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INSTITUTE FOR DEFENSE ANALYSES

Chemistry in Space

(Presentation)

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About This Publication

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Executive Summary

Background

The Defense Advanced Research Projects Agency requested that the Institute for Defense Analyses (IDA) explore the challenges and opportunities for chemical and material processing in extraterrestrial environments such as the International Space Station (ISS), the moon, or Mars. Specifically, IDA investigated possible manufacturing methods in these environments, as well as differences in processing physics that might enable improved or novel processing methods.

IDA first identified the key characteristics that distinguish the three environments in question from Earth, including gravity, atmosphere, temperature, and *in situ* resources. Mars and the moon each have reduced gravity and atmosphere relative to Earth, but samples of their soils and atmospheres differ. Previous efforts to identify ways to prepare building materials *in situ* in Martian or lunar environments have targeted pressed and sintered soil simulants, polyethylene, and composites of the two.

Findings

In contrast to Mars and the moon, the ISS is characterized by a microgravity environment with access to a high-vacuum, low-impurity environment. Buoyancy-driven convection and sedimentation are largely eliminated in such an environment, leading to several important effects. Lack of density gradients during solidification produces more uniform microstructures and compositions for materials, ranging from metallic foams to semiconductor crystals. Metallic foams have many applications, including heat exchangers, blast and impact protection, and battery electrodes, and can be prepared from relatively small launch packages. For this reason, metallic foams may be of interest for both Earth-return and extraterrestrial use.

A lack of convection can also suppress nucleation events in glass-forming melts, expanding their working temperature range and reducing the number of crystalline defects in the final glass. This effect, which has enabled the preparation of high-transmittance ZBLAN optical fibers, has also improved our understanding of metallic glass formation. ZBLAN fibers represent a possible Earth-return, in-space manufacturing application, as they require compact (as opposed to large-volume) equipment and derive extremely high value per weight of finished product. In contrast, many materials research efforts on the ISS have focused on making *measurements* of properties such as diffusion coefficients while avoiding complicating microgravity effects. Such measurements can improve both simulation and manufacturing capabilities on Earth, but typically do not feed into any in-space manufacturing plan.

Biological research has benefited from microgravity conditions to produce useful test specimens. Lack of sedimentation, suppressed buoyant convection, and more uniform nucleation-driving forces have enabled many high-quality protein crystals to be grown on the ISS. Microgravity also enables 3D tissue growth by allowing intracellular forces to dominate over gravitational forces, preventing sedimentation effects, which are detrimental to cell growth.

Suppressed convection has a number of other interesting effects, including decreasing the amount of shear forces present in a fluid (which affects the viscosity of non-Newtonian fluids) and weakening processes such as combustion and anti-foam propagation. Shear suppression may be important in some polymer processing, but polymer processing has only been explored to a limited extent in microgravity. For the most part, polymer processing is of interest in the context of additive manufacturing (AM) because of the potential to enable on-demand part synthesis aboard the ISS and other extraterrestrial platforms. The ISS already contains an AM facility that works with polymer feedstock; there are plans to expand this to include other material classes such as metals and bio-inks. AM is still a relatively new category of manufacturing, and there are concerns about reproducibility and reliability that have yet to be solved terrestrially. Any attempt to use AM in space must also be cognizant of these concerns.

Combustion effects, specifically those surrounding controlled combustion and stability, are studied in the context of microgravity via programs such as ACME (Advanced Combustion via Microgravity Experiments). Researchers studying fuels and exhaust use data on soot production obtained in microgravity environments to model combustion without the complicated physical interactions produced by gravitational forces.

The conditions available on the ISS also have the potential to minimize defect formation in crystalline materials. Microgravity conditions enable “contactless processing,” which prevents defect formation by avoiding contact with container side-walls. Similarly, high-vacuum, low-impurity atmospheres minimize the presence of compositional impurities. Note, however, that reactive species (e.g., atomic oxygen) or high radiation fluence can induce defect formation.

Flow chemistry may be a valuable approach for molecular synthesis in microgravity. Flow-chemistry methods are more reproducible than batch syntheses and do not include free head-space that is problematic in microgravity. It is also possible to operate and monitor flow chemistry remotely.

Limited research into materials synthesis has found that microgravity effects enable highly uniform microstructures while suppressing defect formation. These effects can be useful in many contexts, such as glass or semiconductor solidification, metal foam formation, or even preparation of highly uniform nanoparticles. However, it is only recently that an application for in-space manufacturing with Earth return has become viable (ZBLAN). Most research efforts aboard the ISS do not feed into a larger in-space manufacturing vision. Instead, these enable manufacturing and simulation terrestrially by making measurements or preparing standard specimens not otherwise possible. But technologies for in-space manufacturing do exist, such as flow-chemistry, additive manufacturing, and foam-formation. Microgravity manufacturing is limited by cost, volume, and the availability of starting materials and power sources.

Contents

ENVIRONMENT INFORMATION

2

Key Aspects of the "Space" Environment

- Space station:
  - Microgravity
  - Vacuum / low oxygen
  - Low impurity content
  - Radiation

Table 3.5: Unique Features of the Space Environment

Phenomenon	Space	Earth
Ultravacuum [24]	10^{-7} Torr in LEO 10^{-14} Torr in LEO orbital wake 10^{-15} Torr halfway to the Moon	760 Torr
Microgravity [15]	Drag: 10^{-7} g Gravity gradient: 0.3 x 10^{-6} g/m Vibration: 8.4 x 10^{-6} g RMS	1 g
Solar Flux	1367 W/m^2	550 W/m^2 to 1,025 W/m^2
Temperature	40 K (passive) Deep Space: 2.7 K	184 K to 330 K

- Moon and Mars have soils and gasses available *in situ.*

M. T. Moraguez, "Technology Development Targets for Commercial In-Space Manufacturing" (master's Thesis, MIT, 2018).

No single NASA reference outlining features of the space environment has been found to provide adequate descriptions of the space environment. These source provide details on individual aspects of the space environment:

