INFLUENCE OF ZIRCONIA CeO_2 LATTICE STABILIZING AGENT ON BIOGLAZE COATING

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The aim of this research is to study in detail the behaviour of glassy bioactive coatings (Bioglazes®) on zirconia substrates with different stabilising agents. In the case of tetragonal Ce-PSZ, some phenomena arose by applying a glaze coating. The stabilising CeO_2 undergoes to an -even partially reversible- autoredox process (CeO_2-Ce_2O_3), caused by migration of oxygen during the glazing process, (ZrO_2 is known as a proton and oxygen radical conducer at high temperatures), with a macroscopic effect of a grey-green colouring of the Ce-PSZ substrate below the coated surface ("affected volume"). The migration of oxygen can assume an extent for which at the glazing temperature, about 1300°C, it is possible the chemical equilibrium shifts towards formation of Ce_2O_3. Grey-green is the own colour of Ce_2O_3. By eliminating the sealing action of the glaze towards atmosphere, oxygen can diffuse back inside Ce-PSZ lattice, recovering the chemical and thermodynamic equilibrium conditions with CeO_2 and Ce_2O_3 and inducing a decolouring effect in the Ce-PSZ ceramic back to a light colour. The bioactive glass utilised to produce the coatings is a calcium-silicophosphatic one, coded AP40.

INTRODUCTION

Zirconia (ZrO_2) ceramic is a material more and more considered for utilisation in biomedical field. In particular it is appreciated for its high toughness, very high mechanical resistance to compression, sufficiently remarkable flexural strength and high chemical resistance to severe environment. ZrO_2 exhibits suitable mechanical properties, perhaps better than those of alumina ceramic [1-7].

Moreover, it is highly biologically tolerated in contact with tissues and has very good resistance towards physiological and biochemical actions.

Good mechanical performances of zirconia, suitable for biomedical applications, derive from its high temperature phases, cubic or tetragonal; instead, the monoclinic phase, stable at room temperature, does not assure such performances. This is the source of the problems that, together with the high specific gravity, let perplexed the biomedical experts for a wide use of this material. The main problem is that it is necessary to sinter ZrO_2 powders at high temperatures, where cubic or tetragonal phases are stable, to obtain a zirconia ceramic; but, during cooling, a phase transformation towards monoclinic phase occurs. The problem rises for the remarkable volume increase (3-5%) associated with this transformation that generates tangential stresses at the grain boundaries, which bring to a rearrangement of the tensional state of the whole bulk of the ceramic body. This leads to sudden cracking or delayed fractures, so compromising the integrity of the produced ceramic piece. To prevent, at least partially, such transformation from high temperature phases to the monoclinic one, some specific oxides (of Ca^{2+}, Mg^{2+}, Y^{3+}, Ce^{4+}) are added during the production of zirconia powders. These cations substitute randomly Zr^{4+} in its crystallographic lattice site and consequently are here defined as *lattice stabilising agents* (LSA).

Other possible problems concern the sensitivity of stabilised zirconia ceramic to warm wet environment [21], such as that of an autoclave (in case of sterilisation), and even to ageing in liquid environment, like the physiological ones [11]. Possible surface modifications can involve microstructural rearrangement with phase transformation, in particular with ageing [8].

On the other hand, zirconia ceramic material is unfortunately not able to exert some important biological performances such as bioactivity, osteoconduction,

osteointegrativity. Therefore, to impart (at least on the surface) some of these characteristics, a coating (glaze) with a bioactive glass (Bioglaze®) [9-13] was conceived. This coating must have the capability to adhere firmly on the surface of the zirconia ceramic substrate and at the same time to develop the wanted biological performances. The coating of zirconia ceramics is considered useful to drive the surface of the ceramic from inert to biologically active and osteoconductive for a close joining with bone when implanted *in-vivo*. The coating in this case is also useful to prevent any possible modification of the microstructure at the surface.

To produce such a coating, with all these targets, the bioactive glass AP40 [25] was utilised. Previous studies on ceramic samples made with tetragonal zirconia, stabilised, with yttria (Y-PSZ), have proved the feasibility of coating of their surfaces with AP40 bioactive glass [14-20, 25] without any loss of its biological performances. It is perhaps useful to remind that these biological performances are lost in a significant way when bioactive glasses are applied on the surfaces of alumina ceramic samples [12] and this represents a point in the favour of adoption of biomedical devices made with zirconia ceramics.

The target of this investigation was to ascertain if possible differences of behaviour arise when a biological glass is applied with the same procedure on zirconia stabilised with ceria (Ce-PSZ) rather than on zirconia stabilised with yttria (Y-PSZ). Two amounts of LSA addition for yttria and ceria were selected, at low content and high content, both compatible within the range of reciprocal total miscibility with ZrO_2 in forming a solid solution which has the wanted and comparable crystallo-physical and physico-mechanical characteristics.

EXPERIMENTAL

Zirconia powders were prepared through sol-gel technology. The base synthesis solution contains dispersants, colloids (*e.g.* polymethylcellulose), the sol (*e.g.* nitrates) of zirconium ions and of the chosen LSA. Cerium oxide was introduced in the zirconia lattice during its synthesis, by a co-precipitation process in aqueous medium, utilising a Ce^{4+} compound, as well as for Y^{3+}. So the powders in formation incorporated the proper LSA in a due amount, depending on its concentration into the solution of synthesis. An alkaline solution was continuously added drop by drop until the wanted stoichiometric proportions were reached; the precipitate was calcined, ground and spray-dried palletised, obtaining stabilised easy handling powders. Samples of cylindrical shape were moulded by cold isostatic pressing (2000 kg/cm^2) with each of these powders.

