Welcome to the world of freeze-casting!

Bordia Research Group

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This manual should be used as a starter guide for anyone looking to perform freeze-casting. It contains the basic background and procedures needed as well as references for further reading. Slurry preparation, freeze-casting and subsequent sample preparation are all covered.

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1 Background

Freeze-casting is a technique that exploits the highly anisotropic solidification behavior of a solvent (generally water) in a well-dispersed slurry to controllably template a directionally porous ceramic. By subjecting an aqueous slurry to a directional temperature gradient, ice crystals will nucleate on one side of the slurry and grow along the temperature gradient. The ice crystals will redistribute the suspended ceramic particles as they grow within the slurry, effectively templating the ceramic, creating a structure that alternates between ice crystals and ceramic lamellae. The microstructure produced is defined by a parameter λ (microstructural wavelenth) which is equal to the average thickness of a macropore plus its adjacent wall (Figure 1).

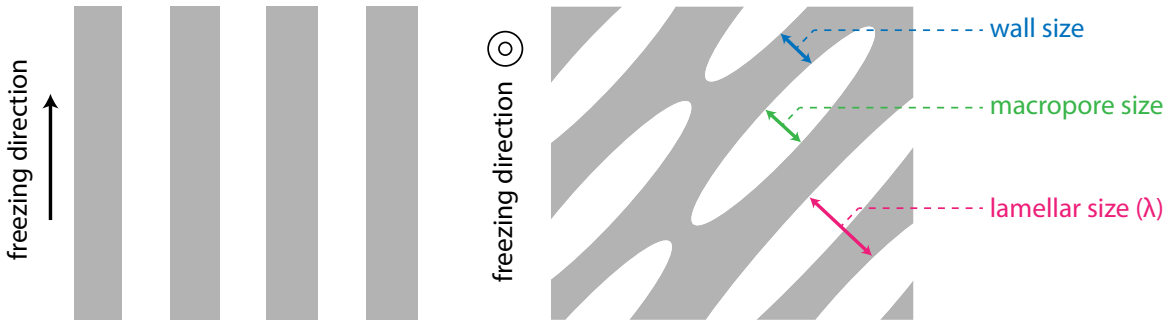

Figure 1: Schematic of freeze-cast microstructure in the longitudinal and transverse views.

Once solidification has ended, the frozen, templated ceramic is placed into a freeze-dryer to remove the ice crystals. The resulting green body contains anisotropic macropores in an exact replica of the sublimated ice crystals and micropores found between the ceramic particles in the walls. This structure is often sintered to consolidate the particulate walls and provide strength to the porous

material. Using freeze-casting it is possible to gain a significant amount of control over the porous microstructure at both the macro (10 - 200 μm) and micro (< 1 μm) levels of porosity.

The main parameters which control the microstructure of a freeze-cast are the freezing rate (which controls λ), solid loading, which controls the ratio of walls to macropore thickness, and sintering temperature, which controls the micropore morphology (Figure 2).

