Influence of Bismuth Oxide as a Sintering Aid on the Densification of Cold Sintering of Zirconia

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Research question

Zirconia (ZrO_2) is a functional ceramic widely used in aerospace, automotive, and medical industries. In the past, 1200°C is the ideal sintering temperature for high quality densification.

- Pros: high density (relative density higher than 80%) and high hardness
- Cons: high energy consumption during synthesis – how to reduce it?

Research goal

Reducing sintering temperature while maintaining high density and high hardness of sintered ZrO_2

Approach #1: cold sintering with solvents

- Liquid phase (solvent) dissolves solid ceramic particulate at low temperature

Pros:

✓ particle rearrangement enhanced by wetting
✓ Kinetic: Mass transport enhanced by diffusion of solute ions;
✓ Thermodynamic: Solvent phase evaporates upon heating, yielding a supersaturated solution for precipitation [1]

Cons:

× low density, thus requiring further annealing/sintering step

Approach #2: liquid phase sintering

- Sintering aid melts at a certain temperature and becomes liquid that fills in between the solid powder particles

Pros:

✓ particle rearrangement enhanced by wetting
✓ due to nonzero solubility of solid powder in the liquid phase, mass transport enhanced by diffusion of solute ions;

Cons:

× sintering T needs to be higher than melting T of sintering aid;
× sintering aid remains in the system, which could alter stoichiometry and affect various properties

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This work:

Combined cold sintering through in-situ conversion of $Zr(OH)_4$ to ZrO_2 and H_2O at 400°C and liquid phase sintering aided by Bi_2O_3 in the temperature range of 817 °C - 900 °C

Experimental methods

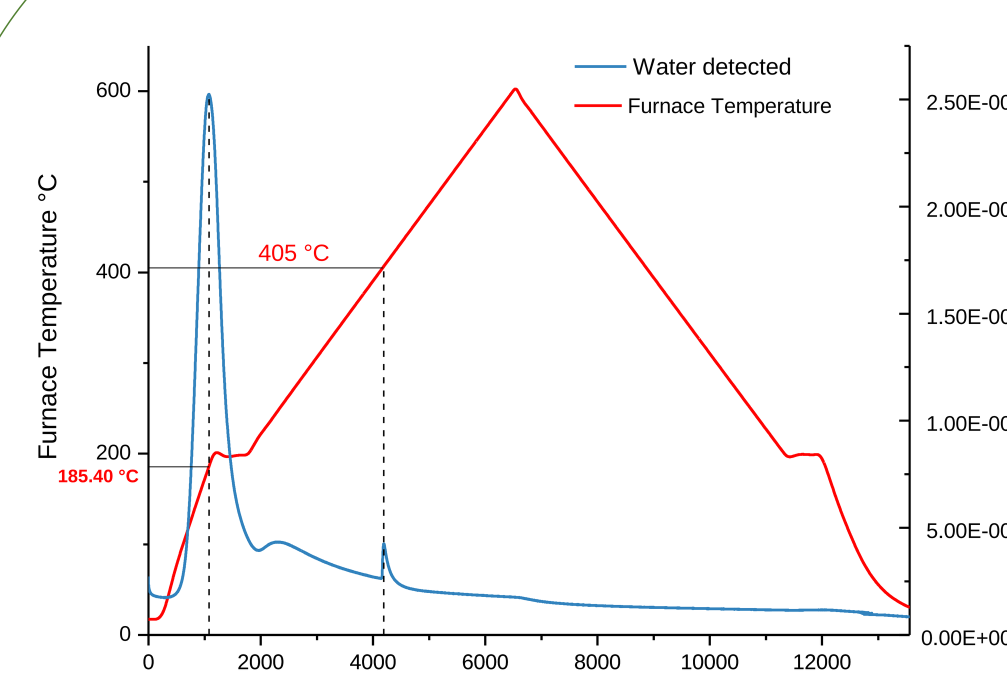
Material: 4 different powder system (a) Pure $Zr(OH)_4$, (b) pure ZrO_2, (c) Pure $Zr(OH)_4$ - Bi_2O_3, and (d) ZrO_2 - Bi_2O_3. Bi_2O_3 weight percentage varies from 5%, 10% and 15%.

