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Influence of Rare Earths on the Sintering of Zirconia-Yttria

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Yttria stabilized zirconia sintered by silicate glass phase with addition of ytterbium or gadolinium was investigated. The grain growth rate was found to be higher in the gadolinium doped samples. The glass phase of the ytterbium doped sample showed partial crystallization on cooling. Grain conductivity was found to be highest in samples with a half hour of sintering, having decreased due to stabilizing ion migration from the grains to the grain boundary glassy phase. The differences observed in the sintering behavior and properties of the sintered bodies are attributed to the different ionic radii of the Yb^{+3} and Gd^{+3} ions.

Keywords: *zirconia-yttria, sintering, electrical conductivity*

Introduction

Pure zirconia has three polymorphic phases that are stable in different temperature ranges. The cubic and tetragonal phases usually become stabilized at room temperatures by doping with ions such as rare earth, yttrium, calcium and magnesium[1-4]. Doping introduces oxygen ion vacancies that can increase the ionic conduction by several orders of magnitude. Grain and grain boundary electric conductivities contribute toward ionic conduction in cubic stabilized zirconia. While electrical conductivity of the grain is dependent on the nature and concentration of the stabilizing ions, that of the grain boundary is influenced by the impurities segregated from the grains[5,6]. It is clear, however, that other causes contribute to low grain boundary conductivity, as has been shown by Verkerk *et al.* in high purity zirconia[7].

Ceramic bodies made from commercial zirconia powders prepared from zirconium silicate have small amounts of remaining silica that, together with other trace impurities, ziconia and the stabilizing oxide, produce a liquid phase during sintering. The liquid phase distribution in the microstructure, both during and after sintering, exerts a strong influence on the microstructural evolution and on the ceramic properties[8-10]. The rare earth ions participate in the grain stabilization and in the liquid phase, the relative concentration between these two phases being dependent on their ionic radius[5]. A systematic study of the influence of the minority ions on the electrical properties of the grain and grain boundary, as well on the liquid phase properties, is currently ongoing.

This work reports on the microstructural evolution of ZrO_2, 7 mol% Y_2O_3, 1 mol% RE_2O_3, where RE = Yb or Gd, by liquid phase sintering.

Experimental

The starting powders for sample preparation were ZrO_2 TZ-0 (Tosoh, Japan), Y_2O_3 (Molycorp, USA), and Ytterbium and Gadolinium Chlorides (Cerac, USA). The basic composition was ZrO_2, 7 mol% Y_2O_3, 1 mol% RE_2O_3, where RE = Yb or Gd. To this composition were added 1 mol% of the following oxides in order to promote the liquid phase sintering: SiO_2 (Cabosil, USA), Al_2O_3 (Baikowski, France) and CaO and TiO_2 (Riedel, USA). Three powders were prepared: ZY-Zirconia-Yttria; ZYLYb-Zirconia-Yttria-Ytterbium-liquid phase, and ZYLGd-Zirconia-Yttria-Gadolinium-liquid phase. The starting powders were mixed in polyethylene jars with zirconia balls and isopropyl alcohol, with polyvinyl alcohol as dispersant. Ceramic discs were prepared by uniaxial conformation, followed by isostatic pressing at 200 MPa. Sintering was done in air in the temperature range of 1400 °C to 1610 °C.

Characterization was done by XRD (Siemens D500), SEM (Zeiss 9600 with Link Analytical QX 2000 microanalyzer), Impedance Spectroscopy (HP 4192 A), and density

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by the Arquimedes method in water. Samples for observation of microstructures were polished with a final diamond paste of 1.0 µm grit and thermally etched for 5.0 min at 100 °C below the sintering temperature.

Results

The XRD spectra of the three studied compositions are shown in Fig. 1. Sample ZY still shows a monoclinic phase after sintering at 1610 °C for 2 h, while compositions ZYLYb and ZYLGd are fully cubic after sintering at 1500 °C for 2 h. The absence of a liquid phase during the sintering of other compositions with rare earth oxides, $ZrO_2 + Y_2O_3 + RE_2O_3$, not shown in this paper, have also shown a monoclinic phase after sintering at 1610 °C for 2 h. Therefore, liquid phase sintering promotes the formation of a solid solution. This effect can be seen in the microstructures depicted in Fig. 2. Microstructures of the ZY sample show small and large grains; the EDS analysis shows that larger grains are yttrium richer.