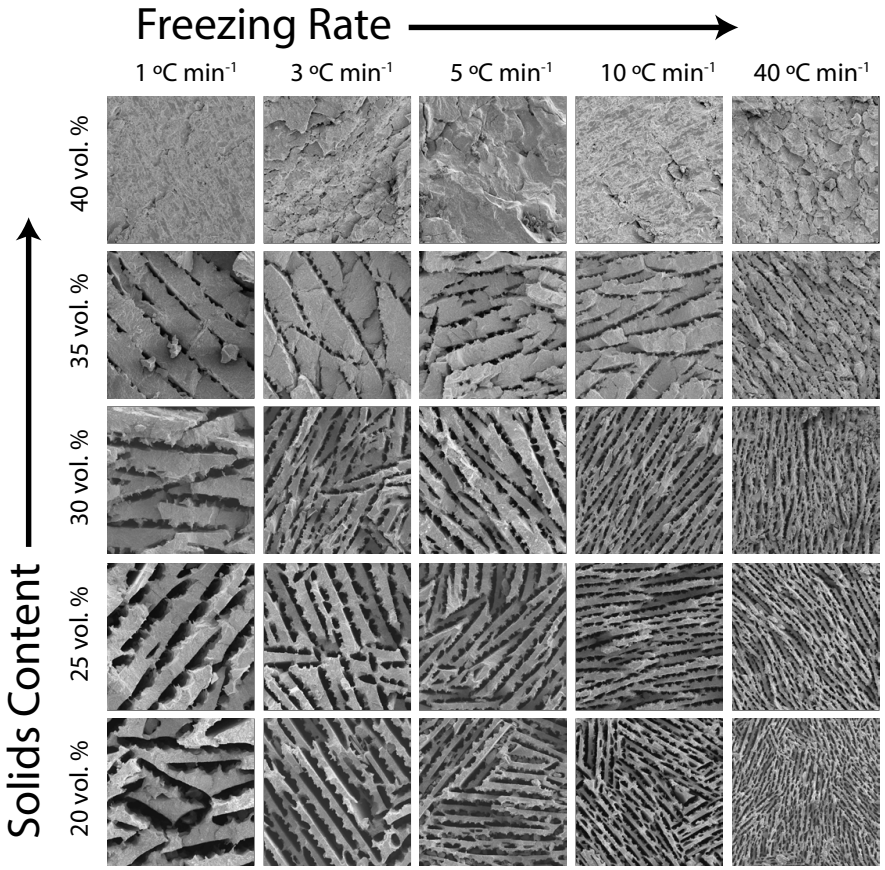

Figure 2: Processing map of LSM-YSZ freeze-casts. The freezing direction is out of the page. Note that no 40 vol. % samples experienced templating, indicating that freeze-casting is not possible at this solid loading for this particular materials system.

Morphology in the Freezing Direction

It is important to understand how the ice morphology changes along the length of the freeze-cast. Once the slurry becomes cold enough, ice crystals will nucleate and grow explosively in every spatial and crystallographic direction. This region of the freeze-cast is known as the Isotropic zone (IZ) because there is no directionality to the growth. Eventually, the freezing front slows down and the basal planes of the growing crystals begin to align with the temperature gradient. This section is known as the Transition Zone or TZ. Finally, once all the growing crystals are aligned with the temperature gradient, you have reached the Steady-State Zone (SSZ). It is primarily in this region that we are interested since there is such an obviously anisotropic microstructure. The size and overall morphology of these three zones can be controlled using various temperature profiles (Figure 3).

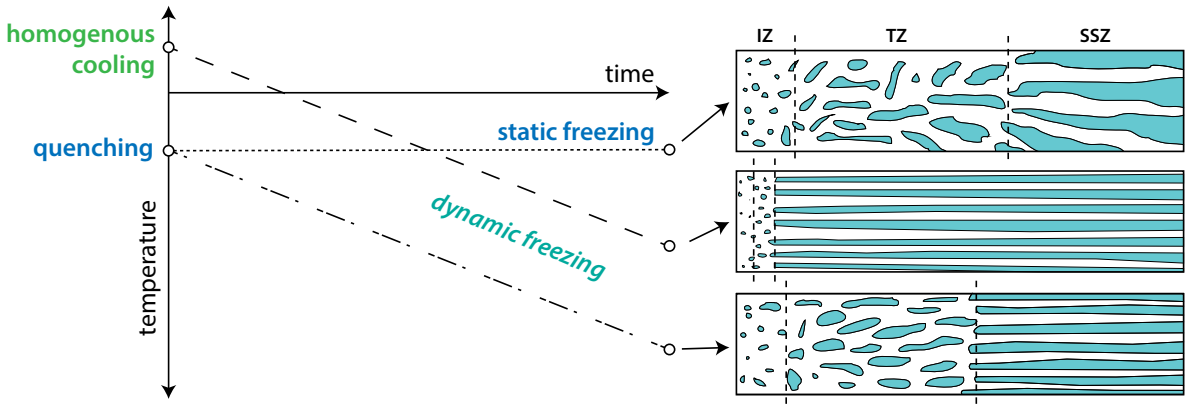

Figure 3: Representative thermal profiles which can be used during freeze-casting and schematic of their associated microstructures.

2 Slurry Preparation

In general, slurries for freeze-casting should have solid loadings ranging from 10 - 40 vol. % ceramics. Loading can be calculated according to the formula below:

$$Loading = \frac{V_{ceramics}}{V_{ceramics} + V_{Solvent} + V_{Dispersant} + V_{Binder} + V_{additional}} \quad (1)$$

Some generic densities are giving below (Table 1) to be used in calculating volumes for solid loading.