All cylinders were fired at 1000°C and sized by machining. Sintering was carried out at 1550°C for 1 hour, and discs with a thickness of about 8 mm and diameter of 25 mm were obtained by cutting the cylinders.

At the end four types of zirconia ceramic samples (coded Z1, Z2, Z3, Z4) were at disposal, stabilised as shown in table 1.

A bioactive glass, coded AP40, elsewhere characterized in detail, proved useful in the role of "*biogla-zing*". Its composition is reported in table 2. It was prepared by melting in a platinum crucible inside a laboratory kiln, at 1450°C, the proper raw materials in precise amounts. After quenching, it was therefore ground in powder at a granulometry ranging from 5 to 40 μm and mixed with polymethylcellulose (as binder) to produce an aqueous slurry.

This slurry vas applied by brushing on the upper base surface of the zirconia ceramic discs, produced as above described, to obtain the coating. A procedure was set up to obtain as much as possible homogeneity in quantity, thickness and distribution of the slurry on the discs surface to be coated. Coating procedure consists in firing samples in a laboratory kiln at 1280°C for 10 minutes to allow the glass powder to melt and forming a layer on the zirconia substrates and to consolidate it, obtaining a glaze. The physico-chemical nature of the obtained coatings was evaluated through by X-ray diffractometry (XRD), optical (OM) and scanning electron (SEM) microscopy techniques. SEM was equipped with an X-ray energy dispersion (EDS) micro-probe analyser.

Tests were also performed to measure the Ultimate Tensile Adhesive Strength (UTAS) on the discs coated with the bioactive glass, according to the relative BS EN Standard 582:1984 "*Thermal spraying determination of tensile adhesive strength*".

Table 1. Composition of the ceramics considered

sample code	stabilised phase	LSA	amount (wt.%)
Z1	tetragonal	Y_2O_3	5.2
Z2	cubic	Y_2O_3	13.4
Z3	tetragonal	CeO_2	12.0
Z4	tetragonal	CeO_2	20.0

Table 2. Chemical composition expressed in wt.% of oxides (except CaF_2) of the bioactive glass AP40.

SiO_2	P_2O_5	$CaO+CaF_2$	Na_2O+K_2O+MgO
44.3	11.2	36.9	7.6

RESULTS

General description of the coated samples

By looking accurately at the OM images coming from the different ZrO^2 ceramic coated samples with the indicated bioglaze® and comparing them, it was disclosed that, while the glass layer on Y-PSZ substrates resulted optimally deposited, clear and plain, the one applied on Ce-PSZ samples changed colour into a dark moss-green, without homogeneity in thickness. A careful investigation on cross-sections of these last samples has displayed two main more relevant aspects which were considered to be unfavourable. To describe them it is necessary to make recourse to the image of figure l, electronically recorded through a scanner directly on a vertical diametrical cross-section of a sample Z4, which explains what happened in the case of Ce-PSZ substrates.

Investigations on the substrate

Most of the glassy coating material originally deposited on the Ce-PSZ discs accumulates near to their periphery (along the perimeter) with a ring-like formation (in the figure defined as "*Ce_2O_3-rich glass toroid*"), the maximum height of which was estimated to be 300~500 µm. Very thin deposition of glass was detected on the remaining area of the surface (the central zone of the discs).

Further, optical microscopy investigations on cross sections of these discs revealed a singular grey-green colour involving the inner body of the substrate (visible even with the naked eye). The volume of material that underwent such a change of colour is defined "*affected volume*" in figure 1.

Measurements of the maximum extension of this darker zone have supplied relevant values in depth inside the samples section, but never reaching the opposite side of the discs.

The colouring looks like the one of the inner part of the glass coating ring-shaped surface: this visibly darker (as above grey-green) core of the Ce-PSZ coated substrate is not related to a glass penetration, as apparently would seem at a first sight interpretation. The penetration of the glass across the interface into the ceramic substrate was ascertained not to overcome 10 µm depth for Ce-PSZ samples (figure 2). The layer formed by the glass infiltration into the ceramic body was defined as "*shell*" as in figure 1.

A careful SEM investigation on the ceramic microstructure was therefore carried out on cross-sectioned and polished samples, before and after deposition of the bioglaze. Except the peripheral parts (near the interface with deposited glass, indicated as "*shell*" in figures 1 and 2), the ceramic microstructure did not exhibit modifications among the samples with same LSA before and after coating, except in the "*affected volume*" (of course not present in the samples uncoated as well). Anyway, the mean grain size of the Y-PSZ samples (Z1 and Z2) resulted to be smaller (0.5-2 µm) than the size (2-5 µm) of the Ce-PSZ ones (Z3 and Z4). Moreover, while the microstructure of the Y-PSZ ceramic samples was very compact, some random clusters of close micro-cavities was revealed in the Ce-PSZ ones.

EDS analyses did not detect differences in composition (even for trace elements) between affected and not affected volumes of the Ce-PSZ ceramic samples. Accurate XRD and EDS analyses on this affected volume did not revealed compositional variations, except weak traces of monazite phase ($CePO_4$) closely to the glass "*shell*" and inside all the glass layer. This affected volume was surely not perfused by glass; however, it is reasonable to suppose that it contains Ce^{3+} ions.