The density behavior of the ZYLYb and ZYLGd samples with sintering temperature is different, as shown in Fig. 3. Apparently, the volume of the glass phase increases with sintering temperature in the Yb doped sample, causing its density to decrease by around 5%. This behavior is confirmed in the microstructures shown in Fig. 4. During thermal etching of the 1500 °C sintered sample, a thin glass phase is expelled while sintering at 1610 °C results in much larger grains and thicker grain boundaries and, therefore, a larger glass phase volume. The 1610 °C sintered samples do not indicate glass phase expelling. The rounded shape of the grains, Fig. 4B, indicates larger grain solubility and glass volume at the triple points. The microstructure of the ZYLGd sample sintered at 1500 °C and 1610 °C is shown in Fig. 5. The microstructure of the 1610 °C sintered sample is similar to that of the ZYLYb sample, however the Gd doped samples have larger grains. Therefore, the relative

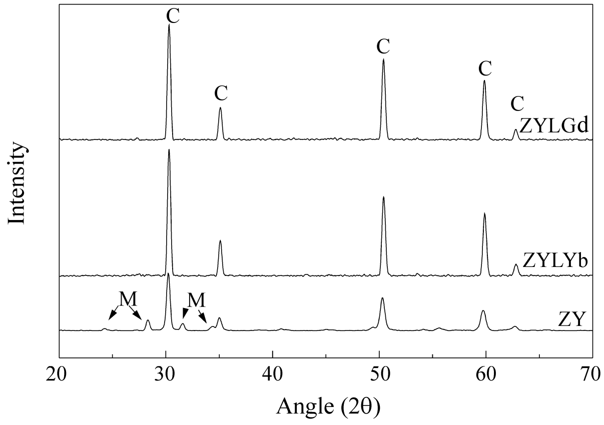

Figure 1. XRD of compositions: ZY sintered at 1600 °C - 2 h, ZYLYb and ZYLGd sintered at 1500 °C - 1 h. M = monoclinic phase; C = cubic phase.

