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Creation and Characterization of Macroporous Ceramics

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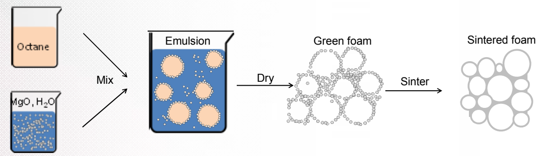
Abstract :

Highly porous and permeable ceramic foams are useful to many applications ranging from catalyst supports, filtering molten metal alloy, tissue engineering scaffolds and high temperature insulation. One potential route for manufacturing ceramic foams is to make concentrated Pickering emulsions stabilized by ceramic micro- or nano-particles which are then dried and sintered. Pickering emulsions are very stable to coarsening or coalescence and because of their yield stress can be shaped and molded. Here, a Pickering emulsion is generated using surface modified magnesium oxide particles resulting in high interfacial area emulsions which are very stable. The emulsion is dried and sintered resulting in a robust ceramic foam with very high porosities of up to 90%. Because of the microstructured arrangement of the magnesium oxide, the porous structure has good mechanical strength. We will discuss the impact of processing parameters on emulsion stability and ceramic foam properties. Results will be compared with some traditional tape casting methods of creating ceramics.

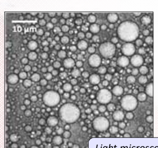
Control of Ceramic Foam Microstructure:

The creation of a ceramic foam using Pickering emulsions is a multi-step process, offering many parameters that have impact on the final microstructure and performance. As the foam is made, there are many characterization techniques that are useful for understanding the effects of these process parameters.

Pickering emulsions are created following the work by Akartuna et al.[1] where short chain amphiphiles are used to modify the wetting behavior of the magnesium oxide so the particles are most stable at the interface of the octane-water emulsion. The resulting emulsion has a substantial yield stress, allowing it to be molded or tape-cast. When dried and sintered, the porous structure is retained.

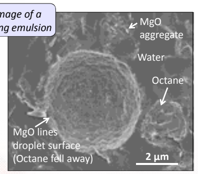


Process Variables: MgO particle size, concentration, mixing time, Amphiphile chain length and concentration, Octane amount, Binder type and concentration, Mixing speed	**Process Variables:** Drying time, humidity, Tape casting or cast in a mold	**Process Variables:** Sintering temperature, sintering rate	
Characterization: Light scattering (MgO aggregate size)	**Characterization:** Light microscopy (droplet size), cyogenic scanning electron microscopy, thermal gravimetric analysis (amount of brucite)	**Characterization:** Measure size, mass (shrinkage, density, and porosity), Scanning electron microscopy (microstructure)	**Characterization:** Measure size, mass (Shrinkage, density, and porosity), Electrochemical impedance spectroscopy (permeability), Indentation (fracture strength), SEM (microstructure)

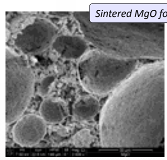


Light microscopy image of a MgO Pickering emulsion.

CryoSEM image of a MgO Pickering emulsion

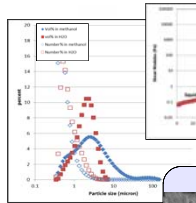


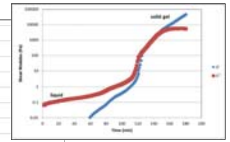
Sintered MgO foam



Effect of Brucite Formation on Microstructure:

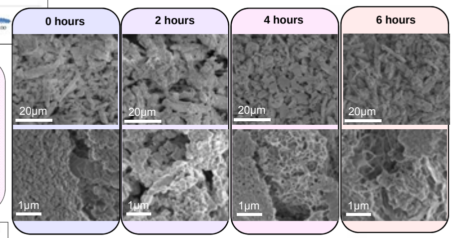
Relative humidity can be used to influence the amount of time it takes for the emulsions to dry. As the magnesium oxide is in contact with water, it hydrolyzes to brucite, $Mg(OH)_2$. The amount of brucite in the green foam greatly influences the drying and sintering shrinkage, as well as product strength and porosity.

