Estudo da Sinterabilidade de cerâmicas dentárias de ZrO$_2$(Y$_2$O$_3$)-Biovidro usando dilatometria.

Investigation of the sinterability of ZrO$_2$(Y$_2$O$_3$)-bioglass dental ceramics by dilatometry

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Palavra chave:

Dilatometria,

Comportamento de sinterização,

Compósito ZrO$_2$-biovidro.

Resumo:

O objetivo deste trabalho é estudar por análise dilatométrica à sinterização por fase líquida da cerâmica ZrO$_2$ utilizando biovidro como aditivo. Pós de ZrO$_2$ estabilizados com Y$_2$O$_3$ foram misturados com 3%, 5% e 10% em peso de biovidro com a composição baseada no sistema 3CaOP$_2$O$_5$-MgO-SiO$_2$. As amostras foram preparadas por prensagem uniaxial a frio sob 80 MPa e a densidade relativa à verde foi determinada. O comportamento de sinterização nas diferentes temperaturas foi estudado medindo a retração linear das amostras num dilatômetro. As velocidades de aquecimento e resfriamento usados neste estudo foram de 10ºC/min. A temperatura máxima de sinterização foi de 1300ºC com um tempo de retenção isotérmica de 120min. Os resultados de retração e das taxas de retração associadas a temperatura de sinterização ou de tempo foram relacionados com a quantidade de biovidro na amostra. As amostras sinterizadas foram caracterizados por sua densidade relativa e pela análise de Difracção de Raios-X. As micrografias indicam microestruturas semelhantes. Um aumento da quantidade de biovidro leva a aumento da fase monoclínica de ZrO$_2$. Os resultados da dilatometria indicam uma redução da temperatura quando o máximo de retração ocorre, em função do aumento da quantidade de biovidro. Além disso, o uso da fase líquida reduz a temperatura máxima de sinterização de 1447ºC para 1250ºC – 1280ºC.

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Abstract:

The objective of this work is to study by dilatometry, the liquid phase sintering of ZrO_2 ceramics using bioglass as sintering additive. Y_2O_3- stabilized ZrO_2 powders were mixed with 3, 5 and 10 wt% of bioglass with the composition based on $3CaOP_2O_5$-MgO-SiO_2 system. Specimens were prepared by cold uniaxial pressing under 80MPa and the green relative density was determined. The sintering behavior was studied by measuring the linear shrinkage of samples in a dilatometer in relation to the temperature. The heating and cooling rates used in this study were 10ºC/min and the maximum sintering temperatures was 1300ºC with a 120 min isothermal holding time. The results of the shrinkage and shrinkage rates in regard of the sintering temperature and time were related to the amount of bioglass added. The sintered samples were characterized by X-ray diffraction analysis and their relative density. SEM micrographs indicates similar microstructure, and an increase of bioglass content leads to increasing of monoclinic ZrO_2 phase content. The dilatometry results indicate a reduction of the temperature where a maximum shrinkage rate occurs, as function of bioglass increasing. Furthermore, the use of liquid phase reduces the maximum sintering temperature of 1447ºC to 1250-1280ºC.

1. Introduction

The uses of dense ZrO_2 based ceramics is proposed in dentistry because of the excellent biocompatibility, high hardness and wear resistance, besides their high mechanical strength and fracture toughness [1].

Pure ZrO_2 cannot be used manufacturing parts without the addition of stabilizers, such as Y_2O_3. Actually, yttria-stabilized ZrO_2 ceramics (Y-TZP) is frequently used as a substitute material for metals and alumina ceramic in structural applications, being also inert body fluids, besides its higher strength, fracture toughness and lower elastic modulus [2-3]. The high fracture toughness of Y-TZP is due to the phase transformation toughening mechanism produced by stress induced tetragonal to monoclinic (t-m), designed martensitic phase transformation of the ZrO_2 grains, accompanied by a volume increase of 3-6% [1,4].

