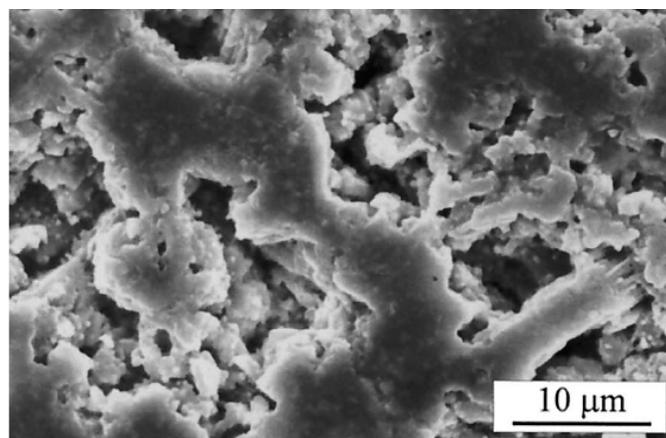


Fig. 4. SEM images showing the microstructure of HA-20- vol%-ZrO<sub>2</sub> composite after sintering at 1350°C for 1 h (source: H. W. Kim et al., 2002a).

A number of approaches have been tried to prepare HA/ZrO<sub>2</sub> composites containing higher fraction of ZrO<sub>2</sub> (20-40 vol%) (Rao & Kannan, 2002; J. Li et al., 1996). However, in these composites, the major problem encountered were the densification of the composites and the decomposition of HA to β-TCP. Actually, the decomposition of HA to β-TCP is accelerated at the higher sintering temperatures (>1300°C). Much effort has been exerted to improve the densification and overcome the reaction between HA and ZrO<sub>2</sub>. However, in most cases, hot-pressing (Kong et al., 1999) or HIP (Takaki et al., 1992) processes are still necessary to obtain HA-ZrO<sub>2</sub> composites with high densities. Nevertheless, there is still a desire for a novel technique to produce dense bodies that use lower temperatures in order to facilitate consolidation but that removes any phase decomposition.

#### 4. Enhancements in the sinterability of HA/ZrO<sub>2</sub> ceramic composites

To overcome the problem of grain growth, unconventional sintering and densification techniques have been proposed. The literature shows that dense HA bodies can be produced by a range of thermal treatments in addition to pressureless air sintering such as conventional HIP, microwave and SPS. However, the application of high temperatures during processing may cause decomposition of the principal components.

To minimize these reactions, some efforts have been made toward reducing the sintering temperature and holding time. Simple economical routes to microstructural improvement are therefore worth investigating. One alternative is the use of the sol-gel process to synthesize a large variety of compositions carefully doped with additional phases, allowing obtain HA nanosized particles and a greater control of the morphology and microstructure of the derived HA/ZrO<sub>2</sub> compacts.

##### 4.1 Hot Isostatic Pressing (HIP)

Dense ceramic-ceramic composites are usually obtained by pressing and conventional sintering of powders using pressure assisted methods, such as hot pressing, hot isostatic pressing, etc.

The high sintering temperatures and long sintering times required for the consolidation of HAP/ZrO<sub>2</sub> powders often result in excessive grain coarsening and decomposition of the HAP into second phases including phase transformation of *t*-ZrO<sub>2</sub> to cubic phase during sintering in air, which are characteristic for conventional sintering methods and results in the deterioration of the mechanical properties of such ceramics.

The advantages of the hot pressing technique are the enhancement of the densification kinetics and the limiting of grain growth, while the disadvantages are the limited geometry of the end product and the expensive equipment required. Ahn et al., 2005, studied the effect of nano ZrO<sub>2</sub> reinforcement on the strength of hot pressed HA/ZrO<sub>2</sub> composites containing 1.5 to 8 wt% ZrO<sub>2</sub>. They observed the highest strength and hardness at 3wt% ZrO<sub>2</sub> which subsequently decreased on higher ZrO<sub>2</sub> loading. They also reported that lower volume fraction of ZrO<sub>2</sub> addition will help to retain both HA and *t*-ZrO<sub>2</sub> phase, which may be due to the combined effect of matrix constraint and uniform dispersion of fine ZrO<sub>2</sub> particles. However, there are still controversial results in the literature about the phase stability of these composites prepared by pressure sintering methods (e.g HIP, hot pressing). Indeed, some reaction has been reported between HA and ZrO<sub>2</sub> by some authors (Veljovic et al., 2007) but not by others (Li et al., 1996). However, there is a general conformity that HA/ZrO<sub>2</sub> composites were considerably stable especially after HIP (Wu & Yen, 1988), even though traces of reaction may be expected due to the increased contact area between HA matrix and dispersed ZrO<sub>2</sub> particles (Adolfsson et al., 2000). On the other hand, a partial reaction between HA and ZrO<sub>2</sub> was observed in the composites prepared by hot pressing but still much less than observed in sintering in air (Evis et al., 2005, 2007). Therefore, the sintering environment and statistical effects on the ZrO<sub>2</sub> distribution within matrix are important parameters that affect the thermal stability of HA and ZrO<sub>2</sub> in the composites. Hot pressing of HA was found to allow the occurrence of densification at temperatures much lower than during conventional sintering (Halouani et al., 1994; Veljovic et al., 2009)

## 4.2 Microwave sintering developments

It is usually accepted that an important issue in ceramics microstructural development is the interaction between densification and coarsening. To control it, parameters such as temperature, pressure, sintering time, and heating rate must be optimized. Rapid heating (RH) has produced high density compacts when compared with slow heating, for similar densities (D. J. Chen & Mayo, 1996). However, differential sintering that causes differential densification is one of the problems most often encountered in RH.

