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Task Description:	Freeze-casting is a novel technique that utilizes ice as a fugitive space holder to fabricate a diverse variety of materials exhibiting elongated, aligned pores. Experimental studies in microgravity inherently simplify the freeze-casting system by minimizing gravity-induced forces that contribute to its complexity, e.g.. sedimentation, buoyancy, and natural convection. Freeze-casting has the potential to produce porous products with specific microstructure including net- and complex-shaped products, provided solidification conditions are properly controlled. Moreover, freeze-casting holds significant promise as an in situ resource utilization technique for space-based materials processing, thus increasing the reliability and safety of access to space while also decreasing overall costs. An improvement in scientific knowledge entails robust and predictive control of materials for a wide variety of applications, thus enabling optimized fabrication on Earth, on planetary surfaces (Moon and Mars), and in orbit.
Rationale for HRP Directed Research:	
Research Impact/Earth Benefits:	Freeze-casting has the potential to produce porous products with specific microstructure including net- and complex-shaped products, provided solidification conditions are properly controlled. Moreover, freeze-casting holds significant promise as an in situ resource utilization technique for space-based materials processing, thus increasing the reliability and safety of access to space while also decreasing overall costs. An improvement in scientific knowledge entails robust and predictive control of materials for a wide variety of applications, thus enabling optimized fabrication on Earth, on planetary surfaces (Moon and Mars), and in orbit.
	This research represents the first microgravity study of quasi-steady state solidification behavior in the freeze-casting process. Given the wide range of typical processing parameters and great number of research-worthy questions that remain unanswered about the technique, an exhaustive literature review was conducted to aid in experiment design. Data linking processing conditions to microstructural characteristics and mechanical properties were extracted from ~900 freeze-casting papers and a systematic analysis of these data was conducted. In accordance with the aim of this program, we created a public freeze-casting data repository (http://www.freezecasting.net) in an effort to facilitate broad dissemination of relevant data to freeze-casting researchers, promote better informed experimental design, and encourage modeling efforts that relate processing conditions to microstructure formation and material properties. A description of the resulting SQL database/website and results of our analysis were published in a review article in Progress in Materials Science [Scotti and Dunand, 2018]. Typical processing parameters that have been identified will be utilized during experiment design to ensure maximum generalizability of these results. Experimental data from the database will also be utilized to test models developed during this project. Succinonitrile (NC(CH2)2CN; SCN) was chosen as the suspending fluid for freeze-casting test suspensions due to: (i) known compatibility with the PFMI apparatus [Grugel et al., 2012], (ii) ease of sample transport (the melting point of SCN is ~58°C; thus, transport of test suspensions and solidified samples requires minimal environment control), and (iii) system simplification. It was determined that simplifying the system to the largest possible extent would offer the greatest degree of fundamental knowledge necessary to improve the understanding of microstructural formation and would also offer the opportunity to validate and improve existing freeze-casting models. This fundamental basis shall provide a basis upon which future microgravity work can build. Unlike water, which is the most-often utilized fluid in freeze-casting studies, SCN exhibits a linear temperature-density relationship within the temperature range of interest; thus, a density inversion during solidification is avoided. SCN has not been reported as a suspending fluid for use in freeze-casting suspensions systems. Previous research has shown that anisotropic solidification behavior of suspending fluids is a necessary, but insufficient criterion, for attaining directional pore structures for particle-based suspension systems [Naviroj et al., 2017]. We conducted preliminary tests to verify the feasibility of attaining directional microstructures using SCN-based particle suspensions. Directional microstructures were confirmed via scanning electron microscopy investigation of the fractured surface of a titanium/SCN freeze-cast structure where 20 vol.% titanium particles (20 μm size) was suspended in molten SCN and solidified under the presence of a thermal gradient. There are two main limitations of our preliminary demonstration, including: (i) constant cooling was utilized and the solidified SCN was not sublimated from the sample and sintering steps were not carried out. For the former issue, one side of the molten SCN suspension was cooled using a constant cold plate temperature (~20°C) while the other side was held at a constant warmer temperature (~65°C), whereas controlled cooling will be utilized during experimental operations as it provides greater control over microstructures templated. With regard to the second issue, our previous freeze-casting projects have mainly utilized water as the suspending fluid. In such cases, frozen samples are sublimated using a conventional freeze-dryer. The physical properties and toxicity of SCN necessitate the development of a new sublimation procedure. Progress toward completing these tasks is described below. As SCN is solid at room temperature, controlled cooling requires temperature control of both the top and the bottom of the suspension. We designed a sample container system to conduct these initial controlled cooling tests. The container consists of a Teflon tube (low thermal conductivity) that is covered using top and bottom aluminum plates (high thermal conductivity). Temperature sensors are placed perpendicular to the heat flow inside each of the aluminum plates to measure and control (through feedback loop) the temperature gradient during solidification. Resistance heaters, consisting of nichrome wire wrapped in Kapton (polyimide) tape, were placed on each aluminum plate and are operated using a microcontroller. A basic solidification program has been developed; the loop function involves reading the voltages of the temperature sensors, performing temperature conversions, comparing actual temperature values for each side of the suspension to target temperature values, and independently controlling each heater depending on the aforementioned comparison. Target temperatures are calculated as a function of time using an exponential cooling profile in an attempt to produce a constant solidification velocity during freezing experiments. The temperature of the solidification interface is assumed to be equal to the melting point of pure succinonitrile and an exponential cooling function determine the target temperature of the cold plate as a function of time. The target temperature of the hot side is determined based on a pre-defined temperature gradient which is held constant throughout solidification. The first stage of the program involves heating the aluminum plates to a starting temperature. During such time, the SCN/particle suspension is kept several degrees warmer than the melting temperature using a hot plate and magnetic stirrer. After the initial temperature is reached for both the hot and cold plates, the plates are kept at this temperature for five minutes during which time, the suspension is loaded into the Teflon mold. Thereafter, the hot plate is kept at a