The martensitic (t-m) transformation causes compressive stresses ahead of the crack tip, thus difficult crack propagation and resulting in an increase of the fracture toughness. These ZrO_2 ceramics are produced by solid-state sintering at temperatures in the order of 1500ºC. Recently, the liquid-phase sintering of ZrO_2 ceramics has been investigated [5-7], reducing the sintering temperatures to 1250ºC

- 1300ºC. The decrease of the mechanical strength caused by the secondary intergranular glassy phase is partially compensated by residual stresses generated between the ZrO_2- matrix and the intergranular phase. Thus, lower sintering temperatures may be used to densify ZrO_2 ceramics maintaining satisfactory mechanical properties, with hardness of 900 to 1000HV, fracture toughness between 5 to 6 $MPa.m^{1/2}$ and bending strength near to 400MPa [6].

In order to optimize the amount of bioglass added and the sintering conditions of these materials, dilatometric studies can e conducted. The instantaneous shrinkage must be determined, and the shrinkage rates permits the development of improved sintering cycles, favoring the obtaining of refined microstructure and high densification of these ceramics. This work investigates the liquid phase sintering of Y-TZP with additions of a bioglass by dilatometric studies aiming the optimization of the sintering parameters.

2. Experimental Procedure

As starting powders, yttria-stabilized tetragonal, 3mol% ZrO_2-Y_2O_3 powder containing binder (ProtMat® Materiais Avançados

- Brazil), Ca(H$_2$PO$_4$)$_2$ H$_2$O and CaCO$_3$, (SYNTH®-Brazil), high purity SiO$_2$ (99.9%) (Fluka®-Germany), and MgO (VETEC®-Brazil), have been used.

2.1. Bioglass Preparation

A bioglass with closed composition of 52.75wt%-3CaOP$_2$O$_5$, 30wt.% SiO$_2$ and 17.25wt.% MgO, has been prepared. This bioglass was studied by Oliveira et al [8-9] and presents high bioactivity. The Ca(H$_2$PO$_4$)$_2$H$_2$O, CaCO$_3$, SiO$_2$ and MgO powders were mixed in a planetary mill for 1h. The bioglass was obtained by melting of the powders at 1550ºC for 2h and a rapid quench in water. The glass was crushed and sieved in a 32μm sieve.

2.2. Sintering Behavior

Powder mixtures of 3Y-TZP mixtures containing 0, 3, 5 and 10wt% bioglass were prepared by attrition milling of the ZrO$_2$ and bioglass powder for 2h at 1000rpm, using alcohol as vehicle. After milling the powder mixtures was dried in a rotary evaporator and in a drying oven at 100ºC for 24h. After drying the powder mixtures were deagglomerated by sieving in a sequence of sieves with apertures of 425, 125, 63 and 32μm. Rectangular green bodies of 5x5x15mm were prepared by cold uniaxial pressing under 80MPa for 60s.

In order to investigate the sintering behavior of the samples, dilatometric studies have been conducted at a maximum sintering temperature of 1300ºC, using heating rate of 10ºC/min with an isothermal holding time of 2h in air, using a Netzsch-DIL 402 PC dilatometer. As a result the linear shrinkage and shrinkage rate as a function of temperature and time have been obtained.

2.3. Characterization

Phase analysis has been performed by X-ray diffraction. The volumetric content of the monoclinic phase, Vm, has been calculated by the integrated peak intensity of the monoclinic peaks, (111)$_M$ and (111)$_M$, and the tetragonal peak, (101)$_T$, according to the equations (1) and (2) [10-11]: (1)

$$X_M = \frac{I_{(\bar{1}11)M} + I_{(111)M}}{I_{(\bar{1}11)M} + I_{(111)M} + I_{(111)T}} \quad (1)$$

$$V_M = \frac{1.311 X_M}{1 + 0.311 X_M} \quad (2)$$

With: (111)$_M$, 2Θ = 28º, , 2Θ = 31.2º and , 2Θ = 30º, represent the integrated peak intensities due the X-ray diffraction on the planes and of the monoclinic crystal structure and on the plane of the tetragonal crystal structure. The specific mass was determined by the immersion method, using Archimedes' principle. The relative density was calculated as the ratio between the specific mass and the theoretical specific mass of each composition. The microstructure were observed in a scanning electron microscope, LEO 1450VP. Polished surfaces were thermal etched at 1300ºC-15min, with heating temperature of 30ºC/min, and grain size average was measured.

