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DENSITY AND GRAIN GWORTH EVOLUTION OF SINTERED YSZ (YTTRIA- STABILIZED ZIRCONIA)

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Density and grain gworth evolution of sintered YSZ (yttria- stabilized zirconia)

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ABSTRACT

During sintering and compaction process, powders enters densification process with reduction of open pores volume. In the study YSZ (yttria-stabilized zirconia) is used to verify what the literature tells about sintering process of powders. After compressing at different pressures and stabilize the sample at different sintering temperatures, bulk and apparent density of sample were calculated in order to investigate the density increasing and the presence of pores. The sample after the process was taken under SEM to analyse the microstructure. Second part of the study is the investigation of grain growth mechanism after maintaining a pre-sintered sample at different sintering temperatures for three different times (30 min - 2 hrs -6 hrs). Increasing sintering temperature densification increase, at high temperature relative density become close to theoretical one. Open pores volume for the highest applied pressure and temperature reach 0.0018 cubic centimeters. In grain growth equation we obtain 'n' exponent is equal to 4.36. Activation energy for the grain growth mechanism is equal to Q$\backsim 82.925 \pm 12.4 \frac{KJ}{mol}$.

Introduction

Zirconia is a oxide which exists in three phases with different crystalline structures : monoclinic, tetragonal and cubic(T > 2960 °C)[1]. Addition of Yttrium stabilizes the cubic phase of the zirconia allowing the production of sintered zirconia with cubic structure at room temperature. YSZ (yttrium-stabilized zirconia) is used as thermal coating, solid electrolyte in SOFC (solid oxide fuel cell), as nanofibers and nanowires. Diffusion occurs in any material above the absolute zero but it can be accelerated by means of temperature increase. From a starting powder sintering process is used to obtain a solid body with a crystalline structure with a reorganization of porosity and increasing of density. Sintering for YSZ powder is done with solid-state sintering, process the driving force that gives the lowering of the free energy of the system are the curvature of the particle surfaces, chemical reaction and an externally applied pressure. The sintering process is done at different temperature and the powder is subjected to uniaxial dry pressing at different pressure before sintering. The presence of pores at the end of the sintering process is an important parameter relative to mechanical properties. Presence of trapped pores it is undesirable for mechanical properties but it could be useful for eletric features it depends on the final use of the material. Sintering process is useful for the densification of the solid body but the maintenance at high temperature will lead to the grain growth mechanism, in order to have the best mechanical properties the grain size must remain low, with grain growth even the porosities grows[2]. The work is divided in two part : I. study the density and microstructural evolution of the sample with different pression and sintering temperature; II study of the grain evolution with different sintering temperature and a crescent time holding at these temperature.

Experimental procedure

Material

The raw material is YSZ (yttria-stabilized zirconia) ZrO_2/Y_2O_3 3mol% powder (provided by Inframat® Advanced Materials™) with 99.9% purity ready to press powder granulated with PVA binder. Density 6.10 g/cm^3, melting temperature 2700 °C. Thermogravimetric and differential thermal analysis were conducted to study the thermal behavior of the raw material using NIETZSCH Geraerebau GmbH STA 409 thermobalance (heating rate 20°C/min up to 900°C, air flux 100 cc/min), the result are reported in Fig1. A exothermic peak is recognized at 400° C related to the crystallization of Zirconia[3], TGA analysis help showing 2.5 %m weight loss until reaching 500°C.

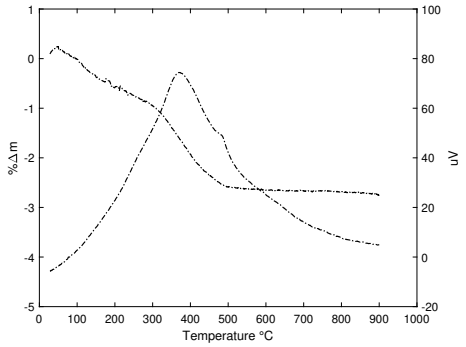

Fig.1 TGA and DTA analysis conducted on the raw material, maximum temperature 900 °C. Exothermic peak is easily detected in the plot.

Dilatrometic analysis is reported in Fig.2 done by L75 PT Horizontal dilatometer by Linseis (heating/cooling rate 20°C/min, $T_{max} = 1550C$).