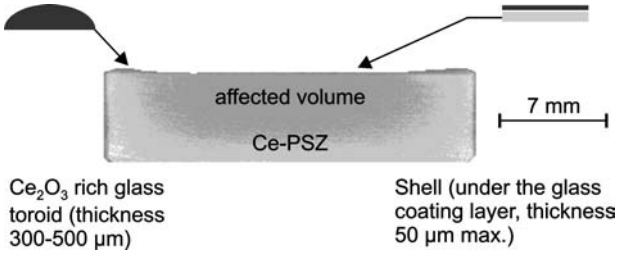

Figure 1. Photographic image (enhanced contrast by graphic elaboration) taken on a section of the bioactive glass coated Ce-PSZ disk sample. Sketched characteristic structures produced by the glass coating are reported.

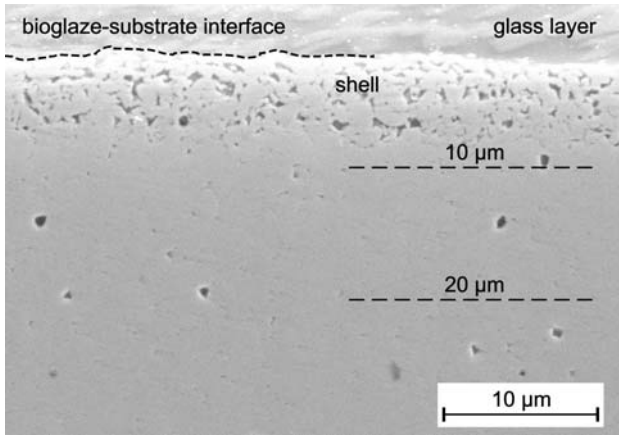

Figure 2. SEM observation at the interface between AP40 bioglaze and Ce-PSZ ceramic substrate (sample Z4). The darker zones inside the *shell*, below the glass layer, are not primary pores but the effect of permeation of glass and consequent enlarging of the microstructure of ceramic substrate. True pores (e.g. internal gaps in densification) are the sparse darker spots in the inner ceramic body. The size of the grains of the *shell* zone is visibly increased, with the intergranular space filled by the glassy phase that acts as cementing medium. This behaviour is common to both Y-PSZ and Ce-PSZ ceramics [16].

Investigations on the coatings

The coating of all samples (both Ce-PSZ and Y-PSZ) exhibited clearly formation of small amounts of $Ca_5(PO_4)_3OH$ (hydroxyapatite, HA) prevalently present on the external surface.

As resulting from a series of optical and SEM investigations on a large number of cross-sectioned samples, the penetration of the glass into the microstructure was revealed to have occurred into the zone of the interface. Figure 2 shows the microstructure of the layer involved in the glass infiltration in a Z4 sample.

The glass infiltration into the ceramic body has formed a "*shell*" zone, the depth of which was detected to be 40÷50 μm for the Y-PSZ samples, and only 8÷10 μm for the Ce-PSZ samples; moreover, it was observed that concerning the glass penetration, the smaller depth corresponded to samples stabilised with the higher amount of LSA (and vice-versa) for both Ce-PSZ and Y-PSZ.

The penetration of the glass in the "*shell*" layer, just below the interface coating-zirconia ceramic body, corresponds to an intergranular infiltration which appears similar to a porous microstructure. However, the microstructure of this "*shell*" differs from that of the innermost parts: as showed in figure 2, it is possible to observe clearly an "*inflated*" microstructure, with enlarged grains just below the coating interface. A considerable difference was observed by SEM in the coating layer on the surface of the different samples. While on the Y-PSZ samples the glass coating retains a consistent thickness (~200-300 μm) in a weakly cambered layer, the Ce-PSZ ones, apart the above mentioned peripheral ring, exhibit a formation of a very thin (<50 μm) layer, the nature of which is not constant all over the coated surface.

XRD investigations were carried out on the coating layers (figure 3). Trace of the monoclinic phase was detected both in the affected and not-affected volume of the cross-sectioned Ce-PSZ samples. However, while the intensity of the detected monoclinic phase remains constantly very weak, that of the tetragonal and also cubic are enormously stronger as expected. This is confirmed also by the adhesion strength of the glass layer to the substrate. In fact, considering UTAS measurements listed in table 3, the adhesion strength of the bioglaze® is twice higher on Y-PSZ substrates [17].

Table 3. UTAS values coming from the adhesion of AP40 coating on the different substrate indicated.

sample	Z1	Z2	Z3	Z4
UTAS (MPa)	30 ± 3	32 ± 2	16 ± 4	15 ± 4

By comparing and crossing investigations carried out on the surfaces of the bioglaze® by XRD and EDS, carried out on cross-sections of the samples, it was ascertained that amount and quality of the crystalline phases formed inside the glaze layer (table 4) changes in relation to the kind of LSA of the zirconia ceramic substrate.

According to a previous study [20], which reveals a very low solubility of zirconium ions in glass systems, Zr^{4+} was not detected in the glass coatings by EDS microprobe. By the way, zirconium oxide is considered to have a role as a nucleating agent in glasses [24].

Figure 3 shows XRD patterns of glass coating of Z2 (top) and Z4 (bottom) samples, which exhibit a remarkable very high [*h0l*] and [*0kl*] peaks families: this indicates an oriented crystallisation of such planes of calcium-phosphosilicate phases reported in the 11-676, 35-327 and 33-1229 JCPDS cards.