3. Results and Discussion

3.1. Compaction

The relative green density of the compacted specimen in regard to the amount of bioglass added is shown in Figure 1.
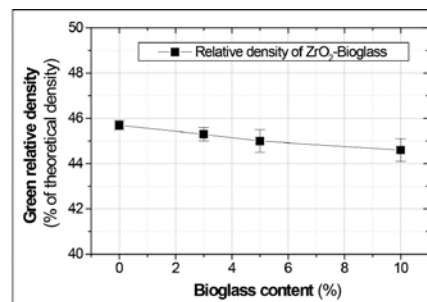

Figure 1: Relative green density of samples in regard of amount of bioglass added.

A slight decrease of the green density can be noted as the amount of bioglass increases. This is attributed to the increasing of the number of irregular shaped bioglass particles [12], in comparison with the spherical shaped ZrO$_2$ particles, see Figure 2. However, as the difference in the green density of the specimen

is less than 1%, its effect on the sinterability has not been considered on the sintering dilatometry results.
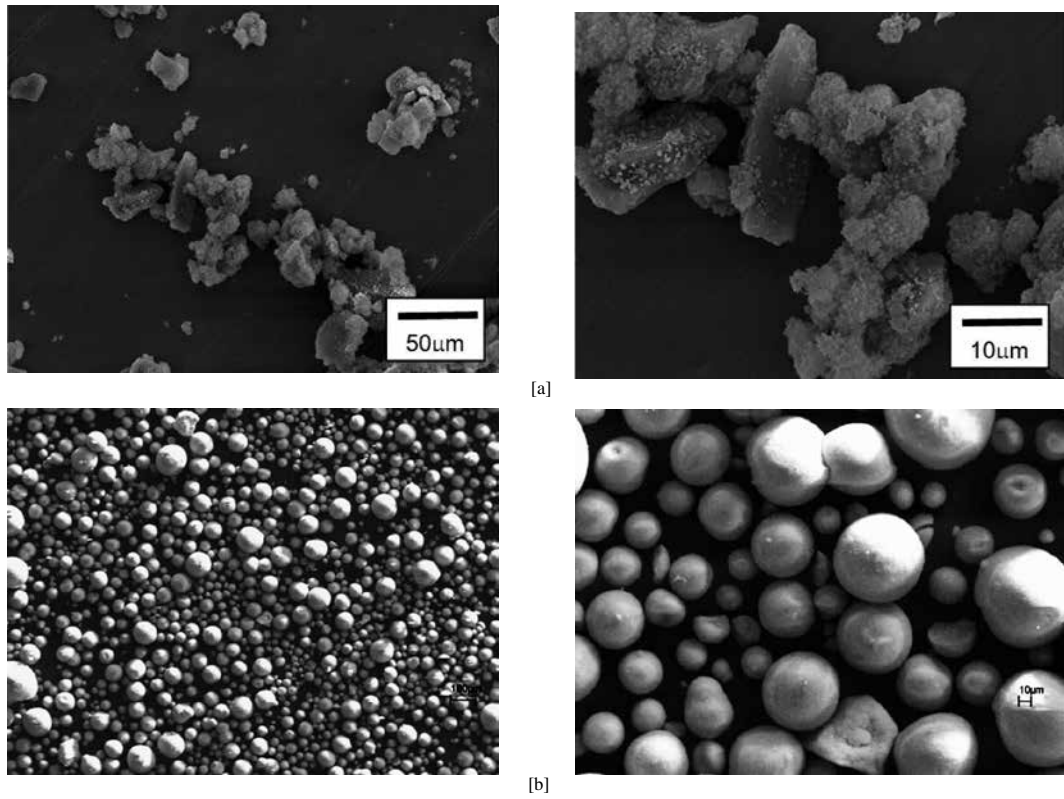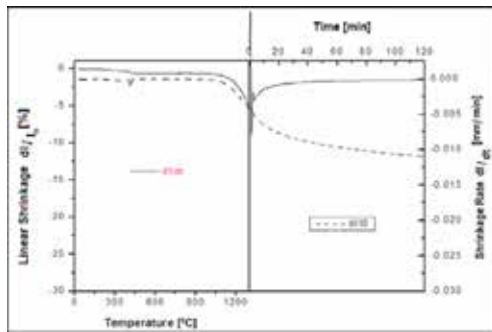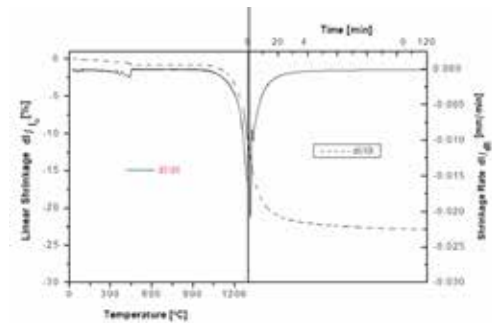