- Air Command and Staff College. *AU-18 Space Primer.* Maxwell Air Force Base, AL: Air University Press, 2009. http://space.au.af.mil/au-18-2009/au-18-2009.pdf; see especially, Chapter 7 (pp. 115–36), "Space Environment."
- Anderson, B. Jeffrey, and Robert E. Smith. *Natural Orbital Environment Guidelines for Use in Aerospace Vehicles.* NASA Technical Memorandum 4527, June 1994. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19940031668.pdf.
- Belk, C. A., et al., "Meteoroids and Orbital Debris: Effects on Spacecraft." NASA Reference Publication 1408, August 1997. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19970034583.pdf.
- Buchheim, R. W., et al. *Space Handbook: Astronautics and Its Applications.* Santa Monica, CA: RAND Corporation), December 1958. https://www.rand.org/pubs/commercial_books/CB136-1.html.
- Dooling, D., and M. M. Finckenor. "Material Selection Guidelines to Limit Atomic Oxygen Effects on Spacecraft Structures. NASA/TP-1999-209260, 1999. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19990064119.pdf.
- Ferguson, D. C., and G. B. Hillard. *Low Earth Orbit Spacecraft Charging Design Guidelines.* NASA/TP-2003-212287, 2003. https://see.msfc.nasa.gov/sites/see.msfc.nasa.gov/files/LEO_Charging_Guidelines_v1.3.1.pdf.
- Herr, J. L., and M. B. McCollum. "Spacecraft Environments Interactions: Protecting against the Effects of Spacecraft Charging." NASA Reference Publication 1354, November 1994. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19950013364.pdf.
- Howard, J. W., Jr., and D. M. Hardage. "Spacecraft Environments Interactions: Space Radiation and Its Effect on Electronic Systems." NASA/TP-1999-209373, July 1999. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19990116210.pdf.
- James, Bonnie F., O. W. Norton, and Margaret B. Alexander. "The Natural Space Environment: Effects on Spacecraft." NASA Reference Publication 1350, November 1994. https://see.msfc.nasa.gov/sites/see.msfc.nasa.gov/files/rp-1350.pdf.

- NASA ISS Program Science Office. "A Researcher's Guide to International Space Station Space Environmental Effects." NASA NP-2015-03-015-JSC, 2015. https://www.nasa.gov/sites/default/files/files/NP-2015-03-015-JSC_Space_Environment-ISS-Mini-Book-2015-508.pdf.
- Vaughan, W. V. et al. "Spacecraft Environments Interactions: Solar Activity and Effects on Spacecraft." NASA Reference Publication 1396, November 1996. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19970034583.pdf.

IDA | **Lunar Environment**

https://moon.nasa.gov/resources/48/the-moons-surface/

- Gravity: 0.17 G (compared to Earth 1 G)
- Temperature range: –173 to 127 °C
- Crust composition: Mix of NaAl, CaAl, MgFe, and other silicates
- Atmosphere composition:
  - "hard vacuum"—14× fewer molecules/cm^3 than Earth
  - Available gasses: Ar, He, O_2, CH_4, N_2, CO, CO_2

Oxide	Lunar soil	Simulant powder
	Concentration (wt.%)	
SiO_2	47.3	47.71 ± 0.10
Al_2O_3	17.8	15.02 ± 0.04
CaO	11.4	10.42 ± 0.03
MgO	9.6	9.01 ± 0.09
FeO	10.5	7.35 ± 0.05
Fe_2O_3	0.0	3.44 ± 0.03
Na_2O	0.7	2.70 ± 0.03
TiO_2	1.6	1.59 ± 0.01

Phuah et al., "Ceramic Material Processing Towards Future Space Habitat—Microstructure and Properties of Field-Assisted Sintering of Lunar Soil Simulant (JSC-1)," presentation at Materials in Space Workshop, 2018.

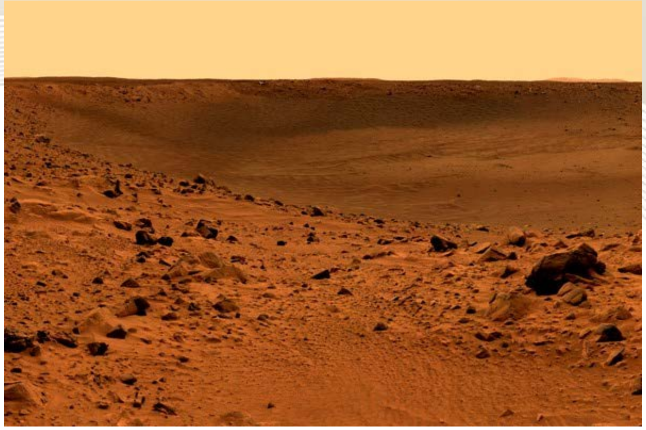
4

For additional information about the lunar environment, see:

- Buchheim, R. W., et al. *Space Handbook: Astronautics and Its Applications.* Santa Monica, CA: RAND Corporation), December 1958. https://www.rand.org/pubs/commercial_books/CB136-1.html.
- Martinez, Isidoro. “Space Environment,” 1995–2019. http://webserver.dmt.upm.es/~isidoro/tc3/Space%20environment.pdf. (Note: Dr. Isidoro Martinez is a Professor of Thermodynamics at Ciudad University (ETSIAE-UPM) in Madrid, Spain; he apparently has expertise in spacecraft thermal control design.)

Martian Environment

- Gravity: 0.38 G (compared with Earth's 1 G)
- Temperature range: –153 to 20 °C
- Crust composition: iron, magnesium, aluminum, calcium, and potassium
  - Known as "Red Planet," resulting from oxidized iron dust
- Atmosphere composition:
  - Thin atmosphere with red suspended dust
  - Available gasses: CO_2 (95%), N_2, and Ar
- Water:
  - Mostly ice
  - liquid water discovered 1 mile below southern ice cap (July 2018)



https://www.nasa.gov/sites/default/files/bonneville_crater.jpg

Pathfinder soil sample

Oxides	Pathfinder (wt%)
SiO_2	44
Al_2O_3	7.5
TiO_2	1.1
Fe_2O_3	16.5
CaO	5.6
MgO	7.0
Na_2O	2.1

Sen, *Adv. Space Res.*, 2010

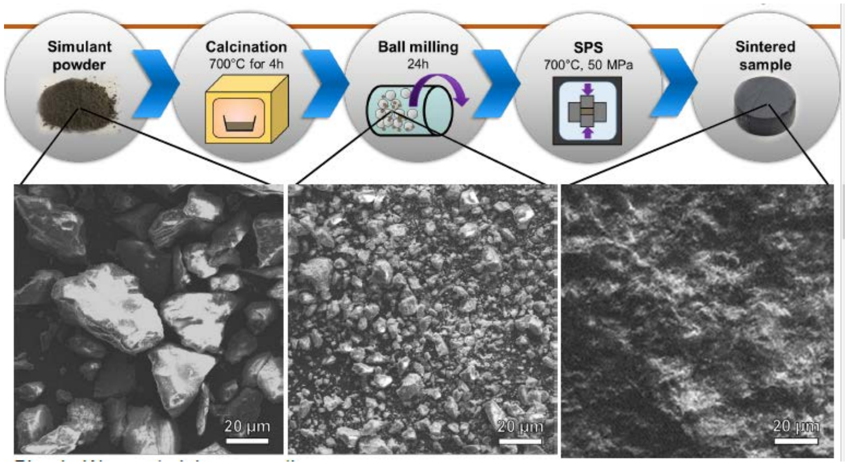
"Mars: In Depth," NASA Science Solar System Exploration, https://solarsystem.nasa.gov/planets/mars/in-depth/; "What is Gravity", NASA, https://settlement.arc.nasa.gov/teacher/lessons/bryan/microgravity/gravback.html; https://www.space.com/16895-what-is-mars-made-of.html.

