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Ultra-Low Temperature Processing of Silica

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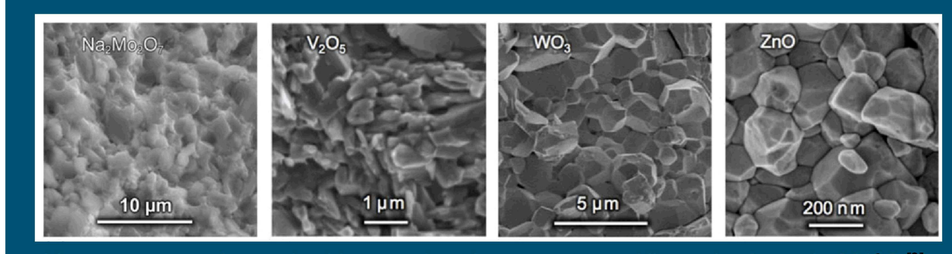
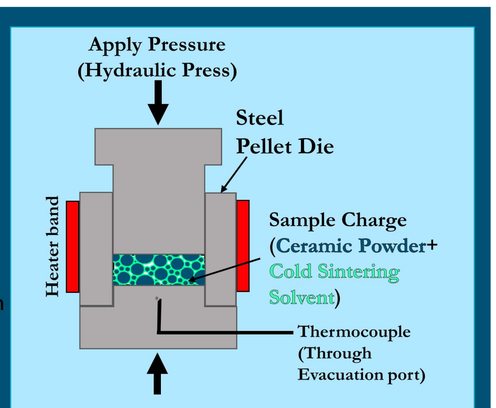
Cold Sintering

A resurgence of interest in ultra-low temperature processing of ceramics has been underway under the umbrella term "Cold Sintering" which encompasses processes which utilize liquid chemistry-driven diffusion to prompt densification as opposed to thermally-driven diffusion. While driving forces for densification are similar, the kinetic enhancement allows for dense samples at temperatures <200°C. Examples (microstructures below) such as ZnO/Acetic Acid[1] and $NaMoO_4/H_2O$ allow for >95% density at these modest temperatures. Alternatively, many technical ceramics such as Al_2O_3, SiO_2, and ZrO_2. Have been attempted with limited success [2].

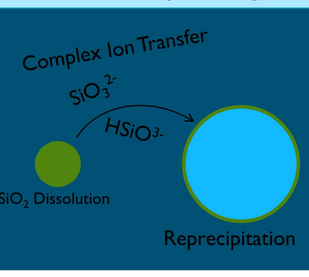


Microstructures of several cold sintered oxide compositions. All samples formed <200°C [2]

Enabling cold sintering on new ceramic systems requires chemical reactions which dissolve, transfer, and precipitate suitable ions/ion complexes of the chosen ceramic.
(Think: Pourbaix diagrams)

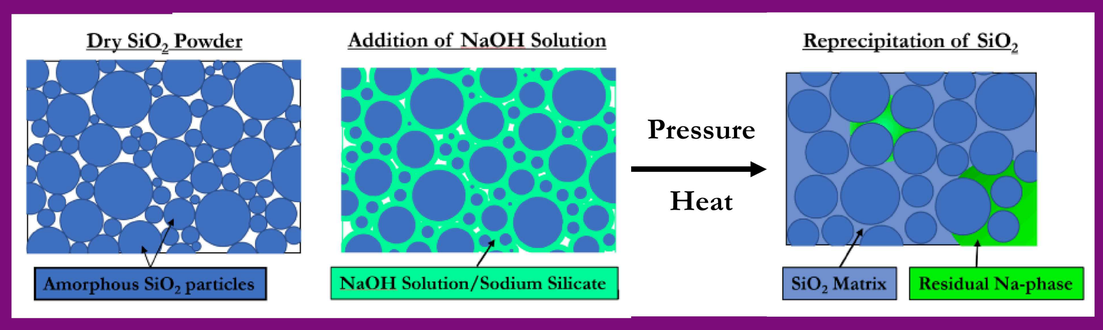


Lab-scale processing is completed on ceramic-powder/solvent mixtures inside heated pressing dies.