[a]

[b]

Figure 2: Morphology of the particles: [a] Bioglass; [b] $ZrO_2(Y_2O_3)$
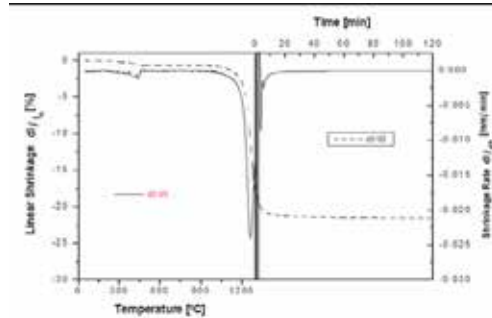
3.2. Dilatometry

Figure 3 shows the shrinkage and shrinkage rates of the samples with 0, 3, 5 and 10 wt% of bioglass additions as a function of the temperature and of the time during the iso-thermal holding time.
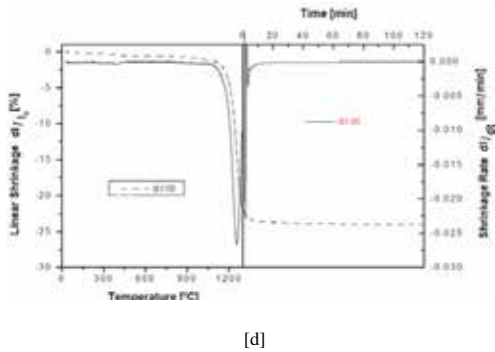

[a]

[b]

[c]

[d]

Figure 3: Shrinkage and shrinkage rates: [a] 0% ; [b] 3% ; [c] 5% and [d] 10% bioglass.

In regard of the dilatometric diagrams the analysis is divides in three regions:

The first region up to 600ºC. The most significant variations talking place in this region around 450 ºC. The observed shrinkage occurring at this temperature is attributed to the burn-out of organic binder from the $ZrO_2(Y_2O_3)$ powder.

A second region up to the isothermal holding time at 1300ºC. As can be seen shrinkage increases, and a maximum shrinkage rate can be observed. Figure 4 presents the temperatures of the maximum shrinkage rates and also the percentages of the shrinkage at these temperatures.
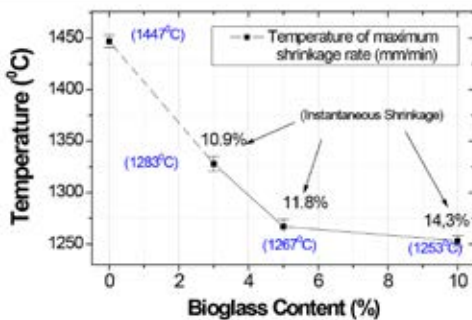

Figure 4: Effect of the amount of bioglass added on the temperature of the maximum shrinkage rates.

It can noted that the temperature of the maximum shrinkage rate decreases with increasing amount of bioglass added, Thus increasing the amount of liquid phase by adding more bioglass, the temperature of sintering may be lowed and still high densification may result.

The samples of pure $ZrO_2(Y_2O_3)$, without bioglass addition, show a distinct behavior, because sintering occurs by solid-state sintering with different sintering mechanisms acting [13]. Sample without addition of bioglass do not reach the maximum shrinkage rate at tem-

peratures below 1300ºC. The temperature of the maximum shrinkage rate has been determined in other works and is near to 1400ºC.

Therefore, isothermal treatments are necessary to achieve total densification at 1300ºC. The temperatures of the maximum shrinkage rates for the samples containing 3, 5 and 10wt% bioglass were 1283ºC, 1267ºC and 1253ºC, respectively.