In this context, microwave sintering has emerged in recent years as an alternative technique to overcome the problems of RH. Because it is a noncontact technique, and the heat is transferred to the body via electromagnetic waves, large amounts of heat can be transferred to material's interior, minimizing the effects of differential sintering. Conventional furnaces heat samples by surface heating transference and, thus depending on the rate of heating, a large thermal gradient from the surface to the centre can be generated within a powder compact. However, volumetric heating via microwave radiation ensures an uniform heating and almost no temperature gradients, which yield higher heating rates and must lower sintering time. Therefore, this technique provides a series of benefits, such as great microstructure control, no limit of the geometry of the bodies, improved mechanical properties and reduced manufacturing costs due to energy savings, lower temperatures of sintering and shorter processing times.

Microwave sintering of ceramic materials with significant time and energy savings has been widely investigated. Microwave sintering of HA was first reported in the 90's. Fang et al., 1995, showed that for transparent HA, the total processing time from start to finish of the sintering process was ~ 20 min for microwave sintering while the same was about 4 h in the case of conventional sintering. Hydroxyapatite ceramics with tailored mechanical properties have also been fabricated by this technique (Rodriguez-Lorenzo et al., 2003). Further it has been shown that HA samples microwave sintered showed better densification, higher density and certainly higher hardness and fracture toughness than samples conventionally sintered at the same temperature (Veljovic et al., 2010). The addition of ZrO<sub>2</sub>, however, can reduce the sinterability of the composite and therefore does not reach a high density. At ~20 years ago, only ~50%-78% of relative density was achieved in conventional sintering of HA/ZrO<sub>2</sub> at 1100-1400° C for 3 h (Wu & Yeh, 1988). Then, a few years later, it was reported an achieved relative density of 93% in microwave sintered HA/10%ZrO<sub>2</sub> composites at 1200°C, for only half hour (Fang et al., 1993). Very recently, a compared study between microwave and conventional sintering was performed on HA/ZrO<sub>2</sub> composites (Declan et al., 2010 ). The effect of microwave heating on green bodies has been investigated in order to understand how microwave energy may affect the physical and mechanical properties of the resultant densified composites. The main difference between the two methods is that materials with different microstructures are formed. The higher levels of interconnected open porosity in microwave sinterized HA-ZrO<sub>2</sub> composites are considered to be useful in promoting osteo-integration.

## 4.3 Spark Plasma Sintering (SPS)

Spark plasma sintering is a newly developed process which makes possible sintering at low temperatures and short periods by charging the voids between powder particles with

electrical energy and effectively applying high temperature spark plasma generated briefly. It is regarded as a rapid sintering method similar to microwave sintering. Therefore, it is capable of sintering ceramic powders quickly to a high density at a relatively lower temperature, compared to the conventional sintering method. Due to the applied electric field, the diffusion rate increases and therefore, powder can be densified at much lower temperature with shorter holding time (only few minutes). However, expensive equipment required limits its generalized employ. Nevertheless, Hap ZrO<sub>2</sub> (Kumar et al., 2005) composites have already been prepared by SPS technique and the results showed improved properties compared to their pressureless sintered composites. For example, HA-40 wt.% ZrO<sub>2</sub> composites were sintered at different temperatures by SPS. After sintering at 1200 °C for 5 min, the relative density of the composite increased up to 93% (Miao et al., 2004). The respective microstructure is presented in Fig.5. One can see that the t-ZrO<sub>2</sub> phase (white spots) is uniformly dispersed in the HA matrix, and the composite is also very dense, since large pores are not found.

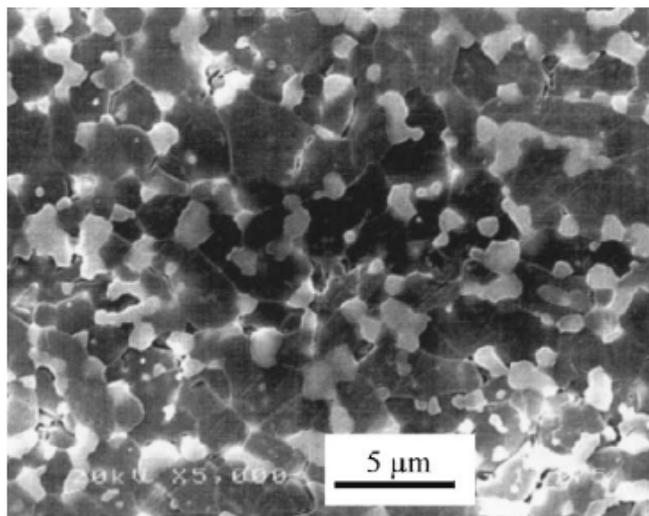


Fig. 5. SEM micrograph of the HA-YSZ composite prepared by spark plasma sintering at 1200 °C for 5 min (Source: Miao et al., 2004).