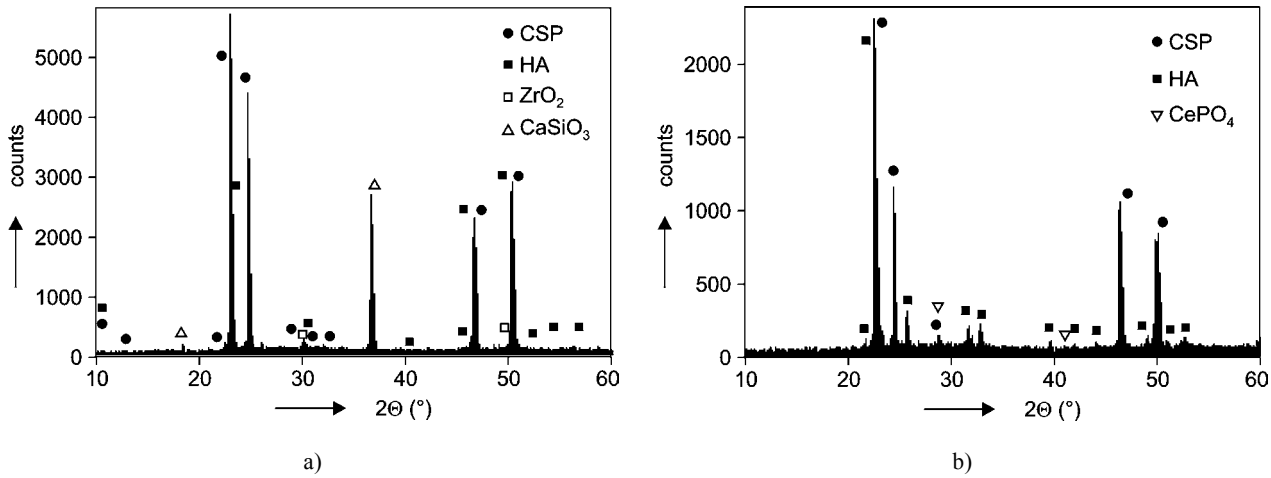

Figure 3. XRD patterns of glass coating of Z2 (a) and Z4 (b) samples.

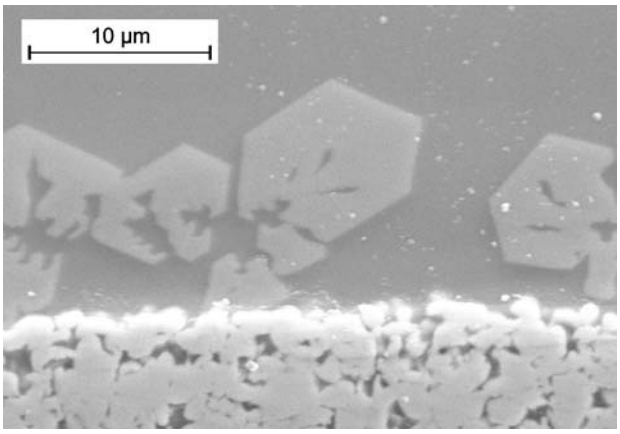

Figure 4. Large pseudohexagonal CPS micro-crystals detected at the interface glass/substrate (sample Z4).

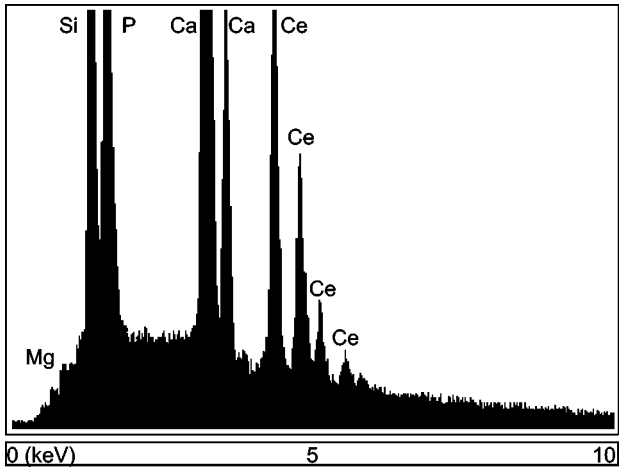

Figure 5. EDS pattern of the crystalline formations visible in the SEM micrography at left (sample Z4).

Table 4. Crystalline phases detected by XRD in the glaze coatings of all kinds of considered substrates, listed following an order of decreasing quantity.

sample	Z1	Z2	Z3	Z4
glass layer	CPS HA♣ $CaSiO_3$	CPS HA♣ $CaSiO_3$	CPS HA♣ $CePO_4$	CPS HA♣ $CePO_4$
interface	$ZrSiO_4$♥	-	$CePO_4$♥	$CePO_4$♥
affected volume	-	-	ZrO_2	ZrO_2

♥: Only sporadically ($ZrSiO_4$), or traces ($CePO_4$);
♣: HA = Hydroxyapatite, grown apparently in epitaxy basal [002] oriented (see figure 2);
$CaSiO_3$ = Para-wollastonite (JCPDS 31-300);
$CePO_4$ = Monazite (JCPDS 32-199);
CPS = Calcium-phosphosilicate, including Nagels-chmidtite family (JCPDS 11-676, 33-1229, 35-327), mainly $Ca_7(SiO_4)_2(PO_4)_2$ at the interface coating-substrate.