For additional information about the Martian environment, see also:

- Buchheim, R. W., et al. *Space Handbook: Astronautics and Its Applications.* Santa Monica, CA: RAND Corporation), December 1958. https://www.rand.org/pubs/commercial_books/CB136-1.html.
- Economou, T. E., R. Rieder, H.Wänke, A. Turkevich, J. Brueckner, G.Dreibus, J. Crisp, and H. McSween, Jr. "The Chemical Composition of Martian Rocks and Soil: Preliminary Analysis," n.d. https://mars.nasa.gov/MPF/science/lpsc98/1711.pdf.
- Martinez, Isidoro. "Space Environment," 1995–2019. http://webserver.dmt.upm.es/~isidoro/tc3/Space%20environment.pdf. (Note: Dr. Isidoro Martinez is a Professor of Thermodynamics at Ciudad University (ETSIAE-UPM) in Madrid, Spain; he apparently has expertise in spacecraft thermal control design.)

Martian and Lunar *In Situ* Manufacturing

- A number of efforts have explored preparing materials from resources available on Mars or the Moon
  - Pressed, field-assisted sintering of lunar soil[1] (Figure)
    - Also, microspheres and fibers made from lunar soil
  - Preparation of polyethylene from Martian atmosphere (Sabatier process + catalytic oxidation)[2]
  - Preparation of poly-ethylene + soil composite by liquid infiltration or extrusion and pressing[2]



Studies are based on soil *simulants*

[1] Phuah et al., "Ceramic Material Processing Towards Future Space Habitat."
[2] S. Sen, S. Carranza, and S. Pillay, "Multifunctional Martian Habitat Composite Material Synthesized from in Situ Resources," *Adv. Space Res., 46: 582–92*.

6

MATERIAL PROCESSING

7

In-Space Manufacturing

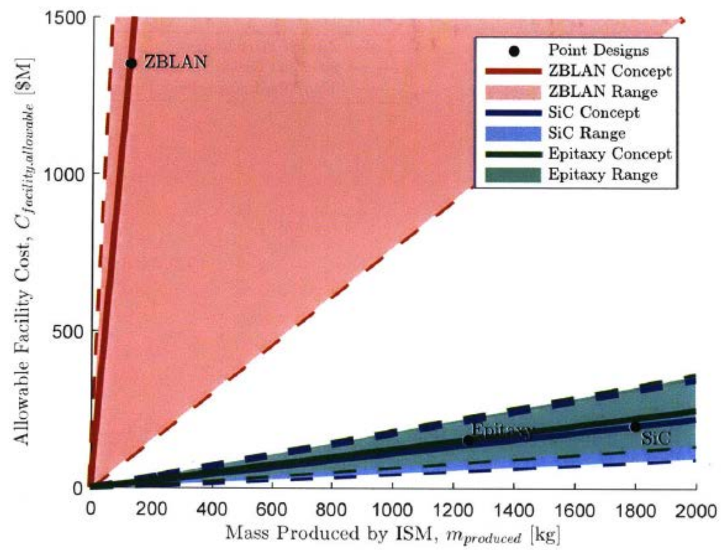
- Earth-return applications of In-Space Manufacturing (ISM) must:
  - Take advantage of unique environment of space (long-term microgravity, vacuum, etc.)
  - Produce better properties than can be achieved terrestrially
  - Retain those properties upon return to Earth
- "Best" applications for ISM have "high allowable facility cost without requiring a large total ISM product mass"
  - ZBLAN fibers fits this description—expected sale price $11 million/kg; required equipment is compact
- Other proposed products: SiC wafers, epitaxial thin films, metal alloys, pharmaceuticals
- There is always a risk that terrestrial methods will be developed that can overtake ISM

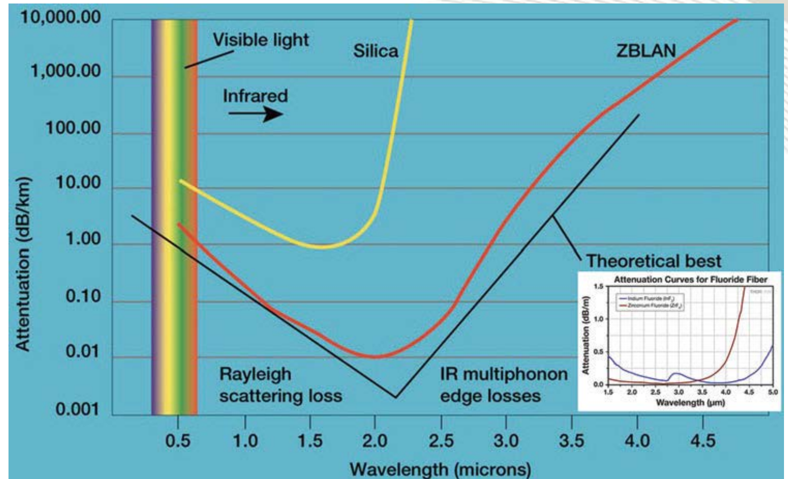
Moraguez, "Technology Development Targets for Commercial In-Space Manufacturing."

8

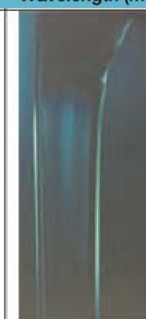
ZBLAN Fibers – Best Business Case to Date

ZBLAN optical fibers fabricated in microgravity can have substantially decreased attenuation compared to SiO_2 fibers





Note crystals in the preform melt.



Fiber pulling in 20 seconds of microgravity. No crystals are present.

Cozmuta, Ioana, and Daniel J. Rasky, "Exotic Optical Fibers and Glasses: Innovative Material Processing Opportunities in Earth's Orbit," *New Space* 5 (3): 121–40.

Materials Processing Methods Uniquely Available in Space

- Substantially reduced buoyancy-driven convection during solidification
  - Highly uniform microstructures and particle, precipitate, or void (for foams) dispersions
    - Monodispersity is valuable in many systems including radiation emitters/absorbers (including quantum dots), filters, and colloids
  - Enables measurement of kinetics without complication of buoyancy—helps with modeling
- Detached growth, levitated solidification (also known as “containerless processing”)
  - Minimizes sites for defect nucleation
  - Enables undercooling
- Minimal environmental impurities / sustained vacuum

Material processing in microgravity can produce more uniform microstructures with reduced defect densities

James Patton Downey, “A Researcher’s Guide to International Space Station: Microgravity Materials Research,” National Aeronautics and Space Administration (NASA) ISS Program Science Office, 1-48, https://www.nasa.gov/sites/default/files/atoms/files/np-2015-09-030-jsc_microgravity_materials-iss-mini-book-508c2.pdf.