#### 4.4 Sol-gel synthesis and powder consolidation on the sinterability of HA/ZrO<sub>2</sub> composites

A currently paradigm of synthesizing and processing of powder compacts emphasizes the tailored assembly of particles, from the atomic scale to the macroscopic scale. One of the trends is prepare finer powder for the ultimate processing and better sintering to achieve dense matrices, with uniform microstructures and high degree of dispersion of the ZrO<sub>2</sub> phase. More is the fineness, more is the surface area, which increases the “reactivity” of powders; The sol-gel process is a very efficient method to synthesize a large variety of compositions carefully doped with additional phases, allowing obtain HA nanosized particles and a greater control of the morphology and microstructure of the following HA/ZrO<sub>2</sub> compacts. Thus, while suitably uniform nanophase powder materials are becoming increasingly available, challenges remain in the fabrication of fully dense nanostructured products. Another important challenge is the production of nanostructures with excellent intergranular distribution of ZrO<sub>2</sub> phase.

Sol-gel chemistry have gained much attention in glass and ceramics fields since the 60ths, as an alternative to the conventional melting techniques, when bulk inorganic gels were formed and converted through low-temperature heat treatments to porous and/or dense glasses or polycrystalline matrixes (Bouquin et al., 1987; Livage, 1998; Brinker & Scherer, 1990). A wide variety of glasses and ceramics with unique properties (materials “à la carte”) can be prepared through sol-gel processing. The possibility to control a number of parameters of the final product such as homogeneity, (from the chemical composition to desired final characteristics, namely the mechanical properties, purity, microstructure (e.g. porosity, surface area, crystalline phases), and sintering temperature are among the advantages of sol-gel processing methods over the conventional ones. The resulting oxide materials have low melting and sintering temperatures, as opposed to the much higher melting temperatures required if they are produced via melting production routes. In addition, by controlling the rheological properties of the *sol* and *gel*, the final product could be shaped into various forms such as fibers, bulks, thin films coatings and powders. The most considerable constraint in the case of industrial sol-gel processing is the cost of raw materials, due to the high quality of the chemicals as precursors.

The expression sol-gel (from a liquid solution to a solid bulk gel) was applied to a colloidal solution (suspension), which is followed by a gel phase. This definition is now changed to the hydrolysis and polycondensation of a precursor and subsequent formation of a gel (Dimitriev et al., 2008). Upon destabilization of the colloidal suspension (sol), a gel which is a rigid network of the sol aggregated particles, is formed. In other words, gel is a transition state between the solid and liquid. The dispersed particles in the sol are small enough to form a stable suspension because of the Brownian motion. By varying the sol conditions, such as dehydration or pH, the colloidal dispersion (sol) transforms into the gel stage.

Although the concept of sol-gel processing covers a large variety of materials, it is specifically suitable to those obtained from hydrolysable metal alkoxides or salts. Hence, metal alkoxides  $M(OR)_n$  are the most common precursors for the sol-gel synthesis of metal oxides. The precipitation of metal oxide particles from solutions was one of the earliest routes to produce ceramics through sol-gel processing.

Considering the numerous applications of HA in biomedical fields, development of various synthesis methods is currently a major issue. A number of synthesis techniques using various sources of Ca and P have been developed which includes wet chemical method (precipitation), hydrothermal synthesis procedure, continuous precipitation, thermal deposition, sol-gel and solid state reaction method (Feng et al., 2005; Thamaraiselvi et al., 2006). However, such techniques can lead to the formation of Ca-deficient apatite structure. Moreover, the presence of  $\beta$ -TCP,  $Ca_4P_2O_9$  or  $Ca_4(PO_4)_2O$  along with the HA phase in the subsequent sintered material is indicative of a Ca/P ratio lower than the stoichiometric value of pure HA (Ca/P = 1.67). Ca/P ratios higher than 1.67 would indicate the presence of CaO with the HA phase (LeGeros et al., 1993). The final composition of dense HA after sintering depend on the sintering temperature, the experimental conditions and Ca/P molar ratio of the HA preparation prior to sintering (LeGeros et al., 1993). In some cases, a well-crystallized HA phase was only developed while approaching a sintering temperature of 1200 °C.

The sol-gel approach provides significantly easier conditions for the synthesis of HA. A currently paradigm of synthesizing and processing emphasizes the tailored assembly of

particles, from the atomic scale to the macroscopic scale. Thus, nanosized particles with high surface area and improved reactivity can be easily obtained by the sol-gel route. Technologically, there are significant benefits from the lower sintering temperatures of HA nanosized particles: possibility of avoiding sintering aids, phase decomposition, deleterious interfacial interactions, and undesirable phase transformations. Compared to the conventional methods, the most attractive features of sol-gel process include (a) molecular-level homogeneity can be easily achieved through the mixing of two liquids; (b) the homogeneous mixture containing all the components in the correct stoichiometry and ensures a much higher purity; and, (c) a lower heat treatment temperature to form polycrystalline ceramics is usually achieved without resorting to a high excessive temperature. As a result, several synthesis routes have been proposed for sol-gel synthesis of HA and HA/YSZ as well as different mixing conditions with various molar ratios among reactants (Han et al., 2004; Bogdanoviciene et al., 2006).