Table 1: Densities of used materials (g cm^{-3})

LSM	YSZ	NiO	Alumina	HAP	Silica	PMMA	Darvan C-N	PEG
6.10	5.90	6.67	3.95	3.16	2.65	1.18	1.1	1.1

General Slurry Making Procedure:

1. Add dispersant[1] and binder[2] into DI water and allow to homogenize while mixing for a minimum of 20 minutes.
2. Adjust pH with HNO_3 or $NaOH$ as needed depending on material system being used (ex. LSM-YSZ requires pH between 7 and 8).
3. Slowly add some powder under continued mixing, allow to homogenize.
4. Repeat until all powder is incorporated. It may be necessary to mix partly by hand or under horn sonication.
5. Slurry can either be used directly or stored for future use in an airtight container.

[1] Darvan C-N, R.T. Vanderbilt Co., Norwalk, CT
[2] PEG - Polyethylene Glycol 400 MW, Carbowax PEG 400 NF, FCC Grade, Union Carbide Inc., Danbury, CT

6. Rather than mixing on a stir-plate, some slurries may benefit from mixing in a rotary tumbler with milling media.

3 Freeze-Casting

We have two freeze-casters (Figure 4). One for low speed (static temperature or 1 - 5 °C min^{-1}) and one for high speed freeze-casting (10 - 40 °C min^{-1}). They are each controlled by the manual addition of liquid nitrogen (-196 ° C) into their respective reservoirs.

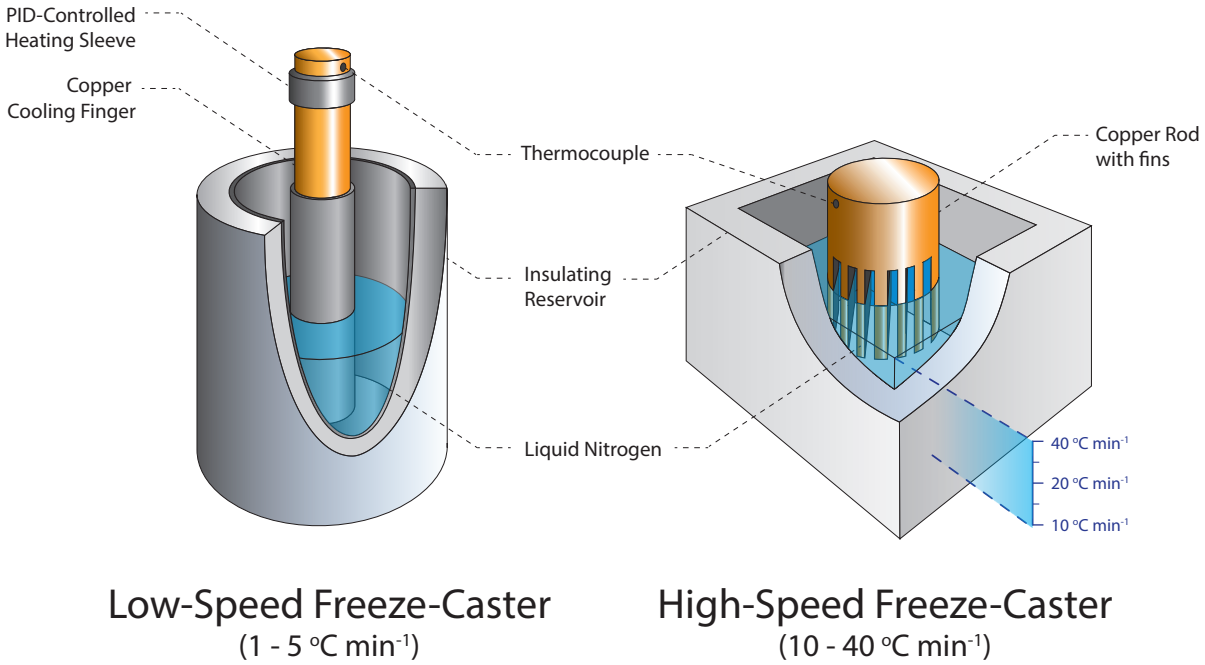

Figure 4: Schematics of our freeze-casters.