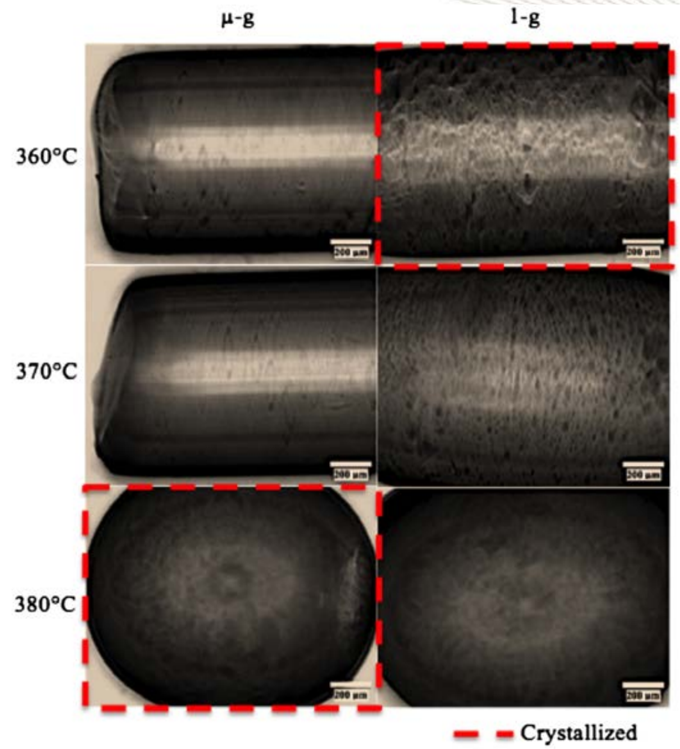
10

Packed-bed reactors (e.g., for heterogeneously catalyzed reactions), photonics, and drug-delivery systems could benefit from highly monodisperse particles.

Some types of controlled-gradient processing (e.g., to make laminates with controlled variations in properties from one side to another) could be enabled in microgravity. Controlled gradients can be important when developing transitional interface layers that minimizes "stress" on either side of a dissimilar environment, such as electrolytes for fuel cells.

Change in Working Temperatures of Non-Newtonian Fluids

- Applies to some polymers and glass melts
- One possible explanation: Microgravity causes reduced convection and therefore reduced sheer—so sheer-thinning fluids will have higher viscosity; sheer-thickening fluids will have lower viscosity than they would at 1 G
- Can suppress crystallization in sheer-thinning glass melts—increases working temperature range, possibly also working time frames



es et al., "Increasing the Working Temperature Range
ZrF4-BaF2-LaF3-AlF3-NaF Glass through Microgravity
ocessing." *Optical Engineering* 53(3): 1–9.

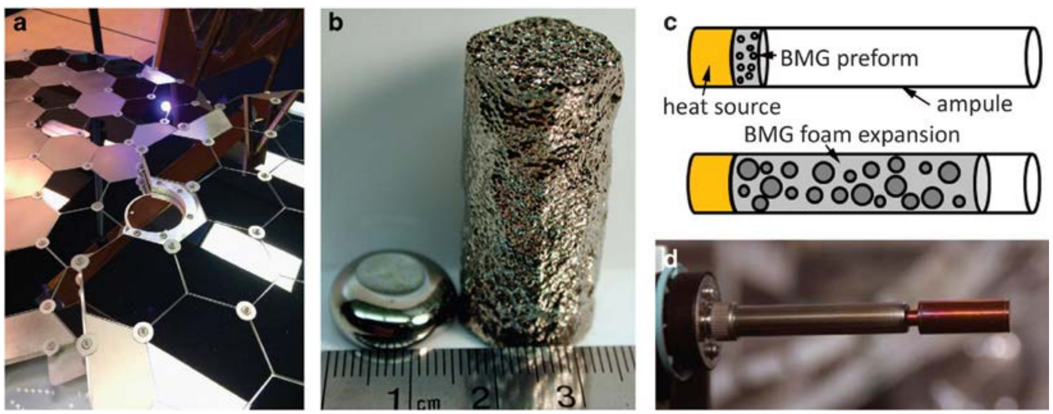
.AN glass optical fibers in space

Dennis S. Tucker and Michael SanSoucie, "Electrostatic Levitation of ZBLAN and Chalcogenide Glasses," Materials in Space Presentation, NASA Marshall Space Flight Center, slides 1–18.

11

IDA | Microgravity Metal Processing

- Foam production[1]
  - Crystalline metallic and bulk metallic glass (BMG) foams
  - Bubble sedimentation velocity impedes foam uniformity on Earth, especially for low-viscosity metals (e.g., Al)
  - Small launch package is expanded during microgravity processing
- Metallic glass production[2]
  - Enhanced by containerless processing and low-impurity environment



*Metal f
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lications of metallic foams: heat exchangers, blast and impact prote
sound absorption, battery electrodes[2]

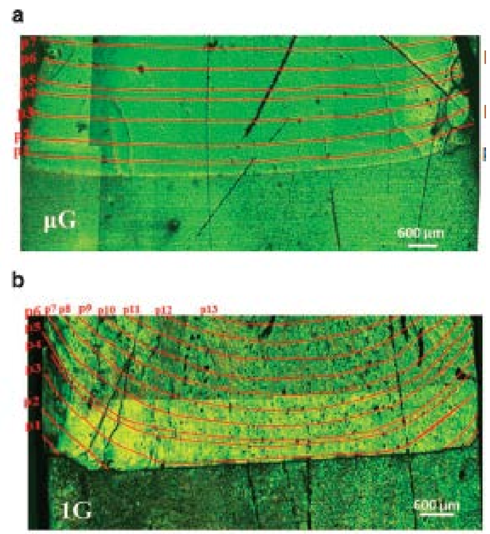
1 Douglas C. Hofmann and Scott N. Roberts, "Microgravity Metal Processing: From Undercooled Liquids to Bulk Metallic Glasses," *NPJ Microgravity* 1 (15003): 1–10.

2 Francisco García-Moreno, "Commercial Applications of Metal Foams: Their Properties and Production," *Materials* 9 (85): 1–27.

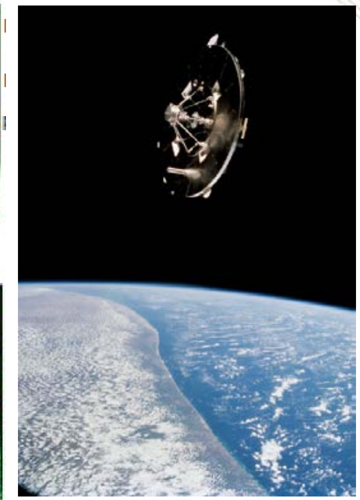
12

IDA | Microgravity Electronic Materials Processing

- Integrated circuits benefit from extremely low defect density and highly uniform composition in supporting semiconductors
- Contactless semiconductor solidification in low-particle-density conditions enables these properties
- Film growth can also benefit from high-vacuum environments



Y. Inatomi et al., “Growth of InxGa1 − xSb Alloy Semiconductor at the International Space Station (ISS) and Comparison with Terrestrial Experiments,” *NPJ Microgravity* 1 (15001): 1–6.