A number of calcium and phosphorous precursor combinations were employed for sol-gel synthesis of HA, namely Ca(NO<sub>3</sub>)<sub>2</sub>, CaO, Ca(OH)<sub>2</sub> and Ca alkoxide as a Ca sources, triethyl phosphite [P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] (TEP) and triethyl phosphate [PO(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>], (P<sub>2</sub>O<sub>5</sub>) and H<sub>3</sub>PO<sub>4</sub> as a P-source. Once more, chemical activity and the temperature required forming the HA structure depends largely on the chemical nature of the precursors. One of most promising combination for the precursors yielding stoichiometric HA with Ca/P ratio of 1.67, is calcium nitrate and TEP using alcohol at the hydrolysis stage (Vasconcelos & Barreto, 2011).

In the development of ceramic sol-gel composites, the different components of the sol may be tailored so that they do not react with each other to form new components. In particular, in HA/ZrO<sub>2</sub> (PSZ; Y<sub>2</sub>O<sub>3</sub>-doped) composites, ZrO<sub>2</sub> particles can be dispersed into a HA sol before gelation, leading to a composite with good homogeneity and intimate contact between the components.

The gel composite slurry is typically dried at temperatures under 200°C, and sintered at temperatures lower than the corresponding calcined ceramics. Due to process synthesis, ZrO<sub>2</sub> particles served as nucleation sites during HA precipitation, so HA crystals were formed on the surfaces of ZrO<sub>2</sub> particles (Vasconcelos & Barreto, 2011). This phenomenon provided a more intimate mixing in these binary composites. Coarsening (i.e. growth of larger particles and pores, and shrinkage of finer ones), frequently observed during sintering of crystalline materials, results in overall grain growth which is in direct competition with the densification processes. However, in the case of sintering of dried gels derived amorphous powders, these competing processes are absent (there is no grains), therefore all the pores shrink during viscous sintering and the body densifies to its full density.

#### **4.5 Nanostructural design and improvement of the mechanical behavior in HA/ZrO<sub>2</sub> ceramic composites**

Fabrication of full dense ceramics composites is not easy. One of the main reasons lies to shrinkage heterogeneities and detrimental grain growth after the density of around 90% of theoretical density, when the continuous network of pores (in second stage of sintering) disintegrates to the closed ones (in final stage of sintering) and leads to an accelerated grain growth in conventionally sintered specimens, in special if the filler is not either

homogeneously distributed. On the other hand, the retention of *t*-ZrO<sub>2</sub> in HA derived composites has to be controlled carefully until is used for implant devices. It has been recognized that the level of toughening is complexly dependent on the microstructure of such composites (i.e., volume fraction, size, shape, location and size distribution of ZrO<sub>2</sub> (Heuer et al., 1982). It can be seen (Fig.6) that toughness ( $K_{Ic}$ ) of HA-based ZrO<sub>2</sub> composites increased with the ZrO<sub>2</sub> content up to 20wt% (Chen et al., 2008). The poor mechanical behavior of the composites with 40 to 60 wt% ZrO<sub>2</sub> is correlated with the presence of high porosities (up to 16%) and phase distribution heterogeneities which tended to retard the densification.

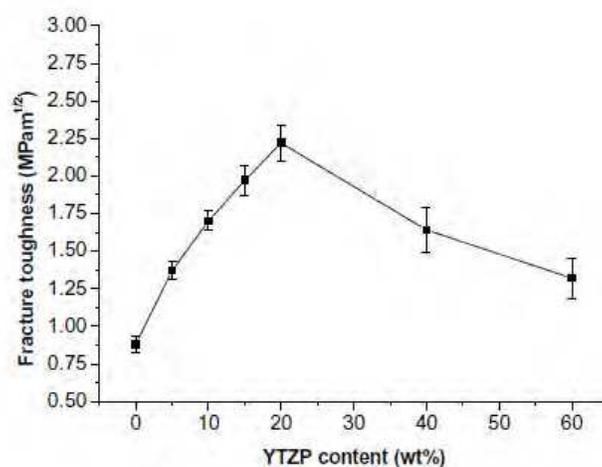


Fig. 6. Fracture toughness vs. ZrO<sub>2</sub> content of HA-based ZrO<sub>2</sub> composites conventionally sintered at 1400°C for 2 hours (Source: Chen et al., 2008).

Homogeneous as well as fine dispersions of ZrO<sub>2</sub> particles in the HA matrix can be obtained by chemical mixing of the constituents in the solution through the sol-gel processing (Vasconcelos & Barreto, 2011). The fine grain size and uniform microstructure of both phases within the composite satisfy the requirements for a toughness improvement; moreover, the toughness can be improved many folds due to the presence of tetragonal phase within the HA matrix, with a potential of 100% of transformation. However, such arguments can change with the phase composition, crystallinity, crystallite size and pore morphology, specific surface area and subsequent shrinkage.

The sol-gel technology offers processing advantages and gives flexibility in tailoring the composite chemistry to obtain the desired properties. Moreover, the processing conditions, composition, retention of the *t*-phase of ZrO<sub>2</sub> the calcination temperature and additives (H. W. Kim et al., 2002b) also control the morphology of the powders and their sintering behavior. An important challenge is the production of composite nanostructures with homogeneous microstructural distribution of ZrO<sub>2</sub> phase. Fig.7. illustrates the SEM of a sintered (950 °C for 1 h) HA/10 mol% ZrO<sub>2</sub> composite (Vasconcelos & Barreto, 2011). As can be seen, the image reveals that ZrO<sub>2</sub> particles are present as both intergranular and intragranular in the HA matrix. However, the presence of intragranular particles is much less compared to intergranular particles. The network of intergranular grain is thus the dominant in the toughening mechanism. The average grain size of HA varies from 0.5 μm to 2μm and is quite homogeneous in the entire matrix. ZrO<sub>2</sub> particles are smaller in size (50-

150 nm) and are trapped at grain boundaries between HA grains. This tailored microstructure provide a more intimate mixing in binary composites, yielding a higher dispersion, allowing ZrO<sub>2</sub> particles to be present mostly at grain boundaries, without agglomerates. Thus, the prepared samples were fully densified with very small isolated voids.