The ready-to-press powder and after sintering was anal-

ysed with SEM (scanning electron microscopy), the samples were sputtered with Pt-Pd coating (using Quorum Q150T ES sputtering machine) and a bit of silver paint. SEM instrument is JEOL JS-5500 microscope.

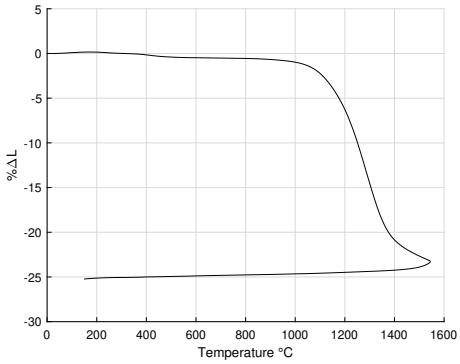

Fig.2 Dilatrometry analysis reaching 1550 °C, linear shrinkage is equal to 25%.

Density and microstructural evolution with different pression and temperature

The samples (about 0.2 g powder) were dry-pressed in a cylindrical die at several pressures and different temperatures, for every specimen diameter,thickness and weight were measured. The die was held under pressure for 5-10 s. The uniaxial dry presser used is 'manual servo-hydraulic press provided by Specac' in a cylindrical die Ø =20 mm. Four compaction pressures values : 30- 70 -110 -150 MPa; and four sintering temperatures : 1050°-1150°-1250°-1500° C were applied. For each combination of pressure/temperature five replicates were measured. To achieve these temperatures from room temperature a Furnace by Nabertherm ® HT16/16 was used with 5° C/min heating rate from room temperature to 600°C, 10° C/min heating rate from 600°C to T_{sint}. The samples stayed at T_{sint} for 2 hours and free cooled down to room temperature. Bulk density were measured on green samples with digital calliper (Borletti) and balance (Gibertini E42S4 digits) using the geometrical method.

In order to find their densities and porosities the Archimedes method were used[4](ASTM Standard). The exterior volume can be obtained by :
$V = M - S$,
where M is the immersion weight and S the saturation weight. The previous formula can be considered if we assume that 1 cm^3 of water weights 1 g. The apparent porosity is calculated by :
$P = [\frac{(M-D)}{V}] \times 100$,
where D is the dry weight. Water absorption (A) can be quantified as the percentage of the weight of absorbed water relative to the dry sample weight:
$A = [\frac{(W-D)}{D}] \times 100$.
The apparent density (T) refers to a portion of the sample that is water proof and is calculated:
$T = \frac{D}{(D-S)}$.
Relative density :
$\%R.D. = \frac{Bulkdensity}{Theoreticaldensity} \times 100$,
where the theoretical density is given by the manufacturer of the powder. Open pores volume :
$V_{openpores} = W - D$.
Closed pores volume :
$V_c = V_{ext} - V_{openpores} - \frac{D}{Theoreticaldensity}$.
Each sample were analysed under SEM and observed the microstructure and the porosity.

Grain growth evolution with Temperature and time

In order to investigate the effect of temperature and holding time on grain growth dog-bone specimen were created from the green powder using a dog-bone die $L_e = 26mm, L_i = 16mm, s_e = 12mm, s_i = 4mm$. Specimens were pre-sintered at 1250 ° C with a heating rate of 10° C/min and held for 1 h in temperature. After that they were inserted in a pre-heated furnace (Nabertherm HT10/18) for four different temperatures (1530°C-1570°C-1610°C-1640°C) and three holding time(30 min- 2 hrs- 6 hrs). Each sample were analysed with SEM for each combination of temperature and time. Grain size were estimated with linear intercept method[5](ASTM standard). The sintered material maintained at high temperature tend to minimize its energy leading to the coarsening of the microstructure. The grain growth relation is given by the next equation :
$G^n - G_o^n = kt$ with $k \backsim e^{\frac{-Q}{RT}}$
G represent the average grain size at a determined temperature and time, G_o is the pre-sintered grain size, Q is the activation energy, R universal constant, T absolute temperature of the annealing process and t is the time of the annealing process. The grain growth exponent 'n' can be estimated by plotting $ln(D)$ in y axes and $ln(t)$ in the x axes. The slope of the straight line obtained by fitting with a linear curve the data is the inverse of the grain growth exponent. The activation energy is calculated from the slope of the line obtained from the plot of $ln((G^n - G_o^n)/t)$ and 1/T.