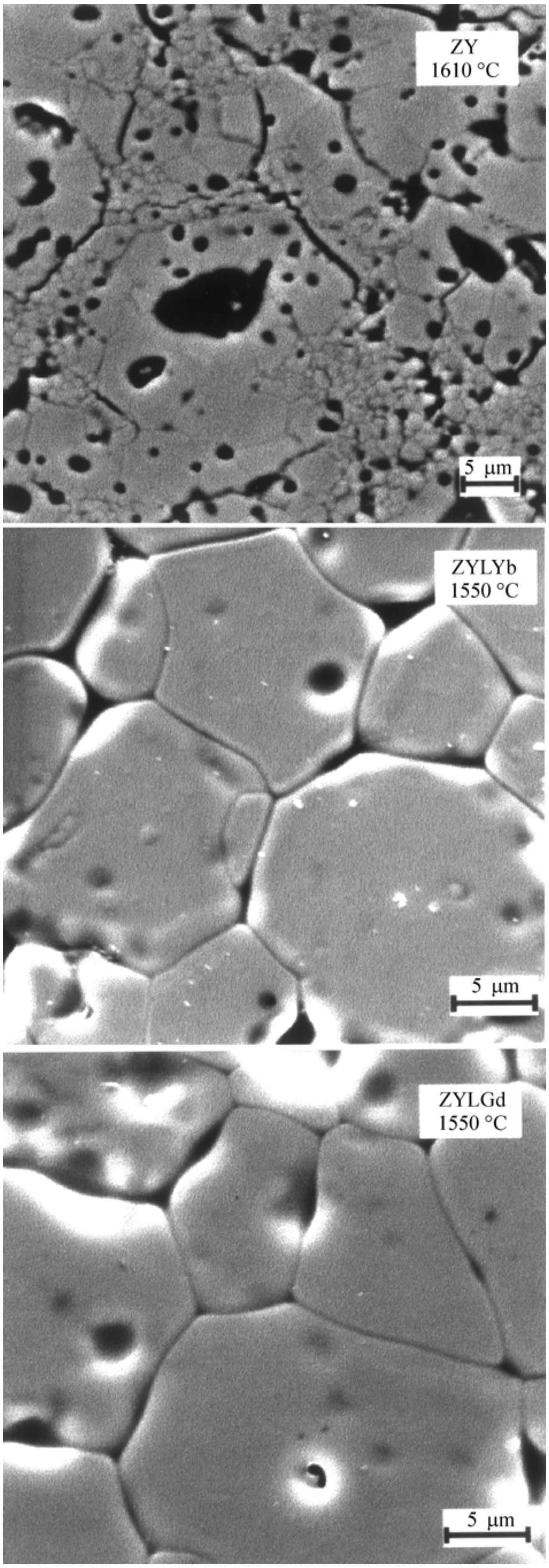

Figure 2. Microstructure of compositions: ZY sintered at 1600 °C - 2 h, ZYLYb and ZYLGd sintered at 1550 °C - 1 h.

amount of glass is higher when compared with the Yb^{+3} doped sample.

The apparent dependence of the density of the Gd and Yb doped samples on the sintering time at 1500 °C is shown in Fig. 6. While the Gd doped sample shows an almost constant density with sintering time, that of the Yb doped sample changes in the first hours of sintering. After four hours, however, both samples have almost the same density. The Yb doped sample shows a peculiar behavior. The highest density is obtained after 0.5 h of sintering; the sample decays nearly 4% for an additional half hour and grows 2%, at a lower rate, to the final value. This behavior indicates that the smaller radius Yb^{+3} ion ($Yb^{+3} < Y^{+3} < Gd^{+3}$) exerts a strong influence on the early

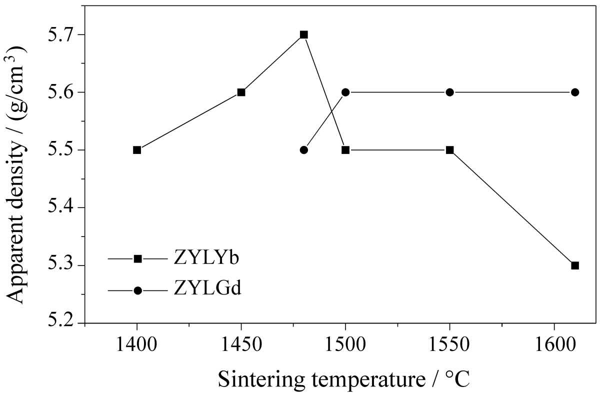

Figure 3. Apparent density dependence with sintering temperature. Sintering time: 2 h.