Slow Freeze-Caster

The slow freeze-caster has a PID-controlled heating sleeve[3] which is able to help control the temperature of the cooling finger making it more precise. It is honestly difficult to describe how to repeatably use this tool. After much practice you will gain intuition about how and when to add nitrogen and apply heat. For example, the colder the temperature gets, the less effective additional nitrogen will have on decreasing the temperature. Also, it should be noted that at temperatures lower than -100 °C it is not possible to apply heat. The temperature will continue to be monitored however.

The slow freeze-caster in addition has a second freezing finger which is suspended above the first, allowing it to perform double-sided freezing, if desired.

[3] CN7800, Omega, Stamford, CT

Fast Freeze-Caster

The fast freeze-caster is able to freeze-cast multiple samples (or one big sample) at the same time. It is controlled by holding the level of liquid nitrogen at various heights along the copper fins. With the bottom 3 mm of the fins submerged in liquid nitrogen, a freezing rate of approximately 10 °C min^{-1} is attained. Halfway up the fins is 20 °C min^{-1} and with the fins entirely submerged a rate of approximately 40 °C min^{-1} can be achieved[4].

3.1 General Freeze-Casting Steps

NOTE: This is a general procedure for freeze-casting a slurry using homogenous cooling (everything starts at room temperature) and dynamic cooling rates. If static cooling rates, quenching or other freezing profiles are desired the steps must be adjusted

1. Clean the freezing surface, making sure that there is no residual grease or powder on it.
2. Attach desired mold to the surface with vacuum grease taking care to ensure that the grease does not touch where the slurry will be.
3. Make sure that the slurry is well-dispersed. If it has been stored for a while it may require mixing/sonication/shaking etc.
4. Remove any air contained within the slurry by placing it in a vacuum dessicator for approximately 5 min.
5. Pour slurry into mold, watching for leaks. Leave some room, approximately 1 mm, at the top to allow for expansion of the slurry during freezing.
6. Control the cooling rate by the addition of liquid nitrogen and applied heat (for the slow freeze-caster).
7. Control temperature (and record) until complete solidification is achieved.

   I typically recorded temperature every minute unless we were specifically looking at freezing dynamics in which case we recorded every 10 - 30 seconds.
8. Remove the entire mold containing the freeze-cast and place into a freezer.
9. Prepare the freeze-dryer. The freeze-dryer must at least reach a temperature of -40 °C and a pressure of < 0.15 torr (< 0.15 mbar). If after freeze-drying there is still visible ice in the chamber or the molds feel very cold, these are clear signs that the pressure was not low enough.
10. If however sufficient temperature and pressure are achieved, the freeze-casts should be placed into the freeze-dryer for a minimum of 12 hours. For larger samples or smaller macropore sizes, freeze-dry for a minimum of 24 hours.
11. After freeze-drying, the samples are very fragile so handle with care.
12. Gently remove the freeze-casts from the molds by pressing a flat cylinder or even a gloved thumb to one end of the freeze-cast. If it doesn't come out easily press from the other side. Continue alternating with increasing pressure until the sample can be easily removed. NOTE: Samples WILL break, make extras. This is particularly true for samples made with low solid loading, low binder, or low freezing rates.

[4]These were calibrated for the climate in Seattle and may be different at Clemson

4 Sintering

Because the freeze-casts contain organic binders and dispersants it is important to add a debinding step to the sintering process. Samples should be heated at 2 °C min^{-1} to 450 °C and held until all organic compounds are burned out (approximately 2 - 4 hours) and then heated at 5 °C min^{-1} to the final sintering temperature.

5 Sample Preparation

Often after freezing it is necessary to section a casting to remove the interior portion (Figure 5). In this way you can remove the IZ and TZ as well as measure the microstructure at set distances along the freezing direction. If the sample is fully sintered and has a high enough solid loading, it is possible to do this without the addition of binder, simply using a slow-speed diamond saw. If quantitative data is needed however (SEM image analysis for example), your best bet is to infiltrate the sample with resin.