The third region of the sintering analysis considers the isothermal holding at 1300ºC. From Figure 4, it can be seen that samples with higher amounts of bioglass additions achieved a higher shrinkages up the maximum sintering temperature of 1300ºC. From this moment on, as can be seen from Figure 5, shrinkage of the bioglass containing samples continues during the isothermal time, but leveling off hand as complete densification is reached. On the other hand the solid-state ZrO_2 samples continue to shrink even after 2h isothermal time.
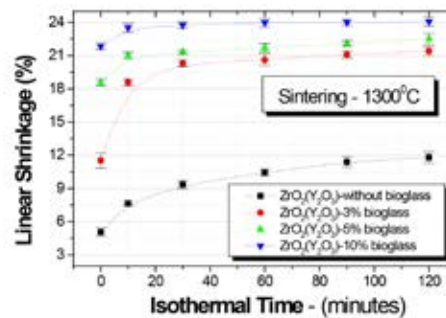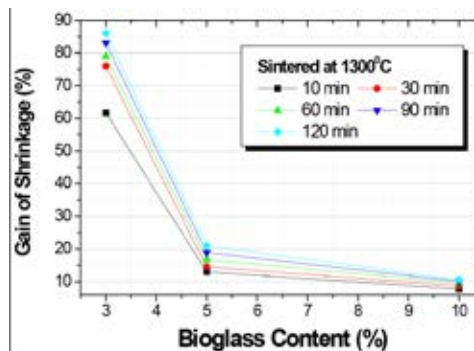

Figure 5: Shrinkage during isothermal walking treatment at 1300ºC.

The results presented above may be represented by the shrinkage gain as a function of the isothermal holding time. In this case, only ceramics containing bioglass addition were studied. These results are presented in Figure 6.
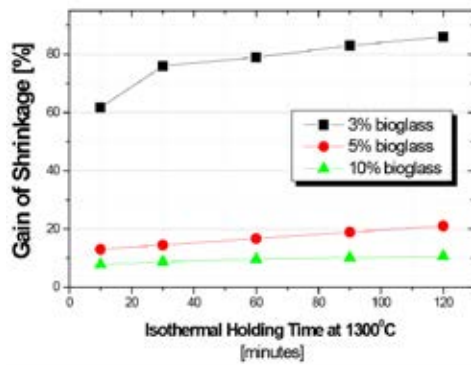
Figure 6: Shrinkage gain during isothermal treatment as function of the amount of bioglass added.

It is evident that samples with 3 wt% bioglass addition show higher gains of shrinkage during the isothermal treatment. After 10 minutes of isothermal treatment the gain in shrinkage is about 60%, while longer holding times up to 120 min lead to shrinkage gains higher than 85%. The densification of samples containing 5 and 10 wt% bioglass is less pronounced during the isothermal sintering at 1300 ºC because; both 5% and 10%, present high shrinkage during heating. Even so, a shrinkage gain of 20% and 10% is observed for samples with 5 and 10% bioglass, respectively, after 120 min. The high levels of shrinkage observed for the samples containing bioglass indicates that a high densification has been achieved; On the other hand it is also evident that the pure ZrO_2 samples did not densify completely under the sintering conditions of 1300 ºC-2h employed.

It is important to consider that all dilatometric analysis was realized at high temperatures, no considering the cooling which the samples are submitted after sintering. XRD patterns of the sintered samples are presented in Figure 7.
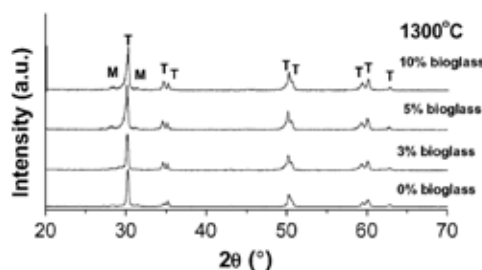

Figure 7: XRD patterns of the sintered samples.