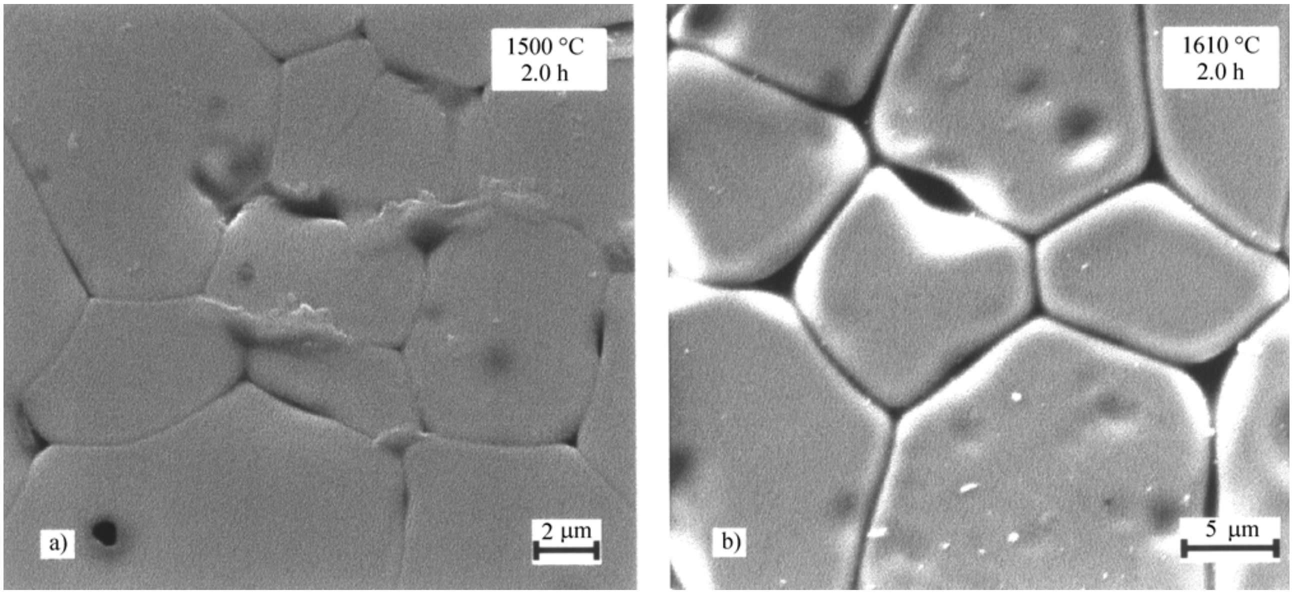

Figure 4. ZYLYb microstructure evolution with sintering temperature. Sintering time: 2 h.

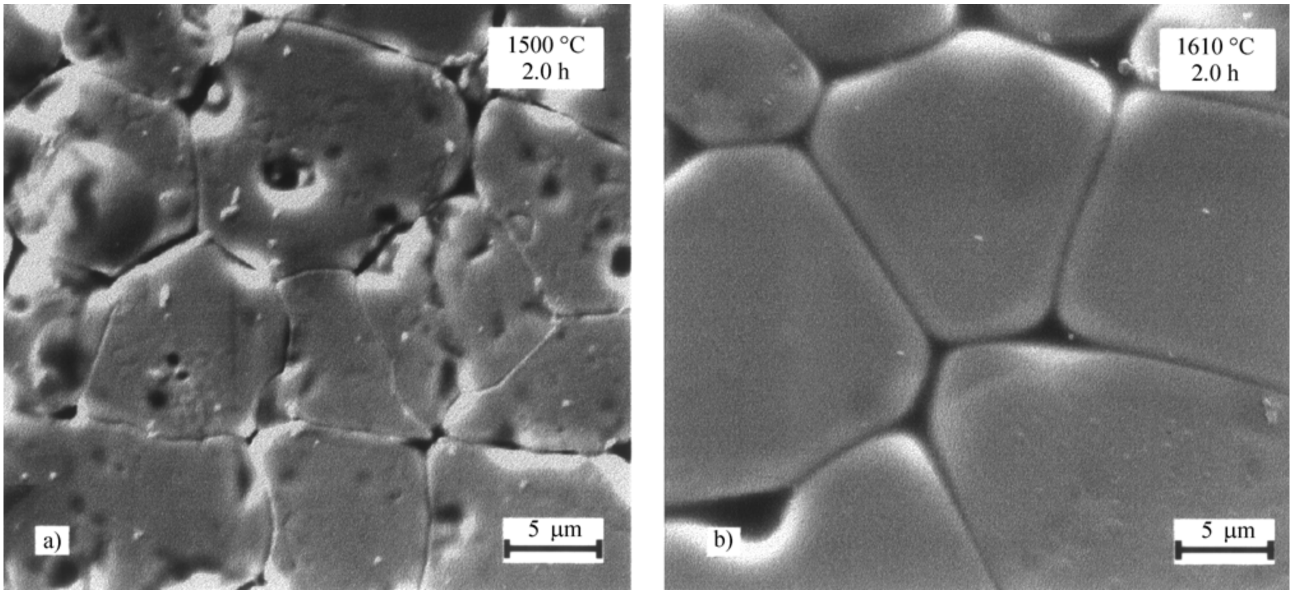

Figure 5. ZYLGd microstructure evolution with sintering temperature. Sintering time: 2 h.