The principal merit of the microstructure observed in these particular composites, obtained by the sol-gel route, is the adequate relative grain size ratio and phase distribution between the both phases, allowing ZrO<sub>2</sub> particles to be present mostly at grain boundaries without agglomerates. During the HA grain growth, residual pores were eliminated throughout the sinter of the HA matrix, and thus an equilibrium-point between densification and coarsening were achieved. Simultaneously, ZrO<sub>2</sub> particles, trapped in the grain-boundaries acts as effective abnormal grain growth inhibitor of HA

Other approaches were also used to obtain better mechanical properties. The properties of these materials are determined by their microstructures; therefore, to control their microstructural development and achieve fine microstructures, the sintering parameters must be optimized. For example, partially or fully fluorine-substituted hydroxyapatite (HAF) ceramics (Adolfsson & Hermansson, 2005) have shown a high thermal stability and some level of bioactivity, and they have been used to develop HAF-ZrO<sub>2</sub> composites with aimed improved mechanical behavior (Chen et al, 2008). The HAF-ZrO<sub>2</sub> microstructures exhibited ZrO<sub>2</sub> grains distributed on the grain boundaries and also within the grains of the matrix (Fig.8). Furthermore, with the increase of the ZrO<sub>2</sub> content, more ZrO<sub>2</sub> grains were trapped within the grains.

For mechanical improvement is quite essential that ZrO<sub>2</sub> particles are mainly as tetragonal phase. However, if *m*-ZrO<sub>2</sub> is present on cracked surface, such presence indicates that the transformation toughening is active for toughness enhancement (Vasconcelos & Barreto, 2011). Transformation toughening is induced from the stress-induced transformation experienced by *t*-ZrO<sub>2</sub> particles when interacting with an advancing crack (Fig.9a) (Stevens, 1986).

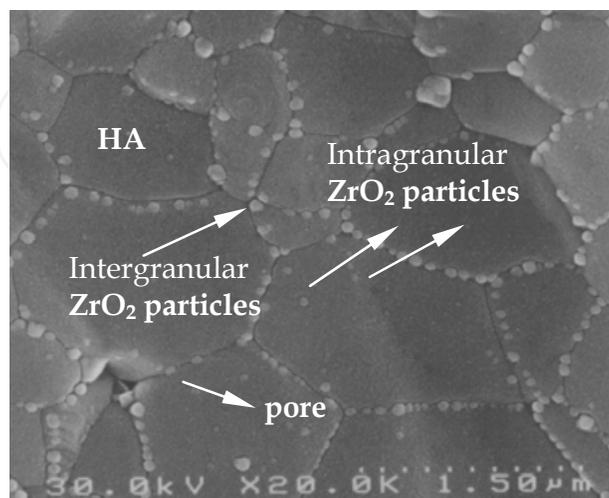


Fig. 7. Tailored microstructure a HA-10 mol%ZrO<sub>2</sub> sol-gel composite (adapted from Vasconcelos & Barreto, 2011).

Moreover, crack deflection toughening by  $ZrO_2$  particles can also contribute to toughening of the composite through crack deflection around the dispersed  $ZrO_2$  particles (Fig.9b) (Vasconcelos & Barreto, 2011). Hence,  $K_{Ic}$  changes with the addition of  $ZrO_2$  may be rationalized by the relative predominance of the toughening mechanism, i.e.,  $ZrO_2$  phase transformation and/or crack deflection.

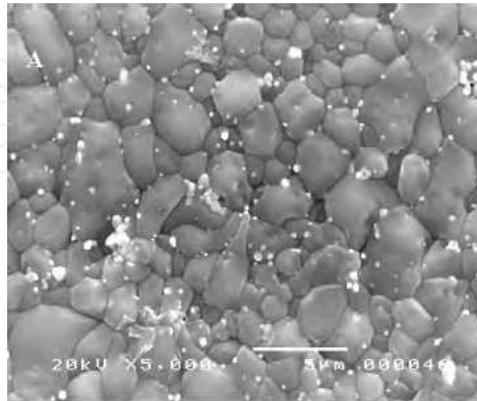


Fig. 8. SEM micrographs of the thermally etched surfaces of the HAF-5wt% $ZrO_2$  composites conventionally sintered at 1400°C (Source: Chen et al, 2008).

In addition, a high degree of densification and homogeneous shrinkage of such composites can be yielded if the formation of Ca-deficient HAP phases during sinterization is avoided. Therefore, through sol-gel process the T-onset of decomposition and the densification at low conventional temperatures of  $ZrO_2$ -doped HA composites leads to more thermally stable HA- $ZrO_2$  composite products than those obtained by other (e.g. coprecipitation) routes.