Results and Calculation

Relative density

Fig.3 represent the relation between green density and applied pressure. Density increases with the pressure increasing, at 150 MPa the density is equal to $2,758 \pm 0.041 g/cm^3$.

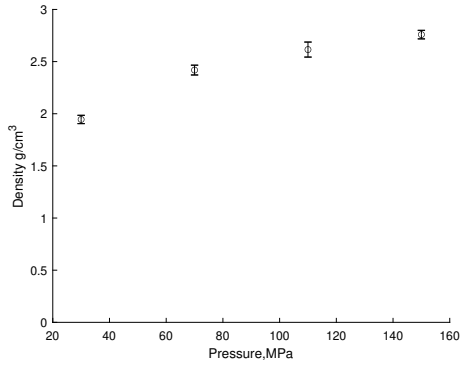

Fig.3 Green density of only pressed powder at 30/70/110/150 MPa. Green density were calculated using the geometrical method.

Fig.4 shows the temperature and the relative density with different applied pressure. As observed the increasing of sintering temperature and applied pressure will lead to an increasing of relative density, the increase in temperature cause the mobility of grain boundaries promoting densification .The relative density reach at its maximum at the value 97.7% at 1500°C with 150 MPa applied pressure.

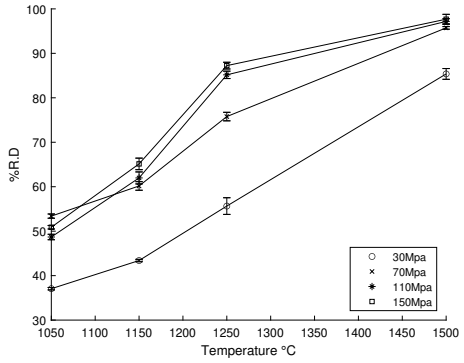

Fig.4 Relative density is giving the relation between bulk density (calculated with Archimedes method) and theoretical density.

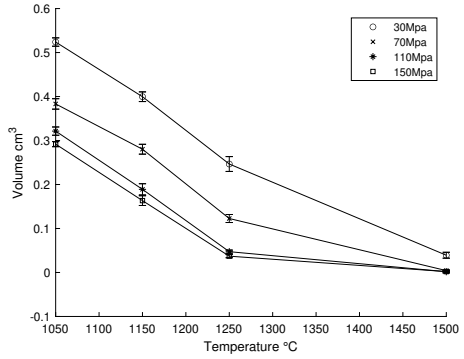

Fig.5 Open pores volume decreasing with increasing of applied pressure and Temperature

Open pores volume drastically drop down reaching value of 0.0018 cm^3 at 1500 °C and 150 MPa applied. The behavior of 110 and 150 MPa applied pressure is similar.

Dilatometric curve

Dilatometric curve shows the 1500° C sintering temperature correspond to the maximum reduction in length of the sample. At 1050-1150 °C sintering temperature correspond to pre-sintering region with surface transort mechanisms. At 1250-1500° C we are in the sintering region and even the relative density at this temperature shows the efficacy of densification. Open pore volume is very low, closed pores are more difficult to remove but at high temperature and pressure the maximum value of closed pores volume is 0.0055cm^3.

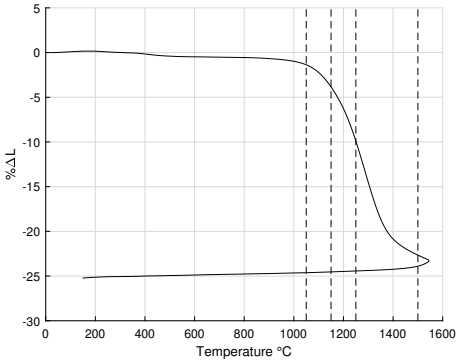

Fig.6 Dilatrometry analysis reaching 1550 °C with the sintering stage

In Fig.7(a) granules are still visible, using x1000 magnification intragranular fractures are possible to identify. Increasing pressure from 30 MPa to 70 MPa at 1050 °C granules are no longer visible.Initial stage is identified at 1050°-1150° C, grains are not visible, neck formation and growth starts. Intermediate stage is visible at 1250°C in SEM images spheroid particles are visible(Fig.7(b)). Final stage is identified with the presence of isolated open pores and the completely visible grain boundaries(Fig.7(c)).

