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Towards long lasting zirconia-based composites for dental implants. Part I: Innovative synthesis, microstructural characterization and *in vitro* stability

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ABSTRACT

In order to fulfill the clinical requirements for strong, tough and stable ceramics used in dental applications, we designed and developed innovative zirconia-based composites, in which equiaxial α-Al_2O_3 and elongated $SrAl_{12}O_{19}$ phases are dispersed in a ceria-stabilized zirconia matrix. The composite powders were prepared by an innovative surface coating route, in which commercial zirconia powders were coated by inorganic precursors of the second phases, which crystallize on the zirconia particles surface under proper thermal treatment. Samples containing four different ceria contents (in the range 10.0–11.5 mol%) were prepared by carefully tailoring the amount of the cerium precursor during the elaboration process. Slip cast green bodies were sintered at 1450 °C for 1 h, leading to fully dense materials. Characterization of composites by SEM and TEM analyses showed highly homogeneous microstructures with an even distribution of both equiaxial and elongated-shape grains inside a very fine zirconia matrix.

Ce content plays a major role on aging kinetics, and should be carefully controlled: sample with 10 mol % of ceria were transformable, whereas above 10.5 mol% there is negligible or no transformation during autoclave treatment.

Thus, in this paper we show the potential of the innovative surface coating route, which allows a perfect tailoring of the microstructural, morphological and compositional features of the composites; moreover, its processing costs and environmental impacts are limited, which is beneficial for further scale-up and real use in the biomedical field.

1. Introduction

The excellent mechanical properties of zirconia-based materials combined with their superior aesthetics and biocompatibility characteristics have enlarged, in the last years, their application in the dental field. Particularly, the high strength (>1200 MPa) [1] exhibited by yttria-stabilized zirconia ceramics (Y-TZP) allows them withstanding intermittent forces that arise throughout mastication, thus becoming very interesting materials in prosthetic dentistry. Nowadays, fully dense, translucent yttria-stabilized zirconia ceramics can be processed with fine grains size (0.3 μm), thus meeting esthetic and mechanical requirements [2]. However, the tetragonal (*t*) to monoclinic (*m*) transformation specific of (meta) stabilized zirconia, which is responsible of these extraordinary properties, can also induce a negative phenomenon known as Low Temperature Degradation (LTD), or aging [3]. It consists in a slow transformation of *t*-zirconia to the *m* phase (without any applied stress) in a wide temperature range, typically from room temperature up to around 400 °C, thus including the temperature used for steam sterilization (~140 °C) and the human body temperature (37 °C) [4,5]. Possible consequences are loss of strength and generation of micro-cracks [6].

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This phenomenon has been well investigated by the orthopedic community since 2001, when a large series of failures of Y-TZP femoral heads was reported [7]. Although the manufacturing process of orthopedic zirconia femoral heads is significantly different from that of dental zirconia, some studies have recently focused on LTD in the dental field [8–13]. Cattani-Lorente et al. [8] and Kohorst et al. [10] observed the reduction of mechanical properties of Y-TZP dental ceramics after LTD. Chevalier et al. [11] evaluated novel porous zirconia dental implants and reported their aging sensitivity. Kim et al. [12] described the influence of different surface treatments on LTD behavior of dental zirconia. Finally, Denry et al. [13] reported that some forms of zirconia are susceptible to aging and that processing conditions can play a critical role in the LTD behavior. Therefore, as well as for orthopedic applications, current research is now focusing on alternative zirconia-based materials to Y-TZP, especially for implants for which the translucency is less important but for which a perfect stability at long durations must be insured in contact with body fluid. Beside the composites in the alumina-zirconia systems [14–17], ceria-stabilized zirconia (Ce-TZP) seems a promising candidate due to its reduced susceptibility to aging and its excellent fracture toughness [18,19]. However, these attractive properties of Ce-TZP are countervailed by its low strength (about 500 MPa [19]) that still prevents its use in biomedical applications. Hence, it is essential to move to composite systems in which the presence of a well-distributed second phase is widely recognized to enhance mechanical properties. Fracture toughness of about 9.8 MPa$\sqrt{m}$ and a mean strength of 950 MPa was reported by Nawa et al. [20,21] for Ce-TZP-based composites containing 30 vol% of Al_2O_3. Higher fracture toughness (about 15 MPa$\sqrt{m}$) and comparable strength (900 MPa) were recently reported by Apel et al. for 10Ce-TZP/$MgAl_2O_4$ composite [22]. Both these systems, characterized by an inter/intra-granular nano-structure, highlight the necessity to carefully tailor and refine the microstructure in order to fulfill the requirements for biomedical ceramics. Since the microstructure is significantly affected by the process conditions (such as powder synthesis and sintering), a deeper understanding of the relationship between microstructure and processing is a key issue to predict mechanical properties.

