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Densification of sintered lead zirconate titanate by hot isostatic pressing

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The effects of hot isostatic pressing (HIPing) on sintered lead zirconate titanate are presented. Densities up to ~ 98% were obtained by HIPing for 1 h at 1300° C with argon gas pressures of either 20.7 or 138 MPa. The microstructural changes observed after HIPing, and the rapid initial kinetics for densification and pore shrinkage, indicate that prssure-enhanced grain rearrangement and solution-precipitation processes are primarily responsible for densification. The persistance of large voids after HIPing suggests that it may be impossible to completely eliminate gross processing-related defects in lead zirconate titanate by HIPing.

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1. Introduction

Hot isostatic pressing (HIPing) is a process that offers many advantages for the processing of metal and ceramic components including near net shape fabrication, improved properties, and reduced processing temperatures. Most industrial applications are centred in the metals industry and include the HIPing of cast metals and various carbide-based cutting tools. Surprisingly, there has been only limited application in the ceramics field.

In this investigation, densities and microstructures of sintered and HIPed lead zirconate titanate (PZT) ceramics were compared to ascertain the effects of HIPing. Specific experiments were performed to determine if macroscopic voids characteristic of the defects which can result due to improper powder processing could be eliminated from sintered PZT by high or low pressure HIPing. In earlier studies on Co-bonded WC, it was shown that such porosity could be eliminated by HIPing [1, 2].

2. Experimental details

A commercial lead zirconate titanate powder* with a composition of $(Pb_{0.94}Sr_{0.06})(Zr_{0.53}Ti_{0.47})O_3$ was used for this study. To prepare the powder for pressing it was granulated with 2 vol% acrylic wax emulsion†. Macropores of a distinct size and geometry were introduced into the sintered microstructure by hand mixing 0.0025 g (~ 5000 in number) of 100 ± 5 μm diameter polymethyl methacrylate spheres‡ into individual 3 g samples of the green powder. Then pellets were formed by first uniaxially pressing at 35 MPa in a 1.27 cm diameter die and then cold isostatic pressing at 172 MPa. Prior to sintering, the binder and pore formers were burned out by heating the pellets at a rate of 10° C $\min^{-1}$ to 500° C and holding for 1 h. A set of control pellets without macropores were also prepared.

Samples were sintered for 15 min in a gradient furnace at temperatures ranging from 1250 to 1320° C. An oxygen atmosphere was used so that during pore shrinkage, the gas entrapped during pore closure could readily diffuse out of the PZT. The dissociation of the PZT during sintering was suppressed by packing the pellets in a mixture of green and sintered PZT powders and enclosing them in a platinum-lined alumina crucible.

The sintered samples were enclosed in a platinum-lined alumina crucible along with a green PZT pellet as a PbO source and HIPed at 1300° C

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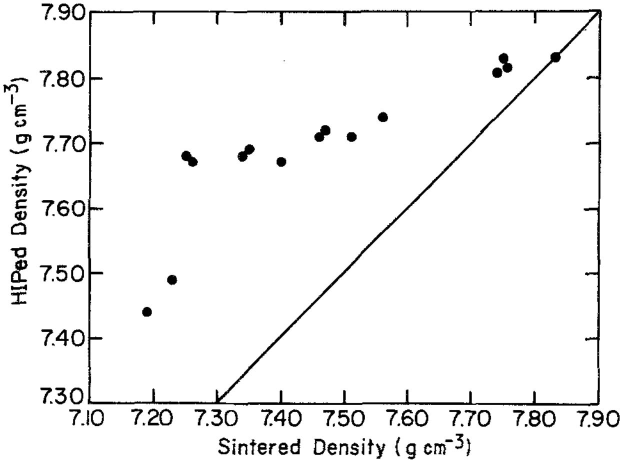

Figure 1 HIPed density as a function of sintered density of PZT after HIPing at 138 MPa for 1 h.

with argon at pressures of 20.7 and 138 MPa for times of up to 8 h. A typical HIP cycle consisted of heating to 1300° C at a rate of 15° C min^{-1}, pressurizing at a rate of 10 MPa min^{-1} to the desired pressure, and holding for the requisite time. The pressure and temperature were then simultaneously reduced at rates of 20° C and 10 MPa min^{-1}, respectively.

The sintered and HIPed sample densities were determined using Archimedes' method. Relative densities were calculated using 8.0 g cm^{-3} as the theoretical density of the PZT. This value was determined from the chemical composition and lattice parameters calculated from X-ray diffraction.