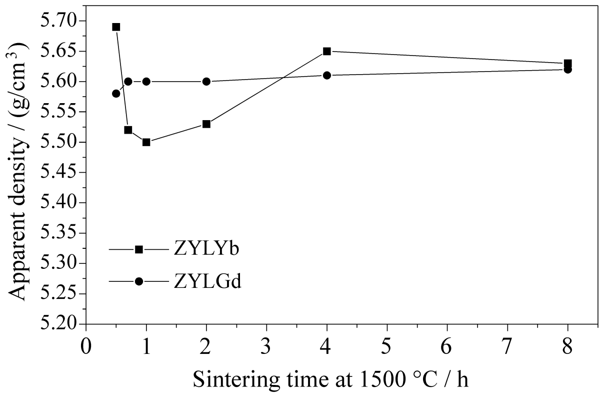

Figure 6. Apparent density dependence with sintering time at 1500 °C.

stages of sintering. The microstructural evolution of the Gd and Yb doped samples with sintering time at 1500 °C is shown in Figs. 7 and 8, respectively.

The main differences between the microstructures of these two samples are in their glass phases:

a) the ZYLGd sample showed a lower wetting angle with grain producing a thin glass film around the grains, as can be seen by comparing Figs. 7d and 8d. This behavior allowed for a higher grain growth rate for the ZYLGd sample, as shown in Fig. 9;

b) the small thickness of the ZYLGd glass on the grains is clearly shown in Figs. 7a (0.5 h sintering) and 7d (8 h sintering), while the ZYLYb glass phase does not show the same behavior, Figs. 8b (2 h sintering) and 8d (8 h sinter-