The X-ray diffraction patterns reveal only t- and m-ZrO_2 as crystalline phases present. No secondary crystalline phases have been detec-

ted; indicating the bioglass added maintained its amorphous state. Figure 8 presents analysis of % martensitic transformation and relative density as function of bioglass content.
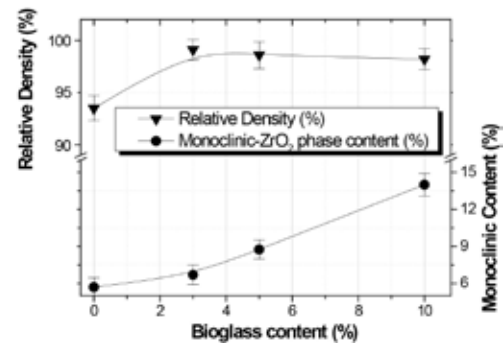

Figure 8: Relative density (T – Tetragonal ZrO_2 ; M – Monoclinic ZrO_2 , as well as the amount of monoclinic-ZrO_2 phase in regard to the amount of bioglass.

An increase of the m-ZrO_2 phase is observed with increasing amounts of bioglass added. Apparently the "t–m" phase transformation occurred during cooling and may have been triggered by stresses caused by the thermal mismatch of the ZrO_2 matrix and the intergranular bioglass phase. This may also be the reason for the porosity as indicated by the decreasing relative density for the samples containing 3, 5 and 10% bioglass.

Figure 9 presents SEM micrographs after sintered samples, indicating ZrO_2 grain size average near 0.4-0.5µm, in different compositions. It is an advantage of the sintering at low temperatures. The obtaining of refined microstructure possibilities the improvement of the mechanical properties of these ceramics, mainly bending strength and fracture toughness.
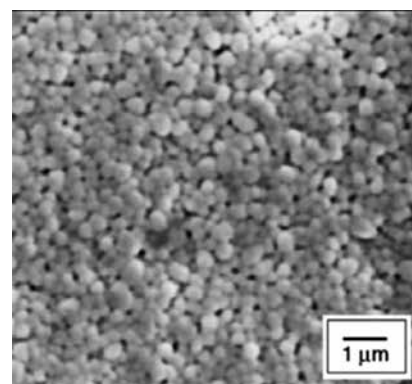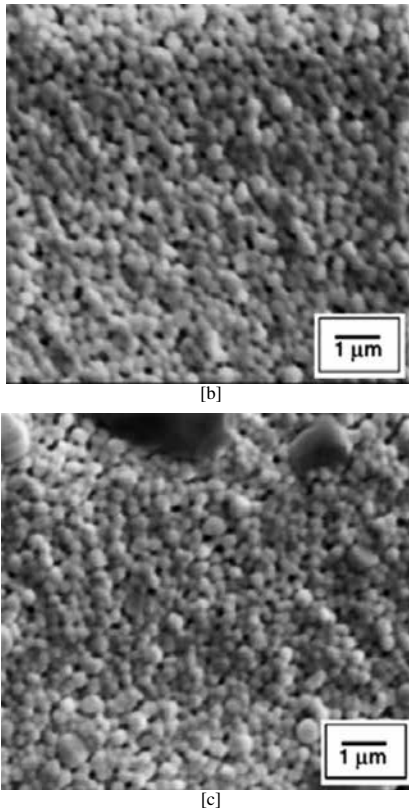

[a]

Figure 9: SEM micrographs of the ZrO2-bioglass ceramics sintered at 13000C: [a] 3% of bioglass; [b] 5% of bioglass; [c] 10% of bioglass.

4. Conclusions

The results obtained in this work indicate that it is possible to sinter ZrO_2 ceramics to high final densities with limited amounts of bioglass as additives at a temperature of 1300ºC. On the other hand, pure $ZrO_2(Y_2O_3)$ could not be sufficiently densified under the same conditions. The maximum shrinkage rates depend on the amount of bioglass and are lower for higher glass amounts. Maximum shrinkage rates occurred at 1253ºC, 1267ºC and 1283ºC for the samples containing 10, 5 and 3% bioglass, respectively. In all cases where bioglass has been used as additive, an isothermal treatment at a sintering temperature of 1300ºC has been necessary in order to achieve high final densities.

Due to stresses generated by the thermal mismatch of the ZrO_2 matrix and the secondary amorphous bioglass phase, part of the ZrO_2 transforms into the monoclinic phase during cooling, which may cause a slight decrease in the final density.

5. References

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