Samples were prepared for microstructural analysis by cutting the pellets in half, polishing with 0.25 μm diamond paste, and etching with a solution of 70 vol% H_2O, 29.5 vol% HNO_3 and 0.5 vol% HF at 80° C for 40 s. Macropore and grain size were determined by the average linear intercept method [3].

3. Results and discussion

3.1. Density

Sintering for 15 min in the gradient furnace produced samples with densities ranging from 7.12 to 7.84 g cm^{-3}. There were no significant density differences in samples with and without macropores indicating that the addition of a small amount of gross porosity to the PZT system does not affect overall densification.

It is apparent in Fig. 1 that there is a strong relationship between the sintered and HIPed density. Interestingly, similar results were obtained for both the high and low HIP pressures. The straight line in Fig. 1 represents the condition for which there is no change in density with HIPing and is presented to indicate the magnitude of the density change on HIPing. Clearly, samples with the lowest sintered densities densify the greatest amount on HIPing. The largest increase is observed in the samples having a sintered density of ~ 7.24 g cm^{-3} (~ 90.5% of theoretical). This density is in good agreement with the value for the closed porosity state as predicted by Budworth [4]. Therefore, this is the lowest density at which the entire sample can be affected by the gas pressure, and thus, it is reasonable that they show the greatest improvements on HIPing. Densification also occurred in the sintered samples having densities less than 7.24 g cm^{-3}; however, this densification is attributed to additional sintering as well as some pressure assisted densification of regions of closed porosity. The results from the Archimedes' technique verified that 7.24 cm^{-3} was the density at which the PZT had only closed porosity.

Above the critical density at which the gas pressure can be transmitted to the entire sample, there is nearly a linear relationship between the HIPed and sintered densities. Although HIP density increases with increasing sintered density, theoretical density was not achieved for any condition. This finding is in contrast to the findings of Engel and Hubner [1] on cobalt-bonded WC in which theoretical density was obtained after HIPing. This difference is attributed to microstructural differences between the two systems.

3.2. Microstructure

Characteristic microstructures of sintered and HIPed PZT are shown in Figs. 2a and b, respec-

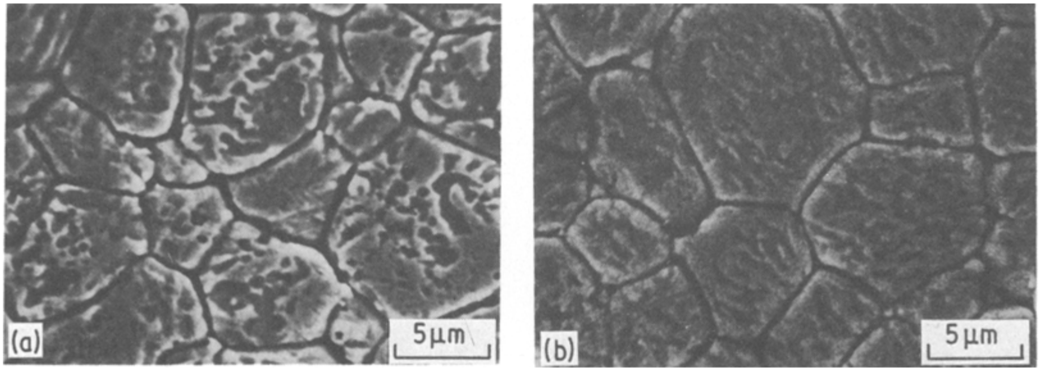

Figure 2 Photomicrograph of the microstructure of (a) PZT sintered for 1 h at 1320° C, and (b) PZT HIPed for 1 h at 1300° C and 20.7 MPa.

tively. Both samples have similar morphologies and grain sizes; however, a second phase is observed at three grain junctions in the HIPed PZT. Although there is no evidence of this second phase in the SEM micrographs of the sintered PZT, Goo *et al.* [5] identified a 10 nm thick amorphous phase at the grain boundaries of the sintered PZT they studied. It is suggested that a liquid phase forms during sintering as a result of excess PbO in the PZT system. It is well known that PbO is commonly added to commercial PZT powders to maintain stoichiometry during sintering. From the 1300° C isothermal section of the PbO–$PbTiO_3$–$PbZrO_3$ ternary phase diagram shown in Fig. 3 [6], it is evident that even a slight excess of PbO in the system will produce a liquid (L_1) in equilibrium with solid PZT. The liquid has an approximate chemical composition of 50 mol% PbO and 50 mol% $PbTiO_3$ at 1300° C and becomes increasingly rich in PbO as the system cools to room temperature. From microprobe analysis of the HIPed samples it was determined that the second phase was lead and titanium rich, which is consistent with what would be expected.