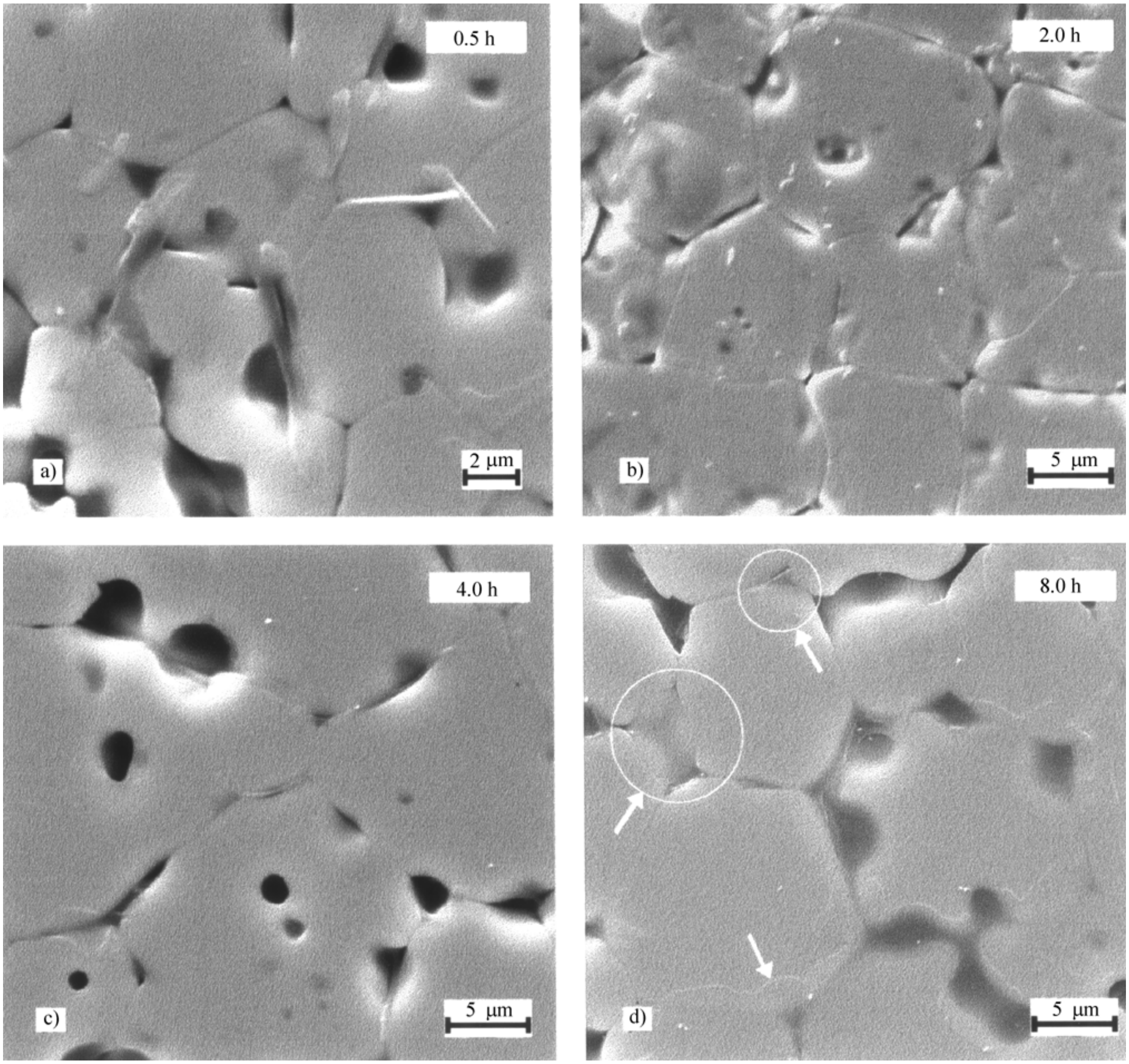

Figure 7. ZYLGd microstructure evolution with sintering time at 1500 °C.