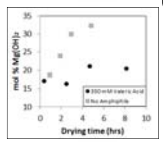


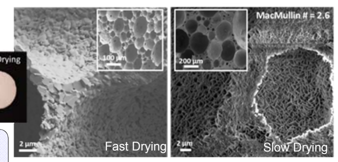


As magnesium oxide is initially dispersed into water, hydrolysis of MgO into brucite is apparent. Fragile brucite breaks into smaller particles than MgO that is ball milled in methanol. The transition can also be seen in the rheology of the suspension. After two hours, the suspension gels as brucite makes a percolated network in the water.

The brucite reaction is also apparent in the shape of the ceramic particles in the dried emulsion. Right we show green samples that were dried for various amounts of time. Below, it seems that the valeric acid amphiphile acts as an inhibitor to brucite formation.



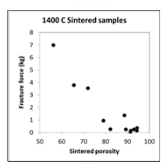


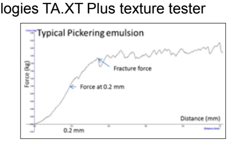


The brucite particle shape is retained, even after sintering the samples. Samples with more brucite also shrink less on drying and sintering.

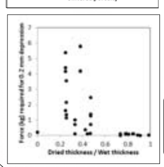
Fracture Strength of Sintered Samples:

The fracture strength is measured by a Texture Technologies TA.XT Plus texture tester using a 2 mm post geometry.



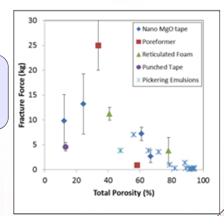


As porosity increases, the fracture strength decreases.



The fracture force of Pickering emulsion foams is comparable to porous MgO ceramics of similar porosity made through other methods.

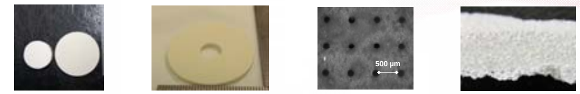
Samples that are high in brucite content tend to shrink less and be weak as opposed to those that dried more quickly and are mostly magnesium oxide.



Comparison to Traditional Porous Ceramic Processing Techniques:

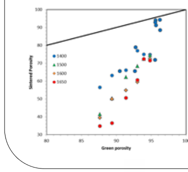
The performance of ceramic foams manufactured from Pickering emulsions are also being compared to other approaches to porous ceramic manufacturing techniques.

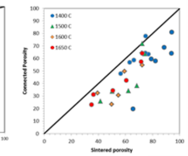
Pressed pellet with added poreformer · *Tape cast with and without poreformer added* · *Tape cast with punched array of holes* · *Reticulated foam*

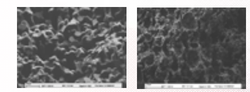


Effect of Sintering Temperature:

Sintering temperature has a big impact on the final structure of the ceramic foam. Higher temperatures reduce the foam porosity as the particles are increasingly consolidated.



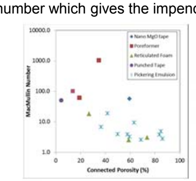




SEM of emulsion samples sintered at 1600 °C (left) and 1400 °C (right)

Ionic Conductivity:

One important measure of the permeability of the ceramic foams is the ionic conductivity, a parameter that includes both the extent of the connected porosity and the tortuosity. The ceramic foams are soaked in conductive KCl solutions and then the impedance is measured as a function of frequency. Where the frequency response is in-phase with the applied AC current, the resistance is measured. Results are reported in terms of the MacMullin number which gives the impendence of the sample relative to the pure salt solution.



$$MacMullin\# = \frac{Sample\ resistance}{Solution\ resistance}$$

Pickering emulsion samples have relatively low MacMullin numbers as compared to porous ceramics made by other traditional methods. This is a direct result of the relatively high porosity of the Pickering emulsion foam.

Conclusions:

Particle stabilized emulsions show great promise as a manufacturing route for ceramic foams. The foam microstructure can be tailored through changes in emulsion processing, allowing higher porosity products than other traditional methods. Hydrolysis of magnesium oxide during the emulsion production can produce very porous samples, yet these samples have very low strength. More work remains to understand the complex interconnections between the composition and processing variables.

References:

1. Akartuna I, Studart AR, Tervoort E, Gaukler LI. *Advanced Materials*. 2008; 20(24):4714.

Acknowledgements:

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