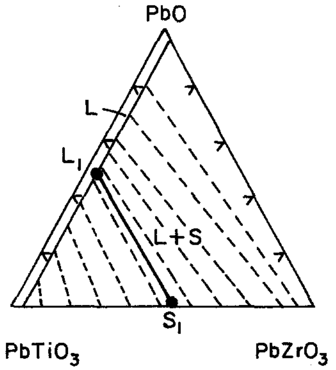

Figure 3 Isothermal section of the system PbO–$PbZrO_3$–$PbTiO_3$ at 1300° C [6].

The presence of "pools" of liquid at three grain junctions indicates that liquid migrates from the grain boundaries to regions of porosity during HIPing. Furthermore, the amount of liquid observed suggests that additional liquid is created during HIPing. This process is similar to the solution-precipitation process which occurs during liquid-phase sintering. When sintering in the presence of a liquid phase, the capillary forces generated by the presence of liquid between grains produces compressive forces between the grains which increases the chemical potential of the liquid. Consequently, more solid goes into solution and the amount of liquid in the system increases [7]. It is apparent that the chemical potential is further increased with the compressive forces created by HIPing, and even more liquid can be produced. This would explain the relatively large amount of liquid observed in the HIPed samples as compared to the sintered PZT, and accounts for the migration of the liquid from the grain boundaries to the pores. Another possibility is that the liquid is physically extruded from high pressure grain boundaries into lower pressure pore sites as suggested by Bowen *et al.* [8].

As expected, similar microstructural differences were observed between the macropores (i.e. those pores intentionally introduced into the microstructure) in sintered and HIPed PZT (Fig. 4). However, a more extensive examination of these microstructures reveals that in addition to the liquid phase, even greater differences exist including changes in grain morphology, pore geometry, and pore size.

The processes active at pore sites located on

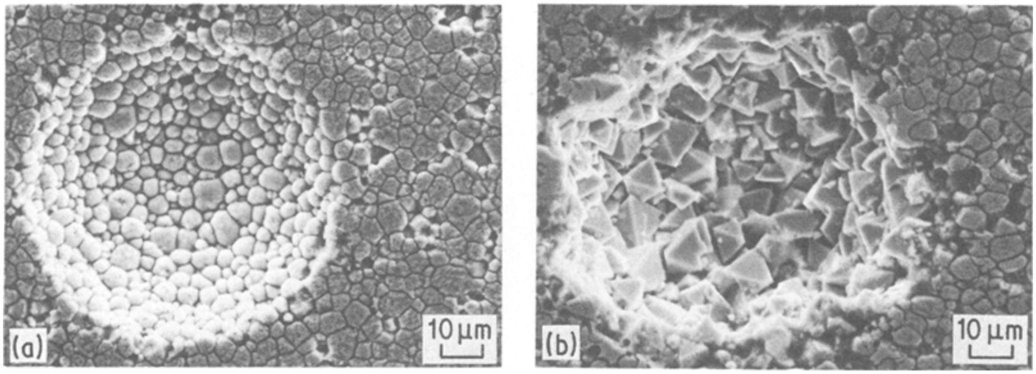

Figure 4 Photomicrograph of a macropore and the surrounding microstructure in (a) PZT sintered for 1 h at 1300° C, and (b) PZT HIPed for 7.5 min at 1300° C and 20.7 MPa.

three grain junctions should also operate at the macropores; however, while the smaller pores are completely filled, there is insufficient liquid available to completely fill the larger voids. Since the large voids constitute only ~0.5% of the total sample volume it is evident that there is little liquid present during HIPing. This may explain why densities less than theoretical were obtained after HIPing as the amount of densification is dependent on the amount of liquid in the system [7].

Another feature of interest is the difference between the morphologies of grains situated on the macropore surfaces in the sintered and HIPed PZT (Fig. 4). The grains in the sintered body are smooth and equiaxed while crystals are observed in the HIPed PZT. Apparently, crystallization occurs as a result of the applied pressure. Interestingly, reheating HIPed PZT to 1320° C at atmospheric pressure reverts the crystals back to a liquid (Fig. 5).

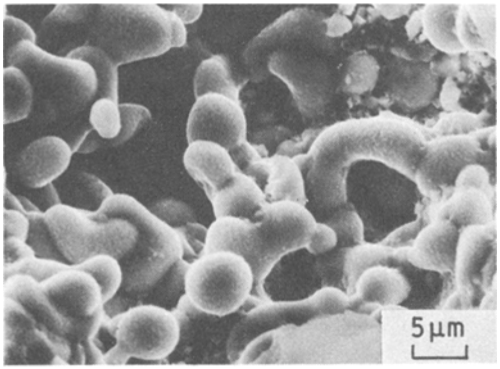

Figure 5 Photomicrograph of the microstructure in a macropore in PZT after heat treating a HIPed sample for 5 h at 1320° C.

