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PI Name:	Dunand, David Ph.D.		
Project Title:	Microstructure Evolution in Freeze-Cast Materials		
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Comments:			
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Key Personnel Changes/Previous PI:			
COI Name (Institution):	Voorhees, Peter Ph.D. (Northwestern University)		
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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.
Task Progress:	1. Solidification studies To study the effect of temperature gradient on solidification structures, different furnace translation velocities were applied. A banding structure is observed and dendritic/spear-like symmetric dendritic features are also observed throughout the microstructure. Primary dendrite arm measurements of naphthalene were obtained from stitched cross-section images taken perpendicular to the freezing direction. Dendrite thickness is expected to increase with decreasing furnace translation velocity; this relationship is observed for all regions. For all velocities, dendrite widths are largest in the outer region of samples and decrease with decreasing distance from the center (e.g., for samples solidified at V = 6.5 μm·s^(-1), dendrite width at the outer and inner regions are 87±11 and 40±9 μm, respectively; for V = 80 μm·s^(-1), these values decrease to 60±14 and 17±4 μm, respectively). The relationship we observe here, with increasing dendrite width at outer regions of samples relative to inner regions, indicates that the local solidification velocity is higher in the central region of the sample relative to the outer region. The corresponding macroscopic convection pattern is likely characteristic of a convex macroscopic interface. Interdendritic convective fluid flow is also likely present, given the observation of asymmetric dendritic features. 2. Freeze-thaw studies As flight ampoules will be filled on the ground and transferred to the international Space Station (ISS) in a solidified state, samples will need to be melted back immediately prior to experimental tests, and suspension stability cannot degrade appreciably due to that freeze-thaw cycle. We conducted freeze-thaw studies using four naphthalene/Cu/surfactant systems to assess suspension destabilization after freeze/thaw. Within the four surfactant types tested, two stabilization mechanisms were studied: steric stabilization and electrosteric stabilization. For suspensions employing low dielectric constant fluids (e.g., naphthalene), steric stabilization is the most commonly employed stabilization method; polymers adsorbed on particles create a hindrance for particle aggregation. Aggregation that does occur when particles overcome steric repulsion is thought to be reversible. Three of the surfactants we tested offered steric stabilization; two of the three (Triton X-100 and Pluronic F-68) produced suspensions that were inconsistently stable even prior to freeze-thaw testing, likely due to thermal degradation of the polymer due to the high melting temperature of naphthalene. The third steric stabilization surfactant, Hypermer KD-13, produced stable suspensions that, however, destabilized after freeze-thaw. AOT is an ionic surfactant that is used for electrosteric suspension stabilization. Electrosteric stabilization in low-dielectric constant fluids offers increased stabilization relative to steric stabilization alone. In this case, we have a non-polar fluid, so the polar head of the surfactant molecule adsorbs to the particle surface (with help from the counterion, which creates a bridge). At the critical micelle concentration, reverse micelles that are charge-stabilized are formed. With this system, we have been able to reliably create stable naphthalene/particle suspensions which, as shown previously, produce anisotropic, directional microstructures upon solidification. Moreover, we did not observe any evidence of suspension destabilization after freeze-thaw. However, tests were conducted after subjecting suspensions to a single freeze-thaw cycle; additional cycles may cause degradation not described in the following. The suspension must remain in the liquid state during various stages of ampoule filling. Also, science requirement 19 specifies a storage transport requirement for suspensions prior to flight testing at <80°C to prevent an uncontrolled freeze-thaw cycle. To assess their freeze-thaw stability, suspensions with 5 vol.% Cu and 1 wt.% AOT (with respect to Cu) were prepared as described previously. Prepared suspensions were subjected to an initial freeze in an ultrasonic bath using bath temperatures of either ~10 or ~50°C, representing slow (FTS) and fast (FTF) freeze-thaw testing, respectively. Solidified suspensions were melted immediately prior to directional solidification. In an attempt to mitigate the risk of particle aggregation during freezing, the sonication step was utilized to promote disordered growth during the initial freeze step, which should reduce the propensity for particle aggregation (Science Requirement 10). Primary dendrite arm measurements of naphthalene were obtained from stitched cross-section images taken perpendicular to the freezing direction, as described previously. As observed previously, dendrite width increases with increasing radial distance from the center. Within a given region, values of mean dendrite width are in relatively good agreement among the freeze-thaw conditions. For the outer region, these values are 60±14, 54±8, and 60±11 for the no-freeze-thaw (STD), freeze-thaw-fast (FTF), and freeze-thaw-slow (FTS) conditions, respectively. For the inner regions, values for STD, FTF, and FTS are 17±4, 21±6, and 20±5, respectively. 3. Pre-Science Requirements Review (Pre-SRR) PFMI furnace testing 3.1 Sample Ampoule Assembly Microgravity solidification experiments are intended for the Pore Formation Mobility Investigation (PFMI). The PFMI furnace allows for a high gradient of 50 °C/cm, low gradient of 10°C/cm, and nominal melt-back and growth velocities of 100 and 1 μm/s, respectively. The Sample Ampoule Assembly (SSA), as designed for the previous PFMI work, was used. Techshot is designing the SSA for this work to be similar in construction to those designed previously, components of which include: the main tube body (composed of Schott 8250 borosilicate glass),