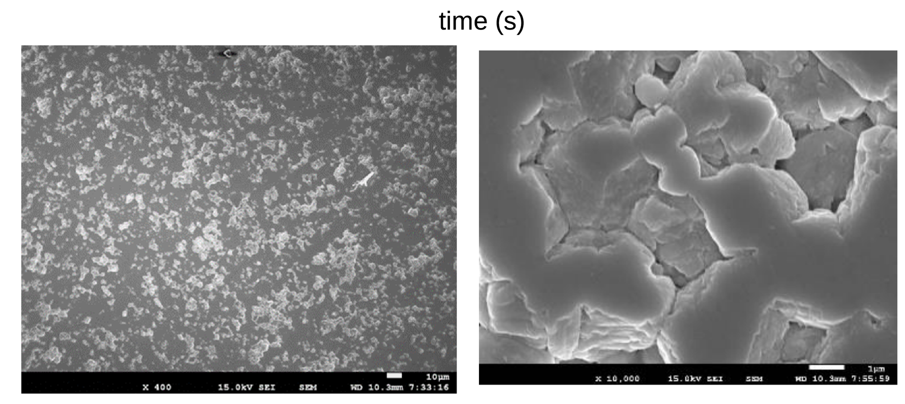
Mixing:
Powders mixed in a planetary ball mill with 2-propanol as a dispenser and ball mass: powder mass ration as 4:1. Milling time: 3h at 300-rpm. Slurry was dried overnight in the fume hood under atmosphere.

Densification:
Spark plasma sintering (SPS) of these mixed ceramic powders was performed using the FCT System Gmbh. Dies made of either (i) Graphite or (ii) Stainless steel, or (iii) Tungsten carbide-Cobalt with maximum mechanical loading 50MPa, 150MPa, and 300MPa respectively, were used depending on the dwell piston pressure of the sintering cycle. Sintering temperature varies between 400°C and 1200°C.

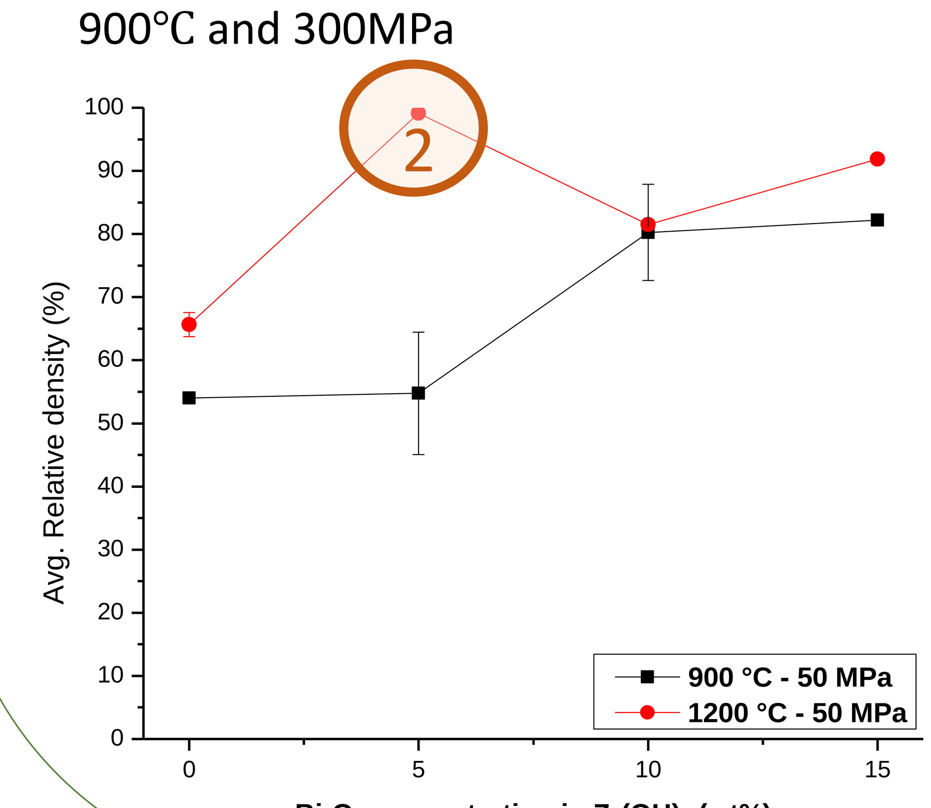
Characterisation:
- DSC, TGA, mass spectrometry for in-situ conversation observation
- XRD, SEM for phase purity check
- density, hardness measurements