Wake Shield Facility for epitaxial growth, NASA image STS069-732-048, 1995, https://archive.org/details/STS069-732-048

SiC wafers and epitaxial films have been prepared in microgravity

13

BIOLOGICAL RESEARCH

14

IDA | Protein Crystal Growth

- Protein crystallization gives insights into the structural properties and function of biochemical macromolecules.
- Can help determine conformational changes in protein's 3D structures in space.
- Achieved through X-ray crystallography methods
- Applications:
  - Biotechnology
  - Pharmaceuticals
  - Genomics
  - Analytical Chemistry

Experiments on NASA Space Shuttle in microgravity crystal growth showed promising results for this methodology.

NASA is working to improve methods for reliability and cost-effectiveness of procedures used to crystalize proteins.

C. W. Carruthers et al., "A Microfluidic, High Thoroughput Protein Crystal Growth Method for Microgravity," *PLOS ONE* 8 (11): 1–12.

15

Further information from Carruthers et al., "A Microfluidic":

> One possibility is to use microgravity to increase the yield of quality crystals. As a crystal forms on Earth it depletes the surrounding solution of protein creating areas of lower density. Because of this, buoyancy driven convection results in the growing crystal rising and falling in crystallographic solution, inducing uneven growth rates.

Terrestrial Challenges in Crystallization

- **Buoyant convection**: many structural models fail because there is a lack of "diffraction quality crystals."
- **Sedimentation**: can cause distortions in the crystal.[1]
- **Nucleation**: gravitational forces at the molecular scale are comparable in magnitude to the intermolecular forces.
  - Microgravity also reduces a phenomenon called secondary nucleation.[2]

1 Carruthers et al., "A Microfluidic, High Thoroughput Protein Crystal Growth Method for Microgravity."
2 Edward H. Snell and John R. Helliwell, "Macromolecular Crystallization in Microgravity." *Reports on Progress in Physics* 68:799–853.

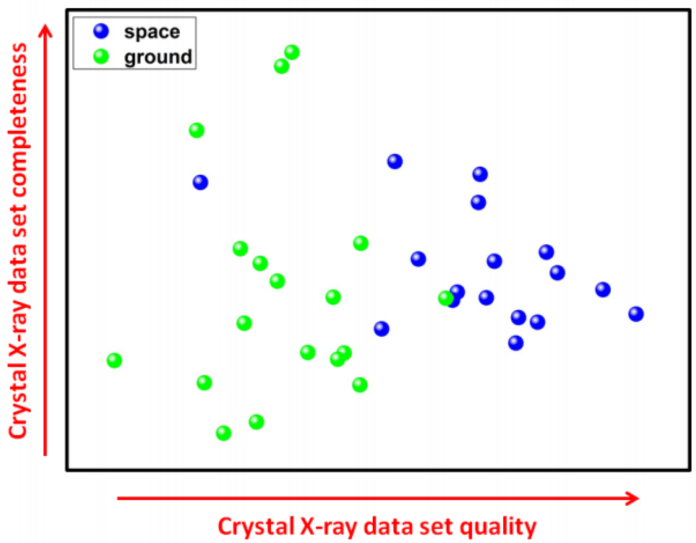
16

Further information from the Carruthers et al., “A Microfluidic” (first two bullets) and Snell and Helliwell, “Macromolelecular” (third bullet):

- Sedimentation: “As a crystal becomes larger, its increasing mass causes it to settle against a drops liquid/air interface or growth chamber wall. This orientation can prevent consistent three dimensional growth…”
- “Together, these effects create a highly dynamic environment that can cause imperfection in a crystal lattice.”
- “Secondary nucleation is thought to be caused by the removal of partially solvated clusters from near the surface of the crystal (the absorbed layer) by this flow (Larson 1991). Reduced buoyancy-driven flows in microgravity reduce this effect.”

Protein Crystal Growth in Microgravity

- There are potentially some Earth-based alternatives.
- It is argued that small-molecule crystals (reduction in the volume of crystallization) can also mimic the effects of microgravity.[1]
- Microgravity effects are dependent on the impurities and the protein itself – case sensitive.[2]
  - It is difficult to predict the impurities in a protein solutions, so we can't always determine if microgravity benefits.



Statistical quality analysis of 35 X-ray data sets of space and ground grown ferritin crystals (Tsukamoto et al. "Do We Need Microgravity?")

1 David Hosfield et al., "A Fully Integrated Protein Crystallization Platform for Small-molecule Drug Discovery," *Journal of Structural Biology* 142: 207–17.
2 K. Tsukamoto et al., "Do We Need Microgravity to Improve the Diffraction Properties of Protein Crystals?" *International Journal of Microgravity Science Application* 34 (1): 1–6

17

Figure caption from Tsukamato et al., “Do We Need Microgravity?”:

> Statistical quality analysis of 35 X-ray data sets of space and ground grown ferritin crystals (17 PromISS-4 “space” crystals and 18 from the ground control) as reported in Ref.1. Sixty-three parameters commonly used as indicative of X-ray data quality were analyzed. This highly dimensional “quality parameter dataset” was reduced using a principal component analysis. The differences between the two groups can be attributed to the first principal component and reflect the superior quality of the space crystals.

IDA | **Tissue Engineering**

- Advantages of tissue engineering in microgravity:
  - Intracellular forces will be more prominent in the absence of gravity
    - Cells and particles (free floating in air or liquid) will eventually interact
  - Cells do not grow at a solid-liquid interface (i.e., no sedimentation) resulting in 3-D growth[1]
    - Assembly → 3-D growth → Matrix formation → Differentiation → Vascularization[2]
  - Cells thrive due to better diffusion of nutrients and O_2[3]
- Joint solicitation between ISS U.S. National Laboratory and NSF to fund tissue engineering projects (submission due 2/25 – 3/4/2019) https://nsf.gov/funding/pgm_summ.jsp?pims_id=505490

1 Neil R. Pellis, "Tissue Engineering in Microgravity," presentation narrative, NASA Johnson Space Center, accessed February 15, 2019, http://www.mainsgate.com/spacebio/Sptopics/bi_resource/TissueEngineering.doc.
2 Neil R. Pellis, "Microgravity Cell Biology," Presentation, NASA Johnson Space Center; slide 12, accessed February 15, 2019, https://www.nasa.gov/pdf/478073main_Day1_P03a_Pellis_Cell_Biology.pdf.
3 Abolfazl Barzegari and Amir Ata Saei, "An Update to Space Biomedical Research: Tissue Engineering In Microgravity Bioreactors," *BioImpacts* 2 (1): 23–32.
See also: CASIS, "ISS U.S. National Laboratory and NSF Announce Tissue Engineering and Mechanobiology in Microgravity Funding Opportunity," press release, SPACEREF, October 23, 2018, http://www.spaceref.com/news/viewpr.html?pid=53255.