The improvements in sinterability and microstructure had a strong influence on the mechanical properties of the HA- $ZrO_2$  composites.

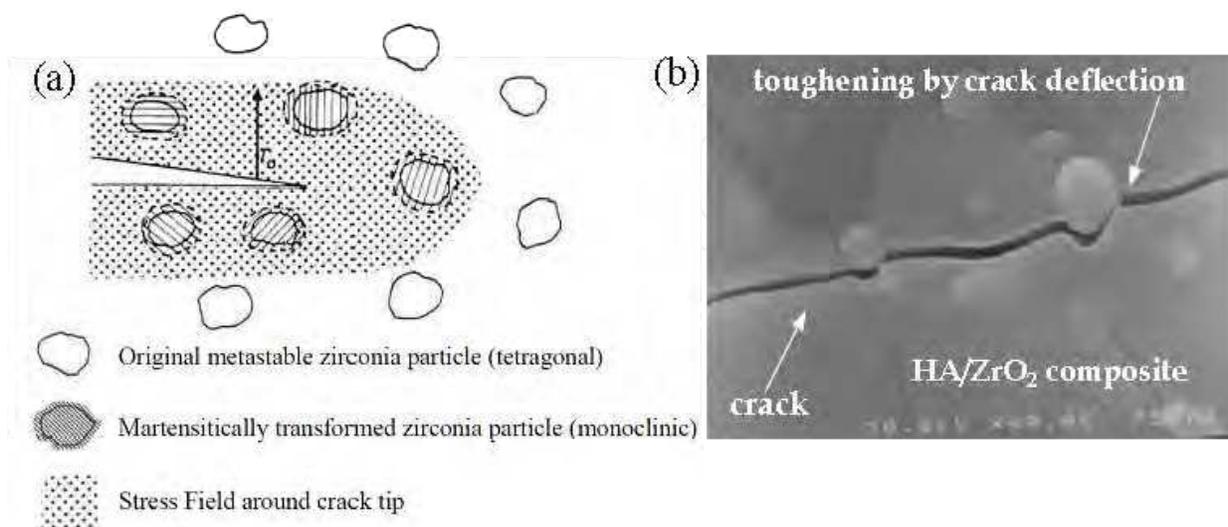
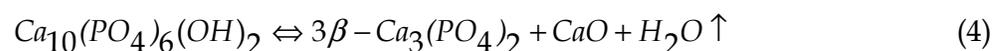
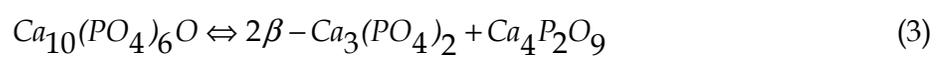
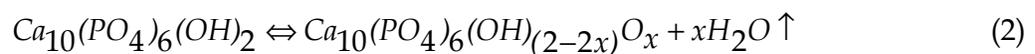


Fig. 9. (a) Stress induced transformation of  $t$ - $ZrO_2$  particles in the elastic stress field of a crack (Stevens, 1986); (b) Indentation crack propagation during indentation fracture of active crack deflection by the  $ZrO_2$  particles (adapted from Vasconcelos & Barreto, 2011).

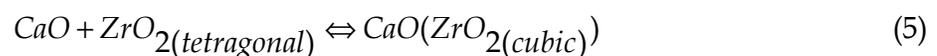
## 5. Sintering advances to suppress the decomposition of the HA phase

Apart from the processing techniques to control the external sintering conditions, other approaches are also used to suppress the decomposition of the HA phase. To minimize the thermal decomposition and improve the densification of the composites, various atmospheres assisted sintering have been employed to produce HA/ZrO<sub>2</sub> composites. However, if this chemical interaction exist, unfortunately would affect the phase purity and the microstructure of the HA/ZrO<sub>2</sub> composites, leading to undesirable mechanical and biological properties.

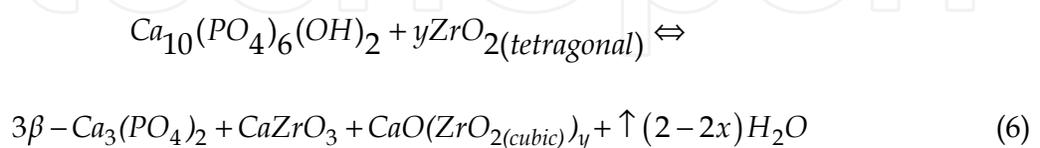
In the spike of that, it was observed that the release of water increases gradually with increasing temperature creating vacancies in HA structure (former OH<sup>-</sup> positions is replaced by O<sup>2-</sup> ions and vacancies) (Adolfsson et al., 1999, 2000). This reaction occurs because HA is a hydrated calcium phosphate material, and begins to dehydroxylate at about 800°C to form oxyhydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2-2x</sub>O<sub>x</sub>, where =vacancy). Further heating, and according to the equilibrium phase diagram of CaO/P<sub>2</sub>O<sub>5</sub>, HAP will decompose in β-TCP (β-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>), forming α-TCP when heated to temperatures in excess of 1350°C. It is well established that HA is thermally decomposed into mostly β-TCP, CaO and H<sub>2</sub>O<sub>(vapour)</sub> (Ahn et al., 2001; Shen et al., 2001; Heimann & Vu, 1997), according to the following reactions (2), (3) and (4):