constant temperature and the temperature of the cold plate is brought down to the melting temperature of SCN using a linear cooling rate (here, the rate is set at 5°C/min). Once the cold plate reaches the starting temperature, the exponential cooling function is used to determine the target temperature for the cold plate; during this time, the target temperature of the hot plate is determined by the pre-determined temperature gradient (the temperature difference between the solidification interface and the hot-plate temperature divided by the height of the molten region). The lowest attainable temperature using this apparatus is room temperature; thus, the solidification experiment is completed after the target cold plate temperature reaches room temperature. The last stage of the program is “thermal hold” wherein the temperatures of the plates are held at a predetermined temperature for a predetermined period of time before demolding; this stage ensures consistency for post-solidification sample handling.

Task Progress:

We previously reported the use of a plastic vacuum desiccator connected to an Edwards RV8 6.9 CFM dual-stage vacuum pump as a vacuum chamber. This design allowed for very heating of the chamber environment (~5°C above ambient) and resulted in extremely slow sublimation times. We re-designed the sublimation apparatus to provide better temperature control of the vacuum chamber. Samples are placed inside a metal vacuum chamber and the temperature of the chamber is controlled via a heating pad and PID temperature controller. A condenser, responsible for collecting and condensing SCN vapor, is connected to the vacuum chamber and cooled using an ice water and pump system. Cooling the condenser with ice water required numerous ice changes during sublimation; thus, we further redesigned this portion of the apparatus by adding a copper chiller that utilizes a cold-water supply source in the lab. The copper chiller is housed in a Styrofoam cooler. The sublimation time for a sample containing ~1.5 g is ~50 h; the time can be reduced by increasing the temperature of the vacuum chamber, however, doing so will increase the propensity for drying cracks to develop; thus, this is a parameter that requires further optimization. After ~80% mass loss, the SCN/CuO sample collapsed during sublimation. Similar tests were repeated and resulted in the same issue. In these cases, some portions of the specimen, especially those corresponding to peripheral regions, can be recovered. Our initial tests were conducted without the use of a binder in an effort to minimize the influence of suspension additives during solidification. We are in the process of testing samples with binder and higher particle volume fractions to mitigate this issue (while still attempting to minimize the effect of suspension additives).

To determine the safe storage requirements of post-experiment (solidified) samples, a series of thin sample studies were performed. This component of the testing was essential because the samples could be exposed to a variety of temperatures and conditions while traveling back from the station and will be stored for an indeterminate amount of time before being sent back for analysis. During that time, if any structural changes occur, microstructures of the samples would no longer be an accurate representation of that which was templated during solidification. Thin samples were used in the place of bulk samples for these tests because the microstructure of thin samples is immediately visible without carrying out post-solidification processing steps (i.e., sublimation and sintering). This distinction allows for the samples to be imaged immediately after solidification so that those images can be compared with ones taken of the same areas of the sample samples at designated time intervals.

A first round of testing was performed using a heating system involving the transmission of heat through nichrome wire wrapped around two aluminum blocks. Two glass slides held apart with a spacer (tape, 2 mm in width) are loaded between the blocks and filled with suspensions containing 5 vol.% CuO particles dispersed in liquid SCN. Samples were solidified using the same temperature profile and solidification program that was used for the bulk samples (described above).

After solidification, thin samples were imaged using a stereoscope once every day for one month. From these images, it was concluded that the microstructure became slightly hazy over time not because of actual structural changes, but because the specimen pulled away from the glass slide (likely due to post-solidification SCN shrinkage). This hypothesis is further supported by the presence of air bubbles in the top corned of the image taken at the one-month mark. These are air bubbles were not present in the image taken immediately after solidification, meaning that there was more space between the glass and the sample for the bubble to insert itself into after the waiting period.

The stereoscope that was used for imaging also provides a high depth of field, which makes focusing on the same area of the sample more difficult when that area begins pulling away from the glass slide (thus, increasing the object distance between imaging days). Thus, the distortion of the features is not significant enough to indicate that they themselves have actually changed, but rather that the methods used to distinguish them are less effective due to a poorer ability to fully resolve all of the same features over time. When comparing the larger highlighted dendritic section immediately after solidification with that same section after one month of storage at room temperature, a significant difference in dendrite width or spacing was not detected.

A second set of tests was used to produce finer microstructures (which should exhibit a higher propensity for microstructural rearrangement after solidification). For these tests, the cold-side aluminum block was refrigerated until it reached 0°C while the slides were heated to 100°C. The length of the slide was decreased such that the sample could be loaded without solidifying prematurely. As expected, the dendrite structure was finer than those observed for the slower solidification tests reported above. Although these finer structures are more difficult to compare due to magnification limitations of the stereoscope, we were not able to observe significant post-solidification processing changes to the microstructures. The same cloudiness and distortion of the image can be observed that was hypothesized earlier to be caused by separation of the sample from the glass but, otherwise, the dendritic structure itself appears to remain unchanged. As we are currently working on modifying the suspension characteristics, these tests will need to be repeated after the suspension preparation process is finalized.

References

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Bibliography Type:	Description: (Last Updated: 11/17/2022)
Articles in Peer-reviewed Journals	Scotti KL, Kearney LG, Burns J, Ocana M, Duros L, Shelhamer A, Dunand DC. "The effect of solidification direction with respect to gravity on ice-templated TiO2 microstructures." Journal of the European Ceramic Society. 2019 Aug;39(10):3180-93. https://doi.org/10.1016/j.jeurceramsoc.2019.04.007 , Aug-2019