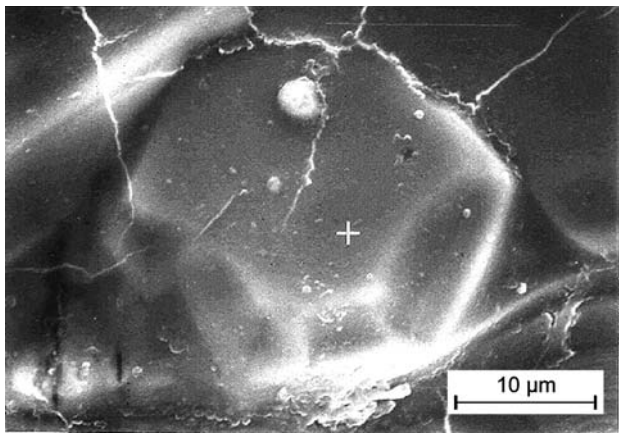

Figure 6. Microcrystal that emerges on the surface of the glaze (sample Z1). According to EDS and XRD investigations, the chemical composition fits with that of parawollastonite ($CaSiO_3$).

Figure 4 shows some pseudohexagonally shaped crystalline formations, inside the glass layer, close to the interface with zirconia. These micro-crystals were investigated by EDS microprobe (figure 5), revealing a composition in agree with a calcium-phosphosilicate phase, polluted (or surrounded by polluted glass) by cerium ions, certainly coming from the dissolved fraction of Ce-PSZ grains of the substrate.

This agrees with the results yielded from the large number of XRD investigations carried out, resumed in table 4, which indicates also the presence of $CePO_4$ in Z3 and Z4 samples. Crystalline formations of pseudowollastonite ($CaSiO_3$) and calcium-phosphosilicates (CSP) were observed by SEM (figures 6, 7) particularly into the glaze layer of Z1 samples.

No presence of the LSA Y_{3+} was revealed inside the glass of Z1 samples coating, while trace was detected inside the Z2 one.

The LSA Ce^{4+} is instead widely diffused in the glaze coating of the samples Z3 and Z4 and reacted chemically with the components of the glass, likely with formation of $CePO_4$ (monazite), as revealed by XRD (although as trace).

DISCUSSION

The presence of cerium trace inside the glass indicates that a migration of it has taken place from substrate towards the glass coating. It is not well clear how cerium has migrated towards glass: what is sure is that a fraction of it has come out from zirconia lattice. This possibility is supported by observing the zirconia grains at the interface substrate/glass ("*shell*" layer) that have changed their microstructure, clearly influenced by the presence of the molten glass. Optical and scanning elec-

tron microscopy investigations on the microstructure have pointed out the enlargement of the grain size, with a general morphology assumed that is more compatible with the monoclinic phase. However, the formation of just trace of monazite indicates presence of Ce^{3+}. As a general observation, it has to be pointed out that the content of LSA for Ce-PSZ is substantially twice as for Y-PSZ. In the case of Z4 sample, the amount of CeO_2 (20%) present inside the zirconia lattice, to guarantee its stability in the tetragonal phase, is so huge that really it could be considered more a mere solid solution between ZrO_2 and CeO_2 rather than a stabilised zirconia. Even at this high CeO_2 concentration the polycrystalline zirconia is not a composite material because no trace of free cerium oxide was found (by XRD). By the way, the interactions of the coating glass with the CeO_2 LSA have still to be studied, on the ability of the glass to extract Ce^{4+} ions from zirconia. What is verified is that the presence of a glass layer induces the Ce-PSZ material to assume an unexpected behaviour, quite different in comparison to that observed when the same glass is deposited on Y-PSZ. As concerns the grey-green colour assumed by the glass deposited on Ce-PSZ ceramics (measured also by an UV-Vis-NIR spectrometer), it was attributed to formation of Ce^{3+}, as well supported by the detection of the cited monazite. The grey-green colour in the ceramic bulk agrees better with the presence of Ce_2O_3, although this last was not directly instrumentally detected (probably because below the XRD threshold limit of sensitivity). Table 5 illustrates the correspondence between colours and compounds of Ce^{3+}. However, the amount attributable to the intense colour observed may derive only from a presence of a very reduced weight percent of Ce^{3+} (Ce_2O_3). Note that Ce-PSZ ceramic is normally light-brown coloured.

To explain the formation of Ce^{3+} from the CeO_2 contained in the zirconia ceramic substrate, some redox reactions must be invoked: being unknown the partner of this redox reaction, some components present in the system during the adhesion interfacial reaction of enamelling, have been taken into consideration. On the base of the electrochemical potentials [22, 23] at first the considered ones were the humidity (as H_2O molecules, coming from burning up of organic binders), or F_2 (present in the chemistry of the coating glass).

Afterwards, it was also considered the possible role of oxygen, reminding that ZrO_2 is a good proton and oxygen radical (O•) conducer at high temperatures.

On the other hand, no evident sign of deep glass infiltration in Ce-PSZ ceramic, after firing treatment, was observed and no ions coming from glass composition (Si, Ca or P) were detected inside the ceramic bulk except, as already reported, the few microns of the "*shell*" layer below the interface.

To verify that, if at the base of the observed phenomenon of the colouring of the underlying substrate volume, there was water or fluorine, a series of planned tests was carried out consisting in coating Ce-PSZ flat samples with different substances listed in table 6. Each test considered one ion in turn among all those present in the coating glass which were suspected to have a possible influence on the redox reaction (including phosphate group). To realise this procedure, a suitable substance was utilised for each test to allow interaction between the specific ion and the ceramic surface. This trial was realized by depositing the powder of such substance on the upper surface of the ceramic sample, with and without slurry. Tests were carried out even using Hench's Bioglass® (45S5) that does not contain fluorine and possible reducing agents, but it has instead a much more low melting temperature. The specimens so prepared were therefore introduced in a laboratory kiln to undergo a firing similarly to the one above described.