Another process that removes CaO from HA is dissolution of CaO into *t*-ZrO<sub>2</sub> as seen in reaction (5):



Some authors (Wu & Yeh, 1998; Rao & Kannan, 2002; Evis et al., 2005;) have reported that the CaO release, due to HA decomposition to β-TCP, enhances the formation of CZ and CaO:ZrO<sub>2</sub> solid solution, according to reaction (6):



### 5.1 Thermal stabilization of HA/ZrO<sub>2</sub> composites with water vapor assisted sintering

Since a gaseous species exists on the products side of the decomposition reactions, sintering atmosphere would be expected to influence the decomposition kinetics of HA. Consequently, sintering under vacuum conditions can induce decomposition at lower temperatures, favouring the formation of water vapour. On the other hand sintering in a

moist atmosphere can neutralize this effect and avoid or delay the decomposition to some degree.

When a specific fraction of vacancies is created, HA will not be stable and it will decompose. However, if  $H_2O$  loss is maintained at a low level, the equilibrium of these reactions is shifted to the left and decomposition into  $\beta$ -TCP,  $CaZrO_3$  and  $ZrO_{2(cubic)}$  will not occur. In order to prevent water loss, it is recommended the use an atmosphere control for sintering (water vapor, for example), or incorporation of additives (e.g. incorporation of F<sup>-</sup> ions) (H. W. Kim et al., 2003) in HA structure. If fraction of vacancies formed is suppressed the temperature stability will be extended.

So far, it has been well recognized that, by pressureless sintering of HA/ $ZrO_2$  composites, it is very difficult to reach full densification in air (Li & Hermansson, 1996; Wu & Yeh, 1988). Therefore, only by introducing pressure water vapor it is possible to densify without any decomposition (Vasconcelos & Barreto, 2011). The obtained HA/ $ZrO_2$  compacts under Water Vapor Assisted Sintering did not contain any phases other than HA and the tetragonal modification of  $ZrO_2$ , as revealed by their X-ray powder diffraction patterns (Fig. 10). The presence of an  $H_2O$  atmosphere during sintering reaction causes a compensation of the partial vapour atmosphere of water inside the furnace. In this way, vacancies formation in the HA structure through reaction (2) could be effectively avoided by a left shift of the equilibrium of reactions (4) and (6), countering the HA decomposition by means of the Le Châtelier principle.

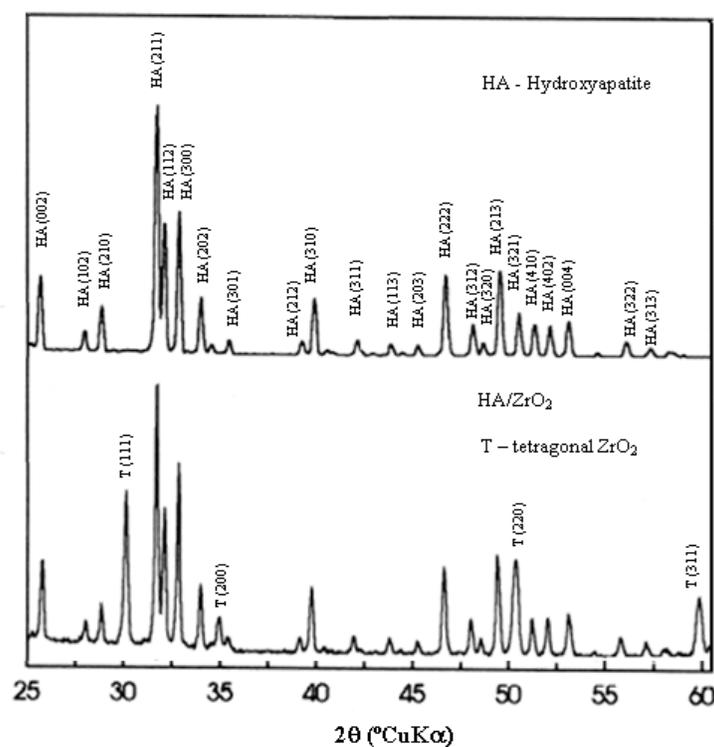


Fig. 10. XRD patterns of HA and HA /10%YSZ powder heated at 950°C, 1 h in  $H_2O$  vapour atmosphere (adapted from Vasconcelos & Barreto, 2011).

Similar approaches, like a flowing H<sub>2</sub>O(g)/O<sub>2</sub> mixtures or hydrothermal sintering conditions have been successful to eliminate or reduce the decomposition of HA or increase the T-onset of decomposition (Ruys et al., 1995). On the other hand, if an intergranular distribution of ZrO<sub>2</sub> particles can be achieved (Fig.4), the decomposition reactions of HA are avoided because diffusion of water from the reaction zone to the surfaces is retarded by the ZrO<sub>2</sub> matrix (intergranular ZrO<sub>2</sub> particles) in boundaries of HA grains, forming a continuous framework (Vasconcelos & Barreto, 2011). Besides, the morphological characteristics of the powders, the good stoichiometry, and their crystallinity are also factors to take into account in sinterability.