Cold Sintering of a-SiO_2 Using a NaOH Solvent

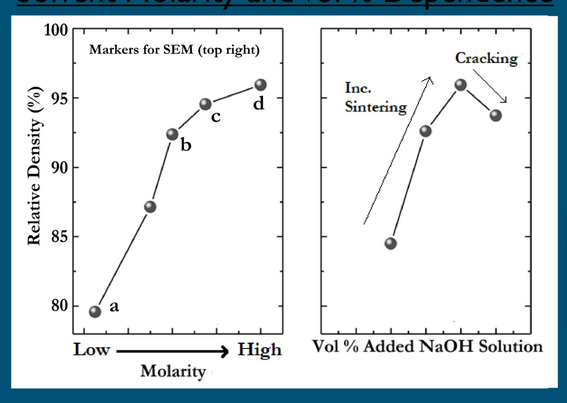
- Enabling cold sintering in SiO_2 requires the selection of an appropriate cold sintering solvent. Dissolution of silica is difficult, while gel creation and precipitation are well studied phenomenon.
- Previous studies attempted a water solvent with limited success [ref].
- NaOH was chosen as an initial cold sintering solvent due to the high dissolution rate constant of silica in NaOH as well as proven ability to precipitate pure SiO_2 from sodium silicate solution upon lowering pH.[3]

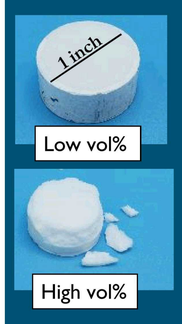


- A raw powder of <5um amorphous SiO_2 is cold-sinterable using NaOH. NaOH is a model system for understanding the process, with the goal of later ideally replacing NaOH with an organic base or alkoxide.

Processing Parameter Dependencies

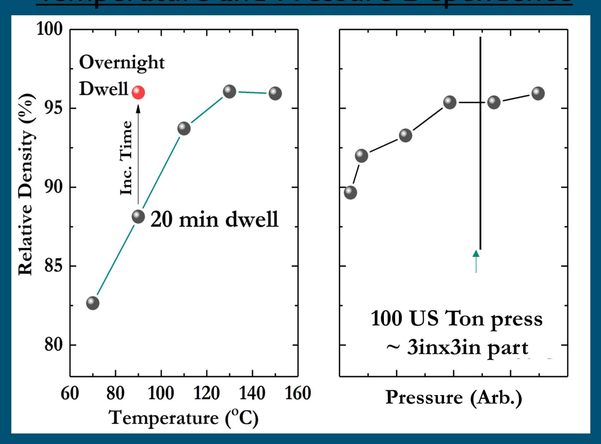
Solvent Molarity and Vol % Dependence





- Higher Vol % of solvent causes increased cracking in samples
  - Liquid likely not fully evaporated during the process, or increasing stresses due to evaporation.
- Increasing molarity of NaOH increases densification
  - If the process is dissolution-rate limited at low molarity, then replacement of NaOH for another solvent may be tricky.
  - Lower particles sizes (nano) may ease molarity constraints