18

CHEMICAL PROCESSING

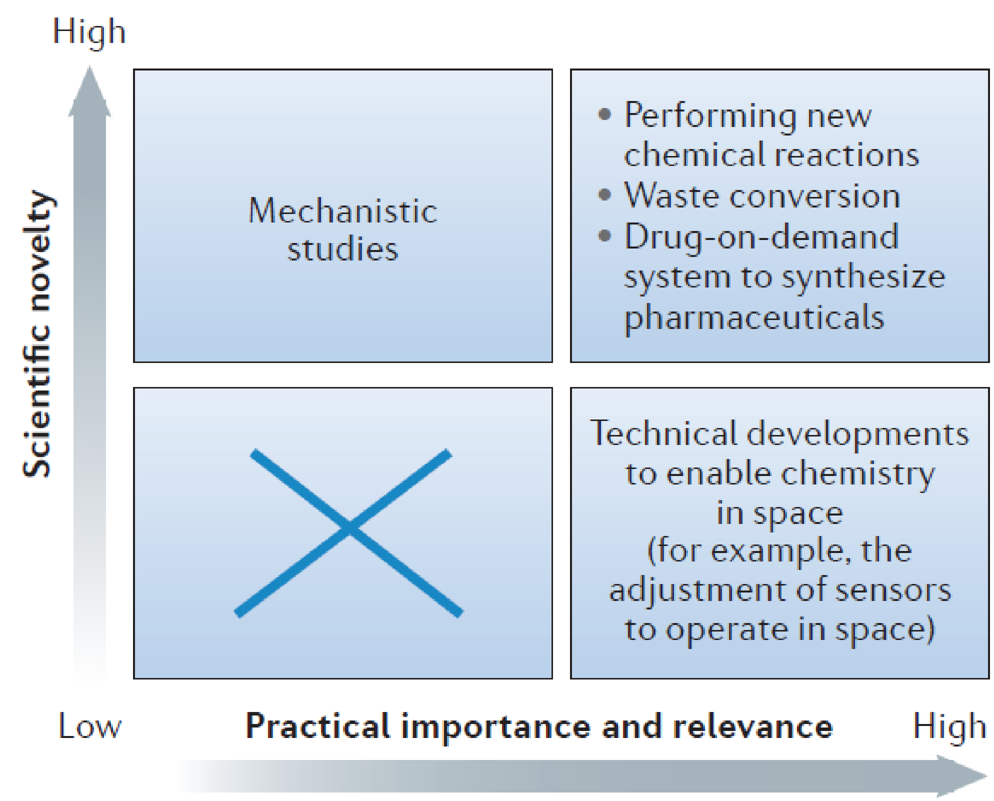
IDA | Chemical Synthesis in Space

- Limited research to date—batch chemical synthesis problematic in microgravity, flow chemistry might be a better alternative
- Why flow chemistry?
  - Better reproducibility compared to batch chemical syntheses: flow cell reactors have no free head space so chemicals are more confined
  - Small scale synthesis of hazardous chemicals
  - Combination of many reaction and purification steps → complex molecules synthesized in a single continuous stream
  - Automated: feasible to operate and monitor equipment remotely

Richard Jones, Ferenc Darvas, and Csaba Janáky, "New Space for Chemical Discoveries," *Nature Reviews* 1 (0055): 1–3.

20

IDA | Prioritizing Possible New Chemistry Projects



Source: Jones, Darvis, and Janaky, "New Space for Chemical Discoveries."

SpaceFlow Project
International consortium of 18 universities, 2 research institutes, and 4 industrial partners

Flow Chemistry Society
Schulstrasse 14, CH-8451 Kleinandelfingen, Switzerland

Flow Chemistry Society, "Chemistry Discovery in Space," accessed February 1, 2019, http://spaceflow.org/index.php.

21

Combustion Effects

- Combustion is typically driven by convection in gravity.
- In microgravity environments, there is random diffusion of oxygen and combustion is weaker.[1]
- Applications:
  - Controlled combustion and combustion stability
  - Study the electrical properties of exothermic combustion [2]
  - Soot control

NASA has been modeling combustion properties and conducting experiments in both space and drop towers via the ACME (Advanced Combustion via Microgravity Experiments) project.

1 Rachel Brazil, "Science in Microgravity," Chemistry World, December 17, 2018, accessed February 7, 2019, https://www.chemistryworld.com/features/science-in-microgravity/3009826.article.

2 A. J. Ata et al., "Effects of Direct Current Electric Field on the Blowoff Characteristics of Bluffbody Stabilized Conical Premixed Flames," Combustion Science and Technology 177 (7): 1291–1304.

22

Further information from Brazil, “Science in Microgravity”:

> In gravity, combustion is driven by convection – gravity pulls down colder denser air to the base of the flame and hot gases rise, feeding fresh oxygen into the reaction. But in microgravity this doesn’t happen; there is only random diffusion of oxygen. This changes the shape of the flame so it is no longer a teardrop. “In a microgravity environment where there is effectively no up or down, there is still the hot gases generated by combustion, but they simply expand in all directions. So a candle flame becomes spherical,” says Stocker.
>
> “Microgravity has a really strong effect on [soot production] because on Earth the hot gas is rising,” says Stocker. “[In] microgravity, flames will be absent of that buoyant acceleration and you get a longer time for the soot to grow within the flame, and you can get very sooty flames.” The project is still underway, but the hope is that they may learn how electric fields could stabilize fuel-lean flames and produce less polluting combustion for terrestrial use.

Soot Production in Space

- Soot production and characterization applications:
  - Fire safety (design of smoke-detecting equipment)
  - High efficiency, low emission combustors
- By having an environment with a lack of sedimentation, other particles that terrestrially can create asymmetrical flow around dropping particles for study (and therefore complicate results) do not exhibit such behavior in microgravity.[1]
- By getting combustion data in a microgravity environment, one can study combustion properties in space to get baseline data for modeling without the complicated physical interactions that happen in gravity.[2]

1. Melissa J. B. Rogers, Gregory L. Vogt, and Michael J. Wargo, *Microgravity: A Teacher's Guide with Activities in Science, Math, and Technology,* EG-1997-08-110-HQ, NASA, https://www.researchgate.net/publication/24322726_Microgravity_A_Teacher's_Guide_with_Activities_in_Science_Mathematics_and_Technology.
2. A. A. Stagni et al., "Numerical Investigation of Soot Formation from Microgravity Droplet Combustion Using Heterogeneous Chemistry," *Combustion and Flame* 189:393–406.