NOTE: This is a good point to perform ***Archimedes Testing*** *on the entire freeze-cast. Density testing can also be conducted after sample preparation, once the resin has been removed.*

Infiltration with resin

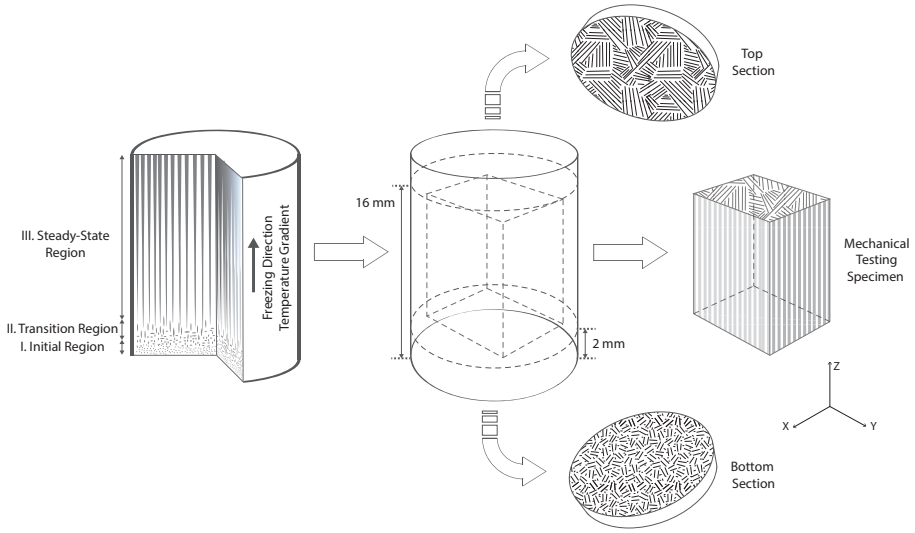

Figure 5: Schematic of anisotropic freeze-cast specimen preparation.

We primarily used EpoHeat[5] resin but EpoThin will also work as long as the pores are large enough (Figure 6). NOTE: The EpoHeat resin can very easily overheat if the warming oven temperature is too high. If this happens it will boil over and result in many bubbles inside the sample making further preparation extremely difficult. Once cured, the sample can be easily cut, ground and polished. They can then be imaged in this state or, if desired, the resin can be removed by slowly heating the sample to 500 °C and holding it there for 2 - 4 hours. Make sure that there is plenty of ventilation and that any large pieces of resin which can easily be removed are removed prior to the heat treatment.

[5]EpoHeat, Buehler GmbH, Irvine, CA, USA

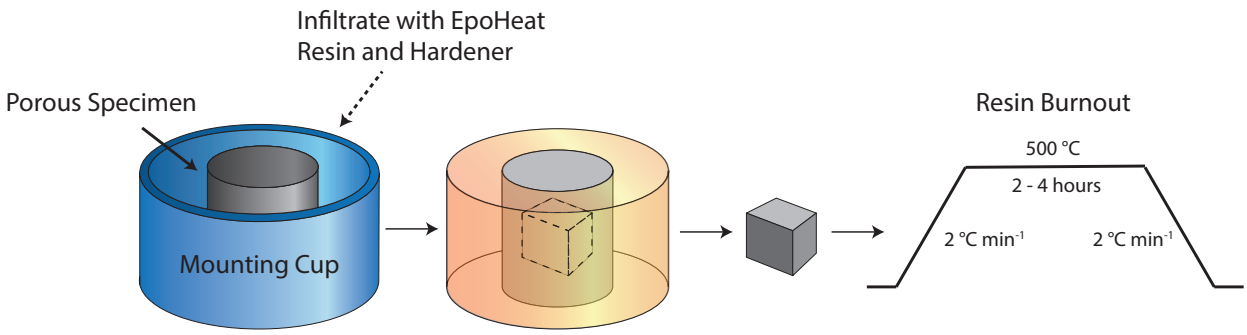

Figure 6: General sample preparation method. The pre-sintered porous ceramic is infiltrated with a low-viscosity resin then sectioned and polished as needed.

6 Further Reading

- Freeze-Casting Wikipedia - Good starter guide on the basic concepts (written by me)
- Website of Sylvain Deville - Freeze-Casting Guru

  Ice-templated porous alumina structures

  Freeze-casting of porous ceramics: a review of current achievements and issues
- Papers from our Group

  Processing of Hierarchical and Anisotropic Porosity LSM-YSZ Composites

  Dispersion, connectivity and tortuosity of SOFC cathodes prepared by freeze-casting