As depicted in table 6, neither fluorine, nor phosphorous, nor silicon were able to affect the ceramic substrate, without production of any significant colouring effect. Also water (humidity, as H_2O molecules) did not produce effect, even in synergy with the above cited suspected ions.

Consequently, according to what expressed in table 6, it was clearly proved that no component belonging to the glass chemical composition takes part to the invoked redox reaction involving cerium ions.

It is instead possible to observe that the colouring effect occurs in Ce-PSZ samples only when a glassy substance covers the ceramic substrate during heating, even if it does not contain a redox partner for the $Ce^{4+} + e^- \rightarrow Ce^{3+}$ half-reaction, such as in the case of the 45S5 Hench's Bioglass®.

Table 5. Correspondence between colour and possible compounds of cerium.

compound	CeO_2	Ce_2O_3	$CePO_4$		CeF_3	$CeFCO_3$
name	ceria	-	Monazite		-	Bastnaesite
phase	cubic	trigonal	monoclinic	rhombohedral	hexagonal	hexagonal
colour	brown-white	grey-green	red	yellow	white	white

Table 6. List of substances proposed as coating to induce comparative effects on the Ce-PSZ substrate.

coating material(s) applied (before coating process: 1290°C/15min; ramp: 100°C/h)	substance(s) or ion(s) expected to react with the ceramic	XRD new phases formed after coating on the glaze layer or on the surface/interface of the substrate		colouring effect	structural effect on Ce-PSZ surface
AP40 glass + + cmc♣ slurry	glass polymer water♦	31-300 35-327÷11-676÷33-1229 9-432 32-199 (?)	$CaSiO_3$-2M $Ca_7(SiO_4)_2(PO_4)_2$ $Ca_5(PO_4)_3OH$ $CePO_4$	✓	T→M♠
CaF_2	fluorine	35-790 34-394 (?) 28-775÷4-733	$CaZrO_3$ CeO_2 $CaO÷Ca(OH)_2$	none	T→M♠ (scarce)
CaF_2 + cmc♣ slurry	fluorine polymer water♦	35-790 34-394 (?) 28-775÷4-733	$CaZrO_3$ CeO_2 $CaO÷Ca(OH)_2$	none	T→M♠ (scarce)
Hench's glass#	glass	47-515	$Na_5Zr_4Si_3P_3O_{24}$	✓	T→M♠ (?)
Hench's glass# + + cmc♣ slurry	glass polymer water♦	47-515	$Na_5Zr_4Si_3P_3O_{24}$	✓	T→M♠ (?)
$CaHPO_4 \cdot 2H_2O$	phosphate	41-489 (?)	$Ca_2P_2O_7$ (γ-phase)	none	-
$CaHPO_4 \cdot 2H_2O$ + + cmc♣ slurry	phosphate polymer water♦	41-489 (?)	$Ca_2P_2O_7$ (γ-phase)	none	-
SiO_2 (silica)	silicon		-	none	-
SiO_2 + cmc♣ slurry	silicon polymer water♦		-	none	-

♦ From burn out of the organic binder (cmc); ♣ Organic binder in the slurry (cmc: carboxylmethylcellulose); # Glass not containing fluorine; ♠ Martensitic microstructural transformation (tetragonal → monoclinic).

The only possible reasonable explanation, deductible from the experimental evidences, is the occurring of the chemical auto-redox equation: $4CeO_2 \leftrightarrows 2Ce_2O_3 + O_2\uparrow$, the equilibrium constant of which is described by:

$$K_{eq} = \frac{K_R}{P_{O_2}} = \frac{[Ce_2O_3]^2}{[CeO_2]^4}$$

K_R is the thermodynamic equilibrium constant, the brackets indicate the concentration of the reported compounds, K_{eq} indicates an equivalent term of equilibrium between CeO_2 and Ce_2O_3 depending on the partial pressure of oxygen (P_{O_2}).

To demonstrate the validity of this hypothesis a series of heating tests were planned. Ce-PSZ ceramic samples, in discs and in fragments, coated or not with AP40 glass, were heated in kilns with different atmospheres (air or argon, always at normal pressure, 101325 Pa). This series of tests allowed the identification of a threshold temperature of about 900°C in air and 800°C in argon, above of which the samples assumed the grey-green colour: higher the temperature exceeding the threshold, and more marked the colour assumed by the ceramic body. In argon atmosphere, the samples coloured more markedly. The coloured samples, not coated with glass, decoloured partially by a successive heating at high temperature in a normal atmosphere and cooled slowly (table 7).

To better follow what happened, Ce-PSZ samples were investigated also through a thermo-gravimetric analysis device (TG) in flowing argon. Their change in weight was followed in a rated heating and cooling, from 1500°C to room temperature (150°C/h). The weight change (loss) occurred only during heating and attributed to O_2 released from CeO_2 (buoyancy drift correction in flowing Argon and thermal expansion of the device were considered in instrumental calibration). As the weight decreased, the contribution of the parts of ZrO_2 were expected to be constant, while the produced weight loss was attributed to a decrease of CeO_2 and an increase of Ce_2O_3.

Through a series of stoichiometric calculations, from the original data coming from TG analysis it was possible to track back to the amounts of CeO_2 and Ce_2O_3.