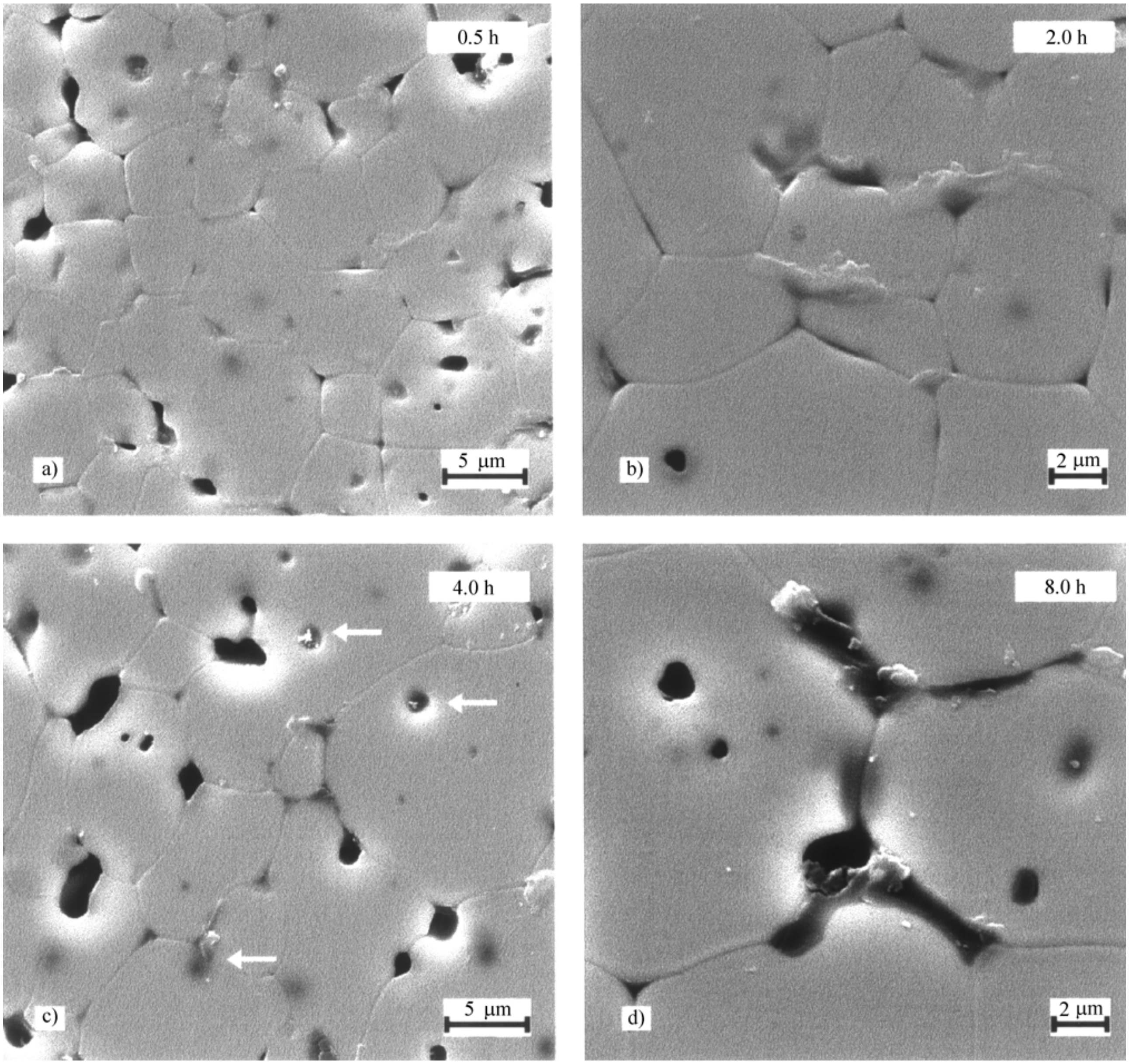

Figure 8. ZYLYb microstructure evolution with sintering time at 1500 °C.

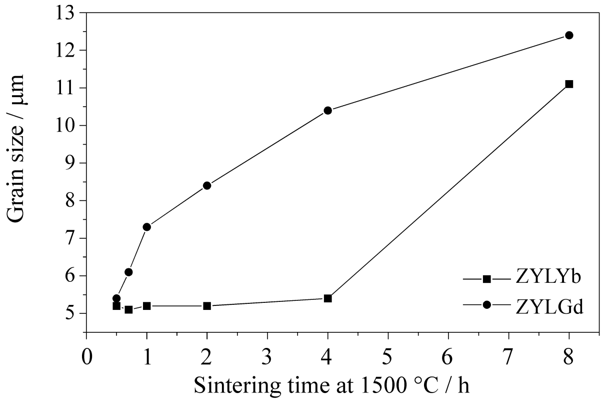

Figure 9. Grain growth with sintering time at 1500 °C.

ing). This composition also shows glass phase crystallization under cooling. Figure 10 shows pores full of glass, part of Fig. 8c with large magnification. In this and other regions of the glass phase one can clearly see that part of it is crystallized. A similar result was recently found in the sintering of Si_3N_4, where ytterbium silicate was used as a sintering aid[11]. It was found that part of the glass phase crystallizes after heat treatment.

The liquid phase composition changes with sintering time at 1500 °C. EDS analyses have shown that the Yttrium concentration increases in the glass phase along sintering time, as has already been discussed previously[9,12]. The segregation observed in the grain boundary should decrease the grain conductivity, as shown in Fig. 11.