23

Further Info from Rogers, Vogt, and Wargo, *Mircogravity: A Teacher's Guide*:

> To date, combustion science researchers have demonstrated major differences in the structures of various types of flames burning under microgravity conditions and under 1 g conditions. In addition to the practical implications of these results in combustion efficiency, pollutant control, and flammability, these studies establish that better understanding of the individual processes involved in the overall combustion process can be obtained by comparing results from microgravity and Earth gravity tests. One clear example of the advantage of these comparison tests is in the area of fire safety. Most smoke detectors have been designed to detect soot particles in the air, but the sizes of soot particles produced in 1 g are different from those produced in microgravity environments. This means that smoke-detecting equipment must be redesigned for use on spacecraft to ensure the safety of equipment and crew.
>
> Comparisons of research in microgravity and in 1 g have also led to improvements in combustion technology on Earth that may reduce pollutants and improve fuel efficiency. Technological advances include a system that measures the composition of gas emissions from factory smoke stacks so that they can be monitored. In addition, a monitor for ammonia, which is one gas that poses dangers to air quality, is already being produced and is available for industrial use. Engineers have also designed a device that allows natural gas appliances to operate more efficiently while simultaneously reducing air pollution. This may be used in home furnaces, industrial processing furnaces, and water heaters in the future. Another new technology is the use of advanced optical diagnostics and lasers to better define the processes of soot formation so that soot-control strategies can be developed. Devices have also been developed to measure percentages of soot in exhausts from all types of engines and combustors, including those in automobiles and airplanes.

POLYMER PROCESSING

Polymer Processing in Microgravity

- Microgravity affects buoyancy-driven convection, but not surface-tension-driven (Marangoni) convection
  - Buoyancy-driven convection can occur as a result of temperature or concentration gradients
  - Microgravity allows decoupling of Marangoni and buoyancy-driven convection, which otherwise is only achieved by changing characteristic length scales
- Less convection means less shear in a fluid, which can potentially affect viscosity, crystallization, defect formation, and polymer dissolution
- Rayleigh number *Ra* describes these effects

$$Ra = \frac{\text{Timescale for thermal transport by diffusion}}{\text{Timescale for thermal transport by convection}} = \frac{g\alpha\Delta T d^3}{\kappa\nu}$$

gravity
thermal expansion
temperature gradient
height of container
thermal diffusivity
viscosity

With the exception of AM, polymer processing has not been a major focus area in microgravity.

James Patton Downey and John A. Pojma, "Polymer Processing in Microgravity: An Overview," *ACS Symposium Series*, 1–15, https://pubs.acs.org/doi/pdfplus/10.1021/bk-2001-0793.ch001.
See also Patton, "A Researcher's Guide to International Space Station."

25

Other notes from Downey and Pojma, “Polymer Processing”:

- Emulsion and dispersion polymerization can produce colloids with different stability when sedimentation is absent. Possibly improved uniformity. Space shuttle flights have produced gels for gas separation.

ADDITIVE MANUFACTURING

26

IDA | Additive Manufacturing (AM) in Space

- **Why AM in Space?**
  - *Scientific goals*: investigate impact of space environment (mainly microgravity) on materials and processes.
  - *Manufacturing goals*: advance knowledge of and capabilities for on-demand manufacturing and repair technologies for in-space uses to support sustainable human spaceflight missions.
- **Recent efforts:**
  - Polymer parts and test structures produced on earth and on ISS.
  - Additive Manufacturing Facility (AMF) is permanent facility on ISS for use by NASA, Made in Space, and others.
  - NASA NextSTEP FabLab program is developing multi-material fabrication capabilities for use on ISS; all efforts are currently using AM.

NASA Technical Reports Server/ NASA Additive Manufacturing Initiatives for Deep Space Human Exploration, 2018, https://ntrs.nasa.gov/search.jsp?R=20180006971&hterms=3D+Printing&qs=Ntx%3Dmode%2520matchallpartial%26Ntk%3DAll%26N%3D0%26No%3D50%26Ntt%3D3D%2520Printing;
NASA, "NASA Selects Three Companies to Develop 'FabLab' Prototypes," 2017, https://www.nasa.gov/press-release/nasa-selects-three-companies-to-develop-fablab-prototypes.

27

Additive Manufacturing (AM) in Space

- **Additive Manufacturing Facility (AMF)**
  - Current materials: ABS, HDPE, and ULTEM 9085 polymers.
  - Other materials (filament, most likely other polymer-based based on extruder temperature range) once approved for ISS operations.
  - An AMF user guide is available.
- **NextSTEP FabLab** (expecting early 2019 launch to ISS)
  - 3D BioFabrication Facility—materials Gel-based bioinks and thermoplastics.
  - Refabricator—integrated plastic recycling and AM equipment.
  - Multi-material AM System—textiles, future metallic and other materials.
- 3D printing of electronic components and traces (current Earth-based demonstration and development).

28

Interlog Corporation. http://interlogcorp.com/new-technology/ http://interlogcorp.com/2017/12/21/december-2017/.

Made in Space. "Additive Manufacturing Facility (AMF) User Guide," April 29, 2016. https://static1.squarespace.com/static/56d9b0528259b560ad38cde1/t/58d2dfda3a0411eedc691ad4/1490214884324/AMF+user+guide.pdf.

NASA Additive Manufacturing Initiatives for Deep Space Human Exploration. https://ntrs.nasa.gov/search.jsp?R=20180006971&hterms=3D+Printing&qs=Ntx%3Dmode%2520matchallpartial%26Ntk%3DAll%26N%3D0%26No%3D50%26Ntt%3D3D%2520Printing.

NASA. "Full Circle: NASA to Demonstrate Refabricator to Recycle, Reuse, Repeat," 2017. https://www.nasa.gov/mission_pages/centers/marshall/images/refabricator.html.

NASA. "Overview of MSFC Additive Electronics Capabilities." PowerPoint Presentation. https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20180004197.pdf.

"SpaceX Mission Will Bring 3D Bioprinter to ISS, Plans to 3D Print Cardiac Patchesfor Damaged Hearts." https://3dprintingindustry.com/news/spacex-mission-will-bring-3d-bioprinter-to-iss-plans-to-3d-print-cardiac-patches-for-damaged-hearts-135635/.

Techshot website (BioPrinter). https://techshot.com/defense/3d-tissue-printer/.

Additive Manufacturing (AM) in Space—Challenges

- **Challenges for terrestrial systems:**
  - Expanding the classes of materials used
  - Advancing understanding of relationships among materials, processing, and properties
  - Repeatedly producing a part having consistent geometry, properties, and performance
- **Understanding the effect of space environment on:**
  - AM processes (mainly microgravity)
  - The relationship among materials, processing, and properties
  - Feedstock materials (potential for long-term storage in space environment)
  - AM parts (long-term space-environment exposure)

29

See previous slide for references.