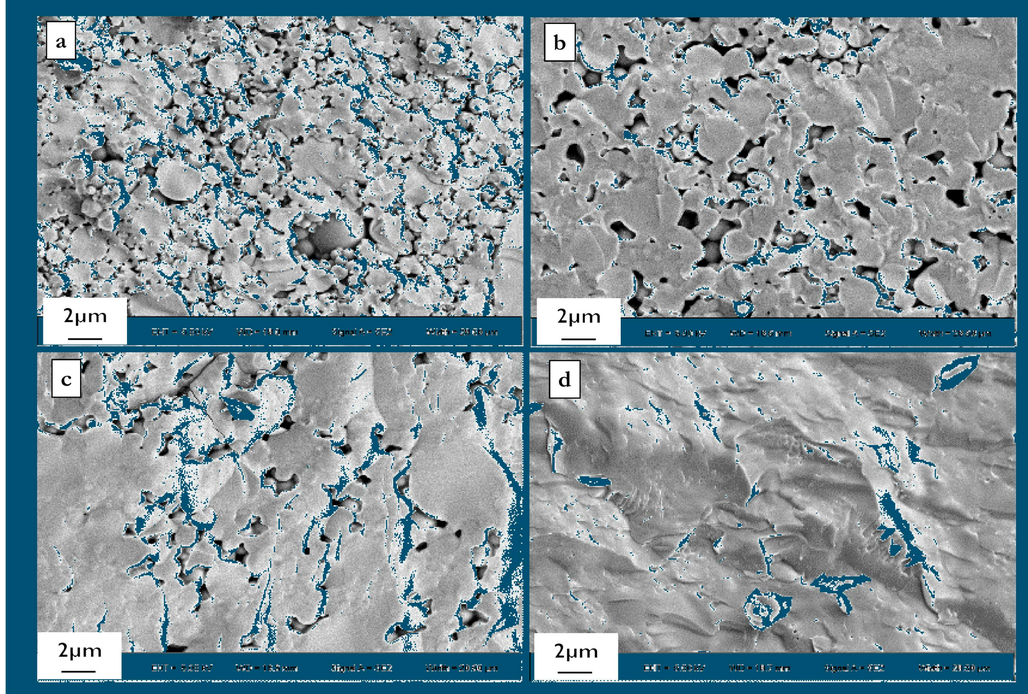
Temperature and Pressure Dependence



- Necessary pressures and temperatures are easily achievable by industrial presses
  - Part sizes will be limited by necessary pressure
- >95% density achieved at 90°C if an overnight dwell is utilized.
  - Availability of sub-100°C processing eases constraints for isostatic processing

Sub-100°C processing
Transparent, but macroscopic cracks

Microstructure Characterization



SEM images of fracture surfaces of cold sintered SiO_2 with increasing NaOH molarity
(Molarity of a<b<c<d)

- Microstructures similar to conventional sintering.
  - Necking, pore volume reduction, etc.
- Local porosity in highest molarity sample is less than the 5% predicted from relative density
  - Lower density secondary phases (gels), macroscopic cracking, incomplete relaxation of SiO_2 matrix, and Si-OH formation are possible explanations
    - Likely Na_2O-SiO_2 gel formation
  - DSC/TGA/SIMS/Crystallization studies are underway to investigate matrix composition/structure
    - Initial SIMS results show different regions – regions which Na^+ is in matrix, regions in which no Na^+ is present in the matrix.
- Smaller particles not identifiable in final samples
  - Ostwald-ripening driven
  - High-pH region should allow for deprotonated SiO_4^{-4} deposition onto particles, similar to high-pH sol gel formation
- Mixed-mode fracture seen even in necking stage. (Only inter-granular fracture surfaces presented).
  - Bonding between particles is strong

Conclusions

- Amorphous SiO_2 has been successfully densified via cold sintering at sub-150°C.
- Reducing sample cracking and replacement of NaOH as cold sintering solvent are key obstacles for furthering practically of the process.
- Necessary pressures and temperatures easily achievable by industrial presses
  - Sub-100°C processing point toward possibility of hydrostatic routes to eliminate die-wall friction and ejection breakage.

References

[1] S. Funahashi, "Demonstration of the cold sintering process study for the densification and grain growth of ZnO Ceramics", J. Am. Ceram. Soc., Vol 100, No. 2 (2017)

[2] J.P Maria et al., , "Cold Sintering: Current Status and Prospects",. J. Mater. Res. 32, 17 (2017)

[3] S. Music, et al. "Precipitation of Amorphous SiO2 Particles and Their Properties", Brazilian Journal of Chemical Engineering Vol 28 (2011)

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