## 5.2 Other approaches

It was reported that one of the main disadvantages of the composite approach applied to HA is related to its processing, leading generally to poor densification. There is an agreement that the addition of ZrO<sub>2</sub> to the HA causes it to decompose at lower temperatures in pressureless sintering, so that several workers have used hot aid pressing to reach higher density. However, it is possible improve densification by applying appropriate sintering additives for HA. The sintering additives should considerably improve composite densification without decomposition of HA. Moreover, the sintering additives could be used as structure stabilizers and/or to control grain size. Thus, several sintering additives (Suchanek et al., 1997) have been used in HA (e.g. sodium, lithium, magnesium, calcium and aluminium fluorides, lithium and sodium phosphates, among others.) Most of them (except NaF and AlF<sub>3</sub>) improved densification of HA, not only by influencing the processing conditions, but also by changing chemical properties of the powders (LeGeros, 1991). In a study of HA-ZrO<sub>2</sub> composites sintered without pressure, small additions of CaF<sub>2</sub> (H. W. Kim et al., 2002b) were added as a sintering aid to thermally stabilize the HA-ZrO<sub>2</sub> composites. Thus, due to the substitution of OH- groups by F- ions, Fluorapatite (FHA) was obtained and thereby restrained the decomposition of HA to β-TCP. As a result, dense bodies with high strength and toughness were obtained.

Apart this, other approaches were also used to suppress the decomposition of the HA phase. For instance, (Kong et. al., 1999) added alumina into HA/ZrO<sub>2</sub> composites to reduce the contact areas between the HA phase and the ZrO<sub>2</sub> phase, and hence suppress the interactions between them. However, the introduction of another metal oxide phase might also result in a high level of residual thermal stresses and lead to microcracking of the sintered bodies due to the large difference in the thermal expansion coefficients of the various composite components. In addition, the presence of CaO may cause decohesion of the material due to stresses arriving from formation of Ca(OH)<sub>2</sub> and related volume changes (Ababou et al., 1995). However, Heimann & Vu, 1997, have shown that addition of CaO to HA/ZrO<sub>2</sub> composite shifts the chemical equilibrium of the product from β-TCP and tetra calcium phosphate (TTCP) towards HA making it more stable. Additional CaO will be effectively fixed by ZrO<sub>2</sub> acting as a sink for Ca<sup>2+</sup> ions resulting in the formation of either *t*-ZrO<sub>2</sub> or CaZrO<sub>3</sub>.

## 6. Conclusion

Bioceramics, used initially as alternatives to metals in order to increase the biocompatibility of implants, have become a diverse class of biomaterials. HA attracts major interest due to

the similarity of its chemical composition and crystallography to mineralized bone of human tissues. However, the mechanical performance of synthetic HA is very poor. In fact, its poor mechanical strength makes it unsuitable for load-bearing. Hence, combination of HA and ZrO<sub>2</sub> have attracted a great attraction since higher strength and fracture toughness can be significantly enhanced either by stress-induced tetragonal (*t*-ZrO<sub>2</sub>) to monoclinic (*m*-ZrO<sub>2</sub>) phase transformation toughening, or by a deflection toughening mechanism. The high sintering temperatures and long sintering times required for the consolidation of HAP/ZrO<sub>2</sub> powders often result in excessive grain coarsening and decomposition of the HAP into second phases including phase transformation of *t*-ZrO<sub>2</sub> to cubic phase during sintering in air, resulting in the deterioration of their mechanical properties. The sol-gel technology offers processing advantages and gives flexibility in tailoring the composite chemistry to obtain the desired properties yielding a particular composite microstructure with homogeneous intergranular distribution of ZrO<sub>2</sub> phase. The presence of H<sub>2</sub>O in the sintering atmosphere prevents the HA decomposition by means of the Le Châtelier principle. However, the main disadvantages of the composite approach applied to HA still is related to its processing, leading generally to poor densification. So, the use of several hot aid pressing techniques to reach higher density is still a possibility. However, it is also possible improve densification and avoid thermal decomposition, by applying appropriate sintering additives for HA.

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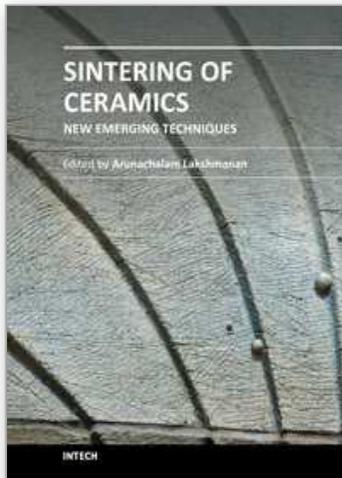
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The chapters covered in this book include emerging new techniques on sintering. Major experts in this field contributed to this book and presented their research. Topics covered in this publication include Spark plasma sintering, Magnetic Pulsed compaction, Low Temperature Co-fired Ceramic technology for the preparation of 3-dimesinal circuits, Microwave sintering of thermistor ceramics, Synthesis of Bio-compatible ceramics, Sintering of Rare Earth Doped Bismuth Titanate Ceramics prepared by Soft Combustion, nanostructured ceramics, alternative solid-state reaction routes yielding densified bulk ceramics and nanopowders, Sintering of intermetallic superconductors such as MgB<sub>2</sub>, impurity doping in luminescence phosphors synthesized using soft techniques, etc. Other advanced sintering techniques such as radiation thermal sintering for the manufacture of thin film solid oxide fuel cells are also described.

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Phone: +86-21-62489820  
Fax: +86-21-62489821

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