Among the several elaboration techniques to process zirconia-based composite powders, the most common are the traditional powder milling and mixing method and the co-precipitation route [23–25]. The former, a simple and fast procedure, often yields to materials with severe limitations for what concerns the final phase purity and microstructural homogeneity. On the other hand, co-precipitation route makes it possible to overcome such limitations, but implies expensive chemical precursors and the whole process is much more complex to manage. Recently, a novel processing route has been developed to produce composite powders via surface coating technique [26–28]. Starting from a commercial powder, its surface is coated (or graft) by precursors of the second phase, which crystallizes on the surface of the parent material under proper thermal treatment. The close mixing between the matrix ceramic particles and the precursor is realized at nano/atomic level, assuring an excellent distribution of the second phase in the composite material [28].

In this context, the European project named *LongLife* "Advanced multi-functional zirconia ceramics for long-lasting implants" (7th Framework Program) aims at developing new multi-functional zirconia-based ceramics having a perfect reliability and a lifetime longer than 60 years. To reach this goal, efforts should focus on the improvement of the zirconia stability in the presence of water, while maintaining high toughness and strength. In this paper the strategy of *LongLife* towards strong, tough and stable zirconia-based materials is presented implying *i)* the design of innovative ultra-fine composite structures and *ii)* the use of a new approach named *nano-powder engineering*. Such approach allows a perfect tailoring of the compositional and microstructural features in the developed materials. This is the objective of the Part I of the work, aimed at developing materials designed for dental applications. A comprehensive set of mechanical properties of the developed materials in terms of Vickers hardness, flexural strength and fracture toughness will be reported in Part II, finally showing the potential use of these composites as dental ceramics. Concerning the composite design, we chose Ce-TZP as composite matrix, due to its reduced susceptibility to aging as respect to Y-TZP, and two kinds of second phases characterized by different morphologies: equiaxed and elongated. The role of well-dispersed, fine equiaxed particles is to refine the Ce-TZP microstructure by a *pinning* effect exerted on the zirconia grain boundaries during the sintering cycle. Although refining microstructure increases strength, hardness and wear resistance [29,30], it inevitably decreases the efficiency of the phase transformation toughening [31]. In order to obtain high transformability under stress even with very fine-grained structures, in the present study the ceria content in the composite materials is carefully tailored. In addition, the formation of elongated second-phase particles is promoted, with the aim of further increasing the toughness by additional bridging/crack-deflection mechanisms [32,33]. Precisely, on the ground of the previous scientific literature [15,32–35] α-Al_2O_3 and strontium hexa-aluminate, $SrAl_{12}O_{19}$, were selected as second-phases and added to the Ce-TZP matrix. A preliminary investigation on the biocompatibility of this composite powder showed already promising results in terms of bacterial adhesion, as reported by Karygianni et al. [36], further supporting its employment in the biomedical field.

Fig. 1 shows a schematic strength-toughness relationship for many Y-TZP and Ce-TZP-based materials, according to literature data [1,19–22,30,32,33,37]. It is striking the lack of materials able to meet all the requirements for dental implants (i.e. perfect stability *in vivo*, very high strength and fracture toughness) thus clarifying the objective of *LongLife*, depicted in the same Figure.

The "Longlife composites" are not a new family of zirconia based composites since some studies on (almost) similar compositions are already present in literature [32,34]. However, the innovation and objective of this work is the development of such composites through an innovative surface coating method, simple but very effective in assuring a perfect control of all the microstructural and compositional features of the composite structures. Other surface-

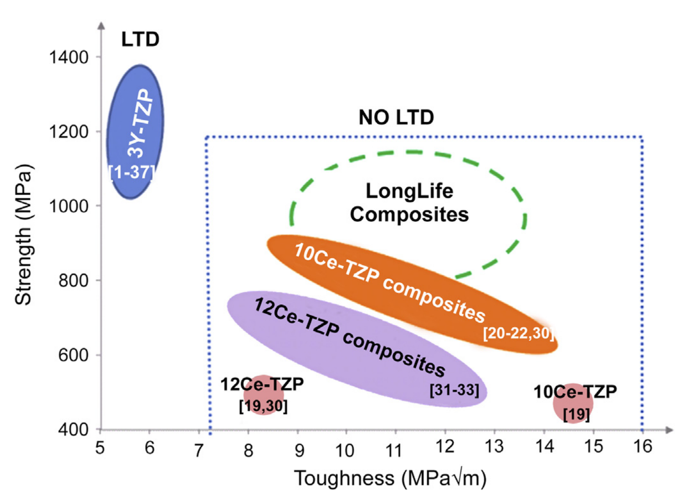

Fig. 1. Relationship strength-toughness for several zirconia-based materials. In green, the objective of LongLife towards LTD-free, strong and tough composites.