Table 7. List of the trials carried out to check the effect of the synergy of environmental atmosphere and heating on Ce-PSZ ceramic substrates.

trial #	condition of the Ce-PSZ ceramic	temperature (°C)	kiln atmosphere	colouring effect on Ce-PSZ ceramic
1	AP40 coating, no colour	1300	air	darkening of the "involved volume"
2	no coating, no colour	500	air	no colouring
3	no coating, no colour	700	air	no colouring
4	no coating, no colour	800	air	no colouring
5	no coating, no colour	900	air	slightly colouring
6	no coating, no colour	1300	air	total darkening of the bulk
7	no coating, no colour	1300	argon	total darkening of the bulk
8	no coating; Ce-PSZ coloured after trial #6	900	air	decolouration along edges and corners

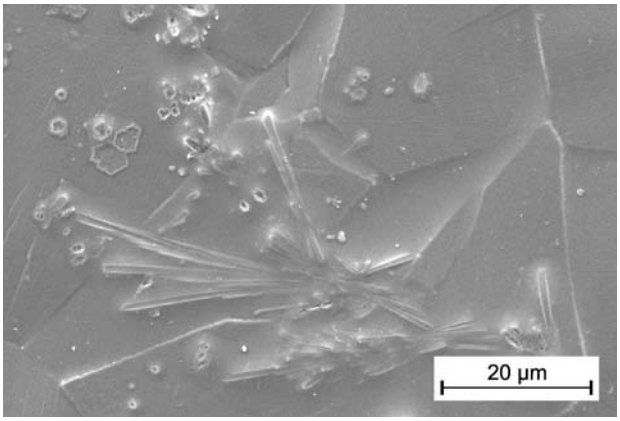

Figure 7. Needle-like shaped CPS (Nagelschmidtite family) microcrystals found on the bioglaze coating, together with HA (common in both Y-PSZ and Ce-PSZ coated samples), as reported in table 4.

Figure 7 shows the weight trends of CeO_2 and Ce_2O_3 with temperature for the sample Z4 and reports also the values of Keq calculated with the equation written above. On 100 parts of the total original weight, the 80 ones of ZrO_2 remain constant, and the variation concerns the remaining 20 parts of CeO_2.

On the other hand, it was already observed in many experiments that Ce^{4+} can change to Ce^{3+} at high temperatures [27]. Literature suggests that the coherency lattice strain of the Ce-PSZ brought about by a partial reduction of Ce^{4+} that results in a diffusion of Ce^{3+} along grain boundaries to free surfaces [29]. A partial reduction of Ce^{4+} would be favoured by the difference of 8-fold coordinated ionic dimensions of Zr^{4+} (0.84 Å) and Ce^{4+} (0.97 Å). This reduction produces 8-fold coordinated larger Ce^{3+} ions (1.14 Å) that however require a lower amount of oxygen and the lattice is allowed to remain tetragonal for the production of a sufficient number of oxygen site vacancies.

The release of the produced oxygen is possible at high temperature for migration towards external surfaces of O• radicals (the most probable form inside the crystal lattice of zirconia), thanks the structure relaxation. In fact, as above anticipated, zirconia lattice is a sufficiently good O• radical conducer at high temperature [26], although the speed of this latter is not very high. This migration can assume an extent for which at the temperature of firing it becomes possible that the chemical equilibrium shifts to right (at least on the covered side).

Consequently, depending on dimension of the sample and imperviousness (given by the microstructure of the ceramic body) of the possible paths through which O• radicals can migrate, if the cooling is too fast the back-migration of O• radicals (in equilibrium with atmospheric O_2) becomes forbidden for the shrinkage of the crystal lattice structure and most of the situation formed at high temperature remains stopped, as observed experimentally [28, 30].

In the ambit of the formulated hypothesis, the presence of the glass lowers the partial pressure of O_2 (PO_2) in an extent for which at the temperature of firing it becomes possible that the chemical equilibrium above written shifts to right.

In fact, the glass interposes itself between the atmosphere of the kiln and the ceramic substrate and does not allow a sufficient permeation of O_2, and the shape and range of the "*affected volume*" let one think that such explanation is autoconsistent. The colouring in the Ce-PSZ ceramic bulk disappears in correspondence of the geometric corners and edges of the volume of the ceramic sample, far off the glass coated surface, much more exposed and permeable to the hot oxidative atmosphere in the kiln during cooling. The melting glass acts likely as an insulator barrier, confining the reducing conditions that occur in the ceramic body.

The glass has reacted in a small extent with the ceramic material with formation of only few $CePO_4$, detected in the thickness of the coating and at the interface (figure 3). The formation of the observed HA, particularly at the surface of the deposited glass, is attributable to a reaction independent from redox events observed, considering that it forms also on the external surface of the glass on Y-PSZ substrates [17]. The observed physical behaviour of the glass on the surface

of all Ce-PSZ samples, as well the intense colouring, clearly indicates that a change in the chemistry of the glass itself occurred, which could in turn induce a change in the chemical and physical interactions at the interface glass-substrate. As concerns the formation of the singular toroidal accumulation of the glass towards the periphery of the disc-shaped samples, a lot of controversial physical reasons could be invoked, but these were not identified with certainty. As the phenomenon appears, it looks likely enough to be connected to the rise of the grey-green colouring of the substrate, interpreted as a pollution of Ce^{3+} inside.

In this way, the kinetic speed of restoring of the thermodynamic state during cooling is not isotropic anymore. This is the only conceivable reason that can come from experimental trials results reported in table 6. Through the not coated surfaces (side and bottom) O_2 permeation is possible, but its speed is not sufficient to restore completely the thermodynamic conditions effective at room temperature, and consequently some Ce_2O_3 remains trapped in those parts of the ceramic volume that are farther from external free surfaces. The geometric profile of the boundary of the "*affected volume*" inside the ceramic body shows this hypothesis to be reasonable.