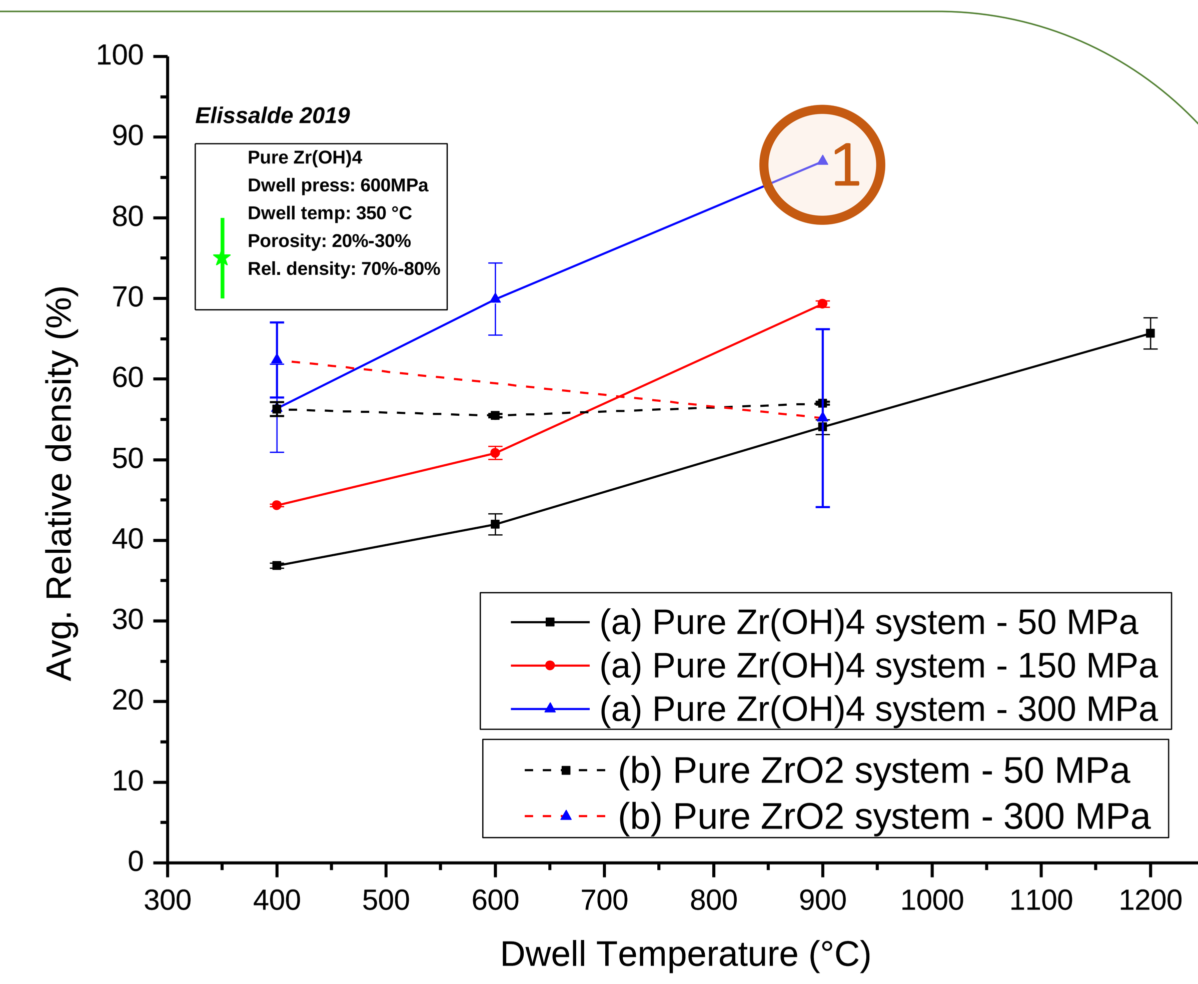
Results

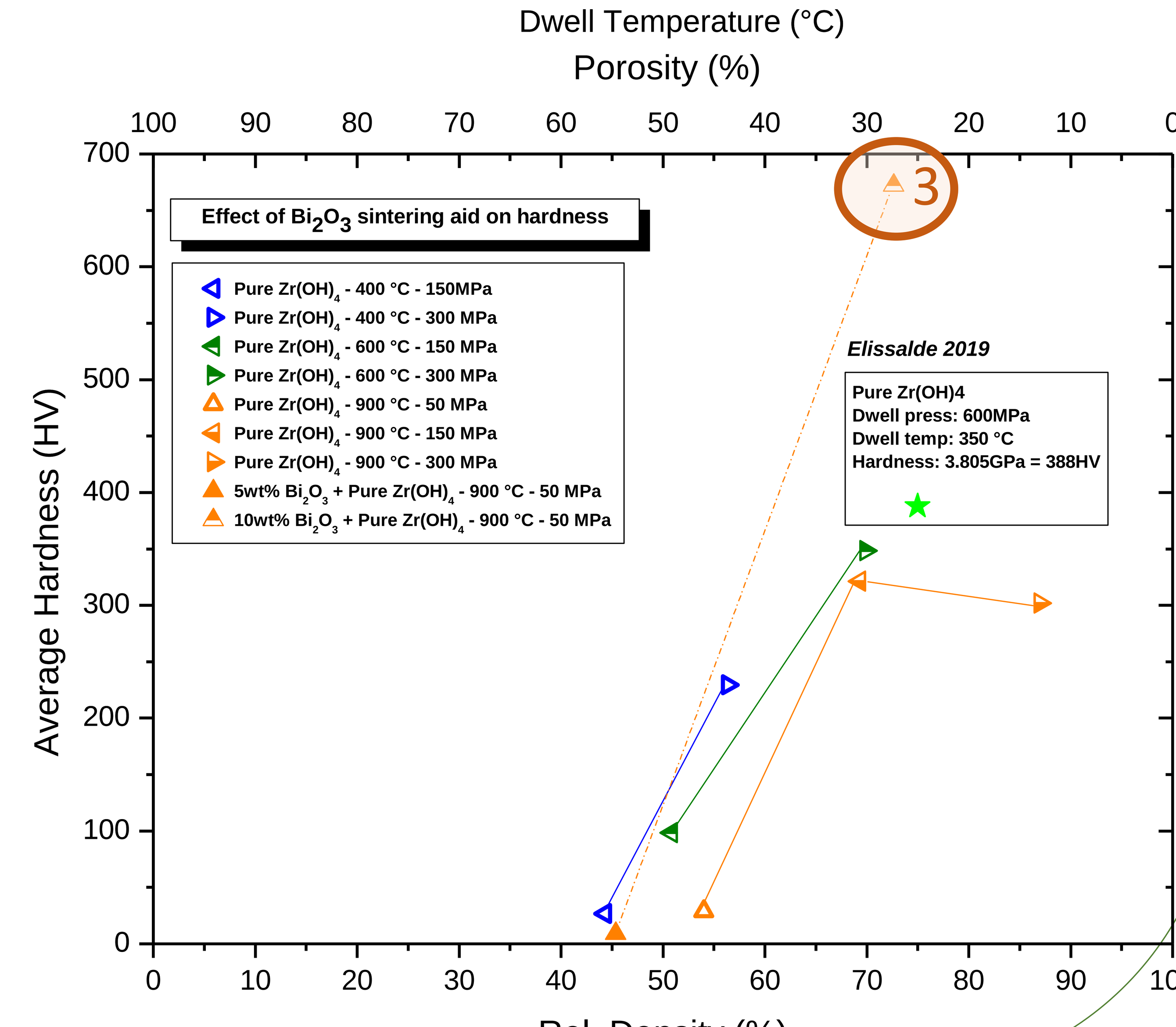




SEM images of ZrO_2 sintered from $Zr(OH)_4$ at 900°C and 300MPa







Conclusion:

1. A density of 87% successfully achieved with a sintering temperature as low as 900 °C in a 'single sintering step' from pure $Zr(OH)_4$ at 300MPa [2]. 2. The 5wt% Bi_2O_3-$Zr(OH)_4$ system achieved the highest relative density (99%) when sintered at 1200 °C and 50MPa. 3. The 10wt% Bi_2O_3-$Zr(OH)_4$ system sintered at 900 °C - 50MPa dwell conditions had the highest hardness of value of 6.6 Gpa at a relative density of 72% [2].

References:

[1] Guo et al., J. Am. Ceram. Soc., vol. 99, no. 11, pp. 3489–3507, 2016, doi: 10.1111/jace.14554.
[2] C. Elissalde et al., Scr. Mater., vol. 168, pp. 134–138, 2019, doi: https://doi.org/10.1016/j.scriptamat.2019.04.037.

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