stainless steel (SS) spring, Kovar piston assembly, cartridge mount head, and six in-situ thermocouples. The inside and outside diameter of the ampoule is ~10.9 and 12.75 mm, respectively. To ensure similar thermal behavior with respect to the glass, Science Requirement 3 specifies an internal diameter tolerance of ±0.2 mm. Based on toxicology assessments conducted by Techshot, the maximum volume of naphthalene that can be used in an individual ampoule is ~6.8 mL. Accordingly, ampoules will be filled with ~5.6 mL of science material, corresponding to an effective science material length of ~6 cm which is shorter than the overall length of the ampoules (~28 cm, not including the piston assembly or insertion of the Kovar head). The first assembled ampoule #1 had an issue with the Kovar piston motion during pumping, which bent thermocouples from designed position which would have affected measurements of temperature gradients (it was thus not used). Ampoules #2 and #3 were assembled with stronger springs to retard the movement of the piston. In addition, a magnetic frame equipped with 4 high strength magnets is also utilized to constrain the piston during naphthalene filling. It was successful, as the piston only moved less than 2 mm under high vacuum after pumping down.

3.2 Naphthalene remelting testing To eliminate bubble formation in solidified naphthalene, induced by air leakage during ampoule filling, the gas lines of the filling station were upgraded using stainless steel pipes, Pirani pressure gauge and Swagelok connectors. A vacuum of 7x10-2 Torr was reached in gas lines after pumping for 40 mins with a roughing pump, indicating good resistance to leaks. As-received naphthalene was distilled first with this upgraded setup.

To test performance and stability of naphthalene melting with the PFMI furnace, sample ampoule #3 with embedded thermocouples was filled with purified, distilled naphthalene at Northwestern University. Filled ampoules were remelted and directionally solidified with different processing parameters in the PFMI furnace at TechShot. Naphthalene solidification was performed with two batches of processing parameters to induce different solidification morphologies, i.e. dendrites and bands, at solid-liquid interface. High furnace translation velocity, V = 100 µm ·s^(-1), and shallow temperature gradient, G = 10 K ·cm^(-1), result in dendritic morphologies. In contrast, the low V =1 µm ·s^(-1) and steep G = 50 K ·cm^(-1) expect to induce bands morphologies during solidification.

The filled ampoule was placed vertically in the PFMI furnace (at Techshot) and heated up to 87 ºC to melt the naphthalene prior to solidification. The cold zone was moved to solidify liquid naphthalene in the molten zone with a defined translation velocity. The temperature as a function of time was measured by 6 thermocouples during solidification with translation velocities of 100 µm/s and 1 µm/s. The solidification of naphthalene was recorded as a plateau (from latent heat release) in temperature profiles during furnace translation.

Temperature gradients in liquid naphthalene during solidification are also calculated from each temperature profile measured by six thermocouples. Cooling rate (k, K/s) was first calculated from the slope of temperature profile, and then divided by furnace translation velocity (V, cm/s) to achieve the temperature gradient (G, K/cm). With a translation velocity of V=100 µm/s, calculated temperature gradient has an average value of 8.4 K/cm, close to the designed value of 10 K/cm. In the case of translation velocity of V=1 µm/s, measured temperature gradients of 26 K/cm are smaller than 50 K/cm. This could be solved by adjusting the distance between electrode 1 and the cool zone.

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