Cerium and its compounds are not generally considered toxic for humans. Only a hint is made in proper literature [24] as having relative low toxic hazard (as well as together with calcium, gold, magnesium, potassium, sodium, yttrium, the zirconium itself, and others). As concerns the bioactivity of the deposited glass no tests were performed to ascertain if it would be unaltered after pollution on the Ce-PSZ samples, at the light of the unsuccessful result, while it resulted unmodified for the Y-PSZ samples. On the other hand, until now ISO standards have certified only zirconia stabilised with yttria as biomaterial. Results coming from this paper bring in some way other reasons as warning at least for zirconia stabilised with ceria.

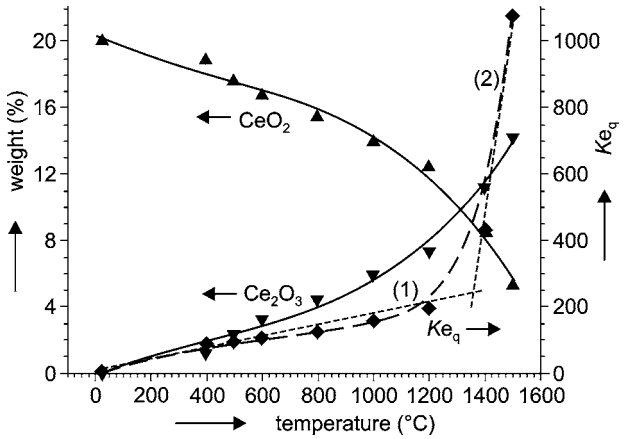

Figure 8. Trend of the weight % content of CeO_2 (▲) and Ce_2O_3 (▼) and of the equivalent constant $K_{eq} = [Ce_2O_3]^2/[CeO_2]^4$ as they can be calculated from O_2 loss determined on a DTG plot. The test was carried out in a flowing argon atmosphere.
The curve of K_{eq} (◆) can be interpreted as the superposition of two linear trends (indicated by dashed lines ---): the first (1) at a slow rate of decomposition, with equation:

$$K_{eq} = -44.492 + 0.166T \text{ (K)},$$

from room temperature up to about 1300°C; the second (2) at a fast rate of decomposition, with equation:

$$K_{eq} = -9279.196 + 584T \text{ (K)},$$

from this last temperature forward.

CONCLUSION

Surface interactions and reactions which have produced the singular arrangement of the glaze on the Ce-PSZ substrates give rise to a degradation of adhesion too, as UTAS data confirm (table 3).

What is sure is that cerium ions present as LSA of zirconia have a fundamental role in the observed behaviour.

Consequently AP40 is (and probably many other similar bioactive glasses are) useless as coating material on zirconia ceramic stabilised with ceria, but remains very useful for the same ceramic stabilised with yttria as previously reported [20]. Consequently, bioactive glass AP40 can be adopted to coat Y-PSZ ceramic devices, with formation of a good and stable coating layer.

On the contrary, Ce-PSZ ones are not able to be coated by this glass because chemically interacting with it, yielding a glass coatings unable for biological applications. This experience reflects also on all possible bioactive glass compositions, all subject to react in the same way with cerium ions. Further, if the attribution to the decreased partial pressure of oxygen is correct, together with the insulated conditions of the ceramic below the glass coating, the observed redox reaction of Ce^{4+} ions to Ce^{3+} should be observed even operating a total surface glass coating, with a complete darkening of the coated Ce-PSZ ceramic. However, if such device were implanted, the presence of ions underwent to a redox reaction, even though in the ceramic below the glass coating, could have a reactive response also with the fluids or living structures surrounding and aggressive on the coating, and this could lead to unpredictable biological situations. Therefore, from these conclusions a new target of research arises aimed to a verification of a complete satisfactory biological compatibility of zirconia ceramics stabilised with ceria. Formation of hydroxyapatite in the glaze is however a good event and this may lead to unexpected developments of information in the study of the biological interactions of materials, particularly for applications on Y-PSZ substrates.

Acknowledgement

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VLIV CeO_2 JAKO STABILIZÁTORU ZrO_2 NA POVLAKY BIOGLAZE®

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Cílem práce bylo podrobně studovat chování skelných bioaktivních povlaků (Bioglaze®) na zirkoniových substrátech s různými stabilizátory. V případě tetragonálního cerem stabilizovaného zirkonia (Ce-PSZ) dochází k některým jevům. CeO_2 stabilizátor podléhá částečně reversibilní redoxní rovnováze CeO_2-Ce_2O_3, způsbené migrací kyslíku během pokrývání glazurou - ZrO_2 je znám jako vodič protonů a kyslíkových radikálů při vysokých teplotách. To se makroskopicky projevuje šedozeleným zbarvením Ce-PSZ substrátu pod glazovaným povrchem („ovlivněný objem“) díky vlastnímu zbarvení Ce_2O_3. Z rozsah migrace kyslíku lze odhadnout jak se při teplotě glazování kolem 1300°C posouvá rovnováha směrem k Ce_2O_3. Snížením bariérního působení glazury pro atmosféru může kyslík difundovat zpět do mřížky Ce-PSZ, obnovit rovnováhu mezi CeO_2-Ce_2O_3 a vyvolat odbarvení Ce-PSZ na původní světlý odstín. Bioaktivní sklo používané na povlaky je vápenato-křemičitofosfátové s kódovým označením AP40.