It is seen in Fig. 4 that macropore geometry also changes during HIPing. The macropores in the sintered PZT have a spherical geometry with a well defined perimeter, whereas macropores in the HIPed PZT have an irregular pore perimeter. The deviation from a distinct spherical geometry suggests that localized grain rearrangement occurs during HIPing. It has been demonstrated that both liquid [7] and pressure [9] enhance rearrangement. This explains why an irregular pore geometry is observed in the HIPed but not the sintered PZT.

Since there is a localized concentration of liquid at the macropores and because densities are relatively high at the onset of HIPing, it is believed that the majority of rearrangement occurs in the localized regions of large voids where there is room for the grains to move. The existence of large voids even after 8 h at pressure indicates that rearrangement is a limited process. This is probably because of the small amount of liquid in the system and the constraint for particle movement due to the dense microstructure adjacent to the pore surface.

Although large voids could not be eliminated, Fig. 6 shows that the size of macropores (i.e. those intentionally introduced into the microstructure) is significantly reduced during HIPing. Macropores shrink from 123 to 85 micrometres in diameter after 1 h at pressure, which is equivalent to a 67 vol% reduction of the macroporosity. The majority of the shrinkage occurs primarily in the first 7.5 min of HIPing. While the pores continue to shrink for extended time at pressure, it is evident that the rate of shrinkage decreases with time. This time dependency was also observed for densification as a function of HIP time. Thus, it is apparent that the mechanism(s) of pore shrinkage

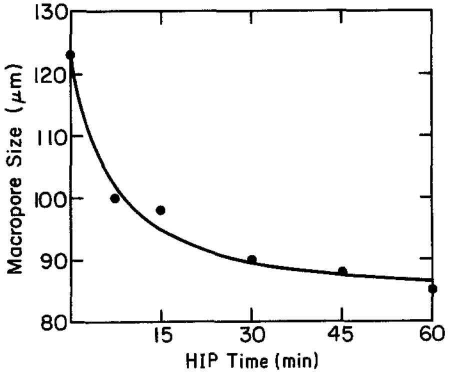

Figure 6 Macropore size reduction in PZT as a function of HIP time at 1300° C and 20.7 MPa.

and densification are primarily active in the early stages of HIPing. The presence of a liquid phase in the HIPed PZT, the irregular macropore geometry after HIPing, and the rapid shrinkage kinetics suggest that pressure-enhanced rearrangement occurs during the initial stages of HIPing. Furthermore, it is likely that a pressure-enhanced solution-precipitation process occurs concurrently with this rearrangement process.

Engel and Hubner [1] presented evidence indicating that rearrangement and solution-precipitation processes are also operative during the HIPing of cobalt-bonded WC. However, one distinct difference between cobalt-bonded WC and PZT is that there is substantially more liquid present in the carbide system. Thus, greater material transport can occur and larger voids can be filled as indicated by the large pools of cobalt present in the microstructure of HIPed cobalt-bonded WC [1, 2]. Consequently, theoretical density is obtained in HIPed cobalt-bonded WC. In the PZT system, where significantly less liquid is present, the amount of densification by rearrangement and solution-precipitation is limited. Consequently, only small pores can be eliminated and large voids are only partially reduced in size. The result is that end point densities less than theoretical are obtained. It is believed that this type of behaviour will be characteristic of most ceramic systems in which little or no liquid phase exists. Thus, HIPing will be incapable of completely eliminating large processing-related defects. Evidence does suggest, however, that with control of the initial stages of processing to keep the pore size small, it is possible to effectively eliminate residual porosity by HIPing.

4. Conclusion

It has been shown that HIPing is a viable means of further densifying sintered lead zirconate titanate. Mechanisms for densification have been proposed on the basis of microstructural changes, densification rates, and macropore shrinkage during HIPing. The presence of a liquid phase in the microstructure of HIPed PZT, the irregular macropore geometries, and the rapid initial kinetics observed suggest that pressure-enhanced grain rearrangement and solution-precipitation processes are predominantly responsible for densification during HIPing. It has also been shown that while small pores can be eliminated during HIPing, large voids can only be reduced in size. This suggests that, in order to obtain the best results, more careful powder processing and sintering should be considered in conjunction with HIPing.

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