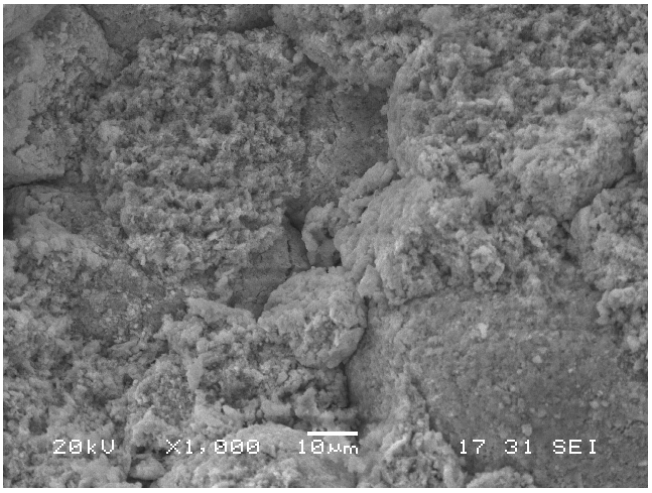

Fig.7.a SEM images, 30 MPa applied pressure , 1050° C sintering temperature

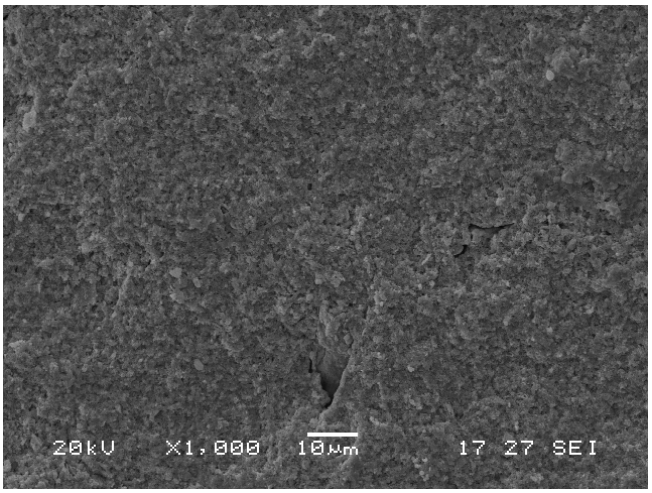

Fig.7.b SEM images, 110 MPa applied pressure, 1250° C sintering temperature

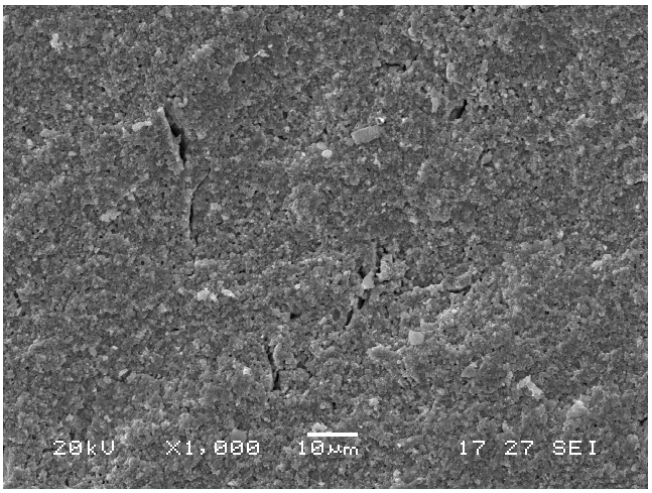

Fig.7.c SEM images, 150 MPa applied pressure, 1500° C sintering temperature

Closed pores don't decrease drastically as open pores, they remain entrapped, increasing the applied pressure closed pores volume is reducing but with pressure higher than 110 MPa the results were similar[6].