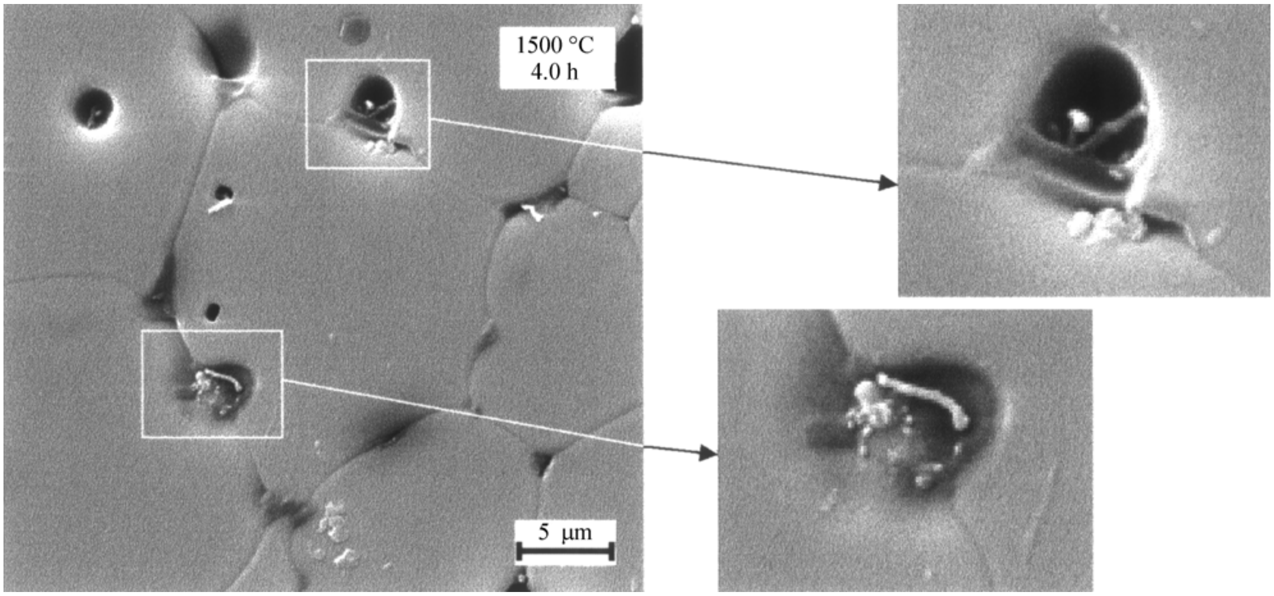

Figure 10. Part of Fig. 8C with large magnification showing pore full of glass. Part of the glass is crystallized.

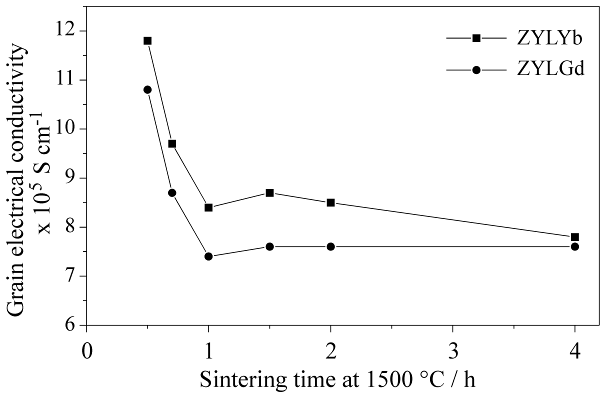

Figure 11. Grain electrical conductivity dependence with sintering time at 1500 °C.

Conclusions

Liquid phase sintering of cubic yttrium stabilized zirconia is very sensitive to minor additions of rare earth ions. Both liquid phases studied in this work were effective in assisting sintering but gadolinium doped samples showed a faster grain growth rate. The thin gadolinium doped glass layer on the zirconia grains close to the grain boundary clearly points to a lower wetting angle for the glass-grain interface. Ytterbium doped glass does not wet grains in the same way as gadolinium doped glass, which is indicative of a higher interfacial tension. We attribute this divergent behavior to the smaller ionic radii of the Yb^{+3} ion. Compared with Gd^{+3}, the Yb^{+3} ionic radii is 8% smaller.

The most interesting behavior observed, however, is the crystallization. The possibility that may be interesting to explore in more depth in a fully crystallized grain boundary phase is the grain boundary electrical properties. Also, the dynamics of concentration of the equilibrium of stabilizing ions between the glass phase and ceramic grains must contribute to a change in the space charge distribution in the solid-glass interface. The slope of the conductivity curves, shown in Fig. 11, indicates flow intensity and direction of the stabilizing ions in the solid-liquid interface, *i.e.*, the segregation direction. Therefore, it seems worthwhile to make a more in-depth study of the liquid phase sintering of these conductive ceramics.

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