Grain growth evolution

Grain size calculated using the linear intercept method are resumed in the Fig.8. Grain growth mechanism follow the equation related to the temperature and time of the annealing process. Increasing the time and the temperature will lead to an increasing in the mean grain size of the material. After 6 hours at 1640° C the mean grain size is eqaul to $0.948 \pm 0.17 \mu m$.The pre-sintered mean grain size was $0.279 \pm 0.026 \mu m$,respect these two values the grain size increasing was 248% of the initial size. The trend of the grain size evolution become leveling after some time, the temperature becomes the main parameter controlling the grain growth mechanism.

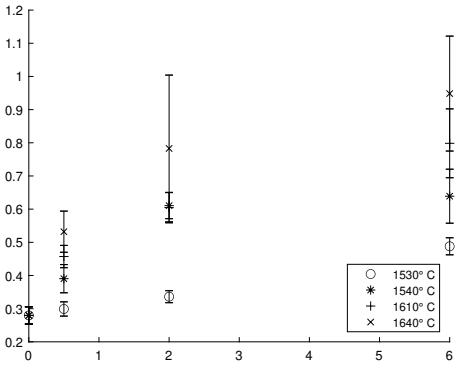

Fig.8 Grain size with the hours and different annealing temperatures

In Fig.9 and in Fig.10 are represented the $ln(D)$ on $ln(t)$ plot and the $ln((G^n - G_o^n)/t)$ on 1/T. The inverse of the slope in Fig.9 is equal to the 'n' exponent of the grain growth equation. $n \backsim 4.36$

The slope of Fig.10 is equal to the activation energy Q, $Q \backsim 82.925 \pm 12.4 \frac{KJ}{mol}$.

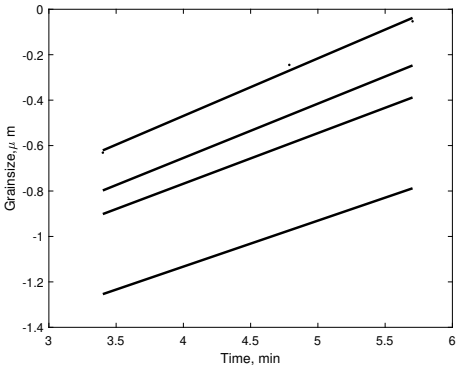

Fig.9 The inverse of the slope is equal to 'n' exponent

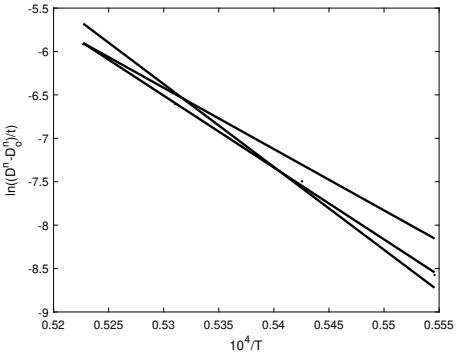

Fig.10 The slope is equal to the activation energy

Conclusion

The effect of sintering in densification process is confirmed in the study, relative density of sintered powder under uniaxial pressing can reach the 97.7% of the theoretical density. Densification related only to applied pressure is irrelevant respect the application of sintering process. Application of an external pressure and applying sintering process helps reducing open pores volume reaching value (for the highest applied pressure) $\backsim 0cm^3$ with a reduction of 99% of open pores volume. Closed pores volume is decreasing but above 110 MPa we are not able to see a further volume decreasing, at 110 and 150 MPa of applied pressure the closed pores volume is the same. Sintering process is also important in increasing mechanical properties of the material, pores are isolated and not interconnected, after sintering granules and intragranular fracture are not present. Maintaining dog-bone specimen at temperature higher than 1530 °C for 30 minutes,2 hours,6 hours grain growth mechanism starts. Pre-sintered specimen have grain size of 0.277 μ m, for 6 hours at 1530 °C the mean grain size reach 0.487 μ m, for 6 hours at 1640° C the mean grain size is equal to 0.948μ m. The trend of the grain size evolution become leveling after some time, the temperature becomes the main parameter controlling the grain growth mechanism and grain growth rate. [7]. At 1640° C for 6 hours in SEM images grains show abnormal grain growth, phenomenon explained in Rahaman M.[2]. Grain growth mechanism follow the grain growth equation with n exponent equal to 4.36 and activation energy $Q \backsim 82.925 \pm 12.4 \frac{KJ}{mol}$.

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