IDA | Useful Websites

- Materials in Space Workshop:
  - https://www.issnationallab.org/workshops/2018-materials-in-space/
- NASA SPINOFF Brochures (technology transfer):
  - https://spinoff.nasa.gov/resources.html
- SpaceFlow Project (consortium):
  - http://spaceflow.org/index.php/contact/

30

BACKUP SLIDES

31

General Effects of the Natural Space Environment

- **Vacuum:** Vacuum causes outgassing, molecules of which can deposit on/contaminate line-of-sight surfaces and cold surfaces; this behavior, in turn, affects optical properties, especially for sensitive optics. Vacuum effects can be evaluated in ground-test facilities.
- **Atomic oxygen (AO):** AO is measured by fluence (atoms/cm^2), and it varies with altitude. AO molecules are at about 5.2 eV energy at International Space Station (ISS) orbital velocity. AO is produced from short-wavelength UV radiation reacting with molecular oxygen in the upper atmosphere. AO oxidizes many metals and reacts with any material containing C, N, S, H bonds (e.g., polymers); if a polymer contains fluorine, its reactivity to AO increases with longer UV radiation exposure. Effects on materials vary depending on spacecraft orientation and altitude and solar activity. AO reactivity is measured as erosion yield (cm^3/atom). Ground testing can be done, but results are mixed—care is required.
- **UV radiation:** UV radiation darkens materials in the presence of contamination; it damages polymers by cross-linking (hardening) or chain scission (weakening). Under high-vacuum conditions, UV radiation can create oxygen vacancies in oxides, leading to significant color changes. Ground testing can be done, but care is required; factors to consider include type of lamp, intensity of lamp, control of sample temperature, and vacuum level.
- **Particulate/ionizing radiation:** Three sources are galactic cosmic rays, solar protons (or electrons), and trapped radiation belts (electrons in the manner of the South Atlantic Anomaly and Van Allen belts). Such radiation can cause cross-linking and chain scission in polymers and single-event upsets, bit errors, and latchups in avionics/electronics. Ground testing can be done, but an understanding of the dose-depth profile is needed.
- **Plasma:** Around the ISS are about equal amounts of positively charged oxygen ions and free electrons, but specific plasma levels vary with solar activity and spacecraft altitude: electrons can impact any spacecraft surface while ions can only impact leading edge surfaces, which can further lead to negative charge buildup, which can, in turn, lead to ion sputtering, arcing, parasitic currents in solar arrays, and re-attraction of contamination to spacecraft component surfaces. Plasma effects can be evaluated in ground testing facilities.
- **Temperature extremes and thermal cycling (CTE mismatch):** The amount of thermal cycling experienced by a material depends on the material's thermo-optical properties (absorptance and thermal emittance), its view of sun and Earth and other surfaces of spacecraft, and its time in sunlight and shade. Other important factors include thermal mass and influence of equipment or components that produce heat. CTE mismatch can cause degradation of protective coatings (16 thermal cycles a day for ISS) and can lead to cracking, peeling, spalling, and formation of pinholes in coatings so AO can attack the underlying material.
- **Micrometeoroid/orbital debris (MMOD):** MMOD size varies from microns to meters, with velocities averaging about 10 km/sec (to a maximum speed of about 60 km/sec) for surfaces facing the ram direction. Speed can vary with solar cycle. MMOD impacts can also cause spalling or shorting out of solar cells. Ground testing is typically carried out at lower velocities (<8 km/sec).

Most of these effects can be evaluated in ground-test facilities, but not in combination.

Source
See, for example: Miria M. Finckenor and Kim K. de Groh, "A Researcher's Guide to International Space Station Space Environmental Effects," NASA NP-2015-03-015-JSC, NASA ISS Program Science Office, 2015, https://www.nasa.gov/sites/default/files/files/NP-2015-03-015-JSC_Space_Environment-ISS-Mini-Book-2015-508.pdf.

Space “weather”—in the form of variable solar winds, solar flares, cosmic rays, etc.—can influence many of the above space environment features and their corresponding effects on the spacecraft.

Sources, e.g.:

- Air Command and Staff College. *AU-18 Space Primer*. Maxwell Air Force Base, AL: Air University Press, 2009. http://space.au.af.mil/au-18-2009/au-18-2009.pdf; see especially, Chapter 7 (pp. 115–36), “Space Environment.”
- Martinez, Isidoro. “Space Environment,” 1995–2019. http://webserver.dmt.upm.es/~isidoro/tc3/Space%20environment.pdf.

International Space Station Experiments by Category

Categories

Biology and Biotechnology

- Animal biology, invertebrates
- Animal biology, vertebrates
- Cellular biology
- Macromolecular crystal growth (114 experiments)
- Microbiology
- Microencapsulation (1 experiment)
- Plant biology
- Vaccine development

Earth and Space Sciences

- Astrobiology
- Astrophysics
- Earth remote sensing
- Heliophysics
- Near-Earth space environment

Educational and Cultural Activities

- Classroom versions of ISS experiments
- Commercial demonstrations (12 experiments, including Made In Space fiber optics demo)
- Cultural activities
- Educational competitions
- Educational demonstrations
- Engineering education
- Student-led investigations

Source:
ISS Experiments by Category as of 2/6/2019 (from https://www.nasa.gov/mission_pages/station/research/experiments_category, accessed 7 February 2019).

From the above link, one can get to lists of experiments by clicking on any one of the specific major categories: biology and biotechnology, earth and space science, educational activities, human research, physical sciences, and technology. Experiment titles are not especially helpful in determining what materials, for example, are being investigated. Additional information for each experiment can be obtained by clicking on the specific experiment.

International Space Station Experiments By Category

Human Research:

- Bone and muscle physiology
- Cardiovascular and respiratory systems
- Crew healthcare systems
- Cross-disciplinary
- Habitability and human factors
- Human behavior and performance
- Human microbiome
- Immune system
- Integrated physiology and nutrition
- Nervous and vestibular systems
- Radiation impacts on humans
- Vision

Physical Science:

- Combustion science
- Complex fluids (42 experiments)
- Fluid physics (42 experiments)
- Fundamental physics
- Materials science (72 experiments)

Source:
ISS Experiments by Category as of February 6, 2019 (from https://www.nasa.gov/mission_pages/station/research/experiments_category, accessed February7, 2019).

From the above link, one can get to lists of experiments by clicking on any one of the specific major categories: biology and biotechnology, earth and space science, educational activities, human research, physical sciences, and technology. Experiment titles are not especially helpful in determining what materials, for example, are being investigated. Additional information for each experiment can be obtained by clicking on the specific experiment.

International Space Station Experiments by Category

Technology Development and Demonstration:

- Air, water, and surface monitoring
- Avionics and software
- Characterizing experiment hardware
- Commercial demonstrations (same 12 experiments listed under Educational and Cultural Activities)
- Communication and navigation
- EVA systems
- Fire suppression and detection
- Food and clothing systems
- Imaging technology
- Life-support systems and habitation
- Microbial populations in spacecraft
- Microgravity environment measurement
- Power generation/distribution systems

Technology Development and Demonstration (cont.):

- Radiation measurements and shielding
- Repair and fabrication technologies (7 experiments including 3 related to additive manufacturing)
- Robotics
- Small satellite and control technologies
- Space structures
- Space materials, 25 experiments
- Spacecraft and orbital environments
- Thermal management systems

Source:
ISS Experiments by Category as of February 6, 2019 (from https://www.nasa.gov/mission_pages/station/research/experiments_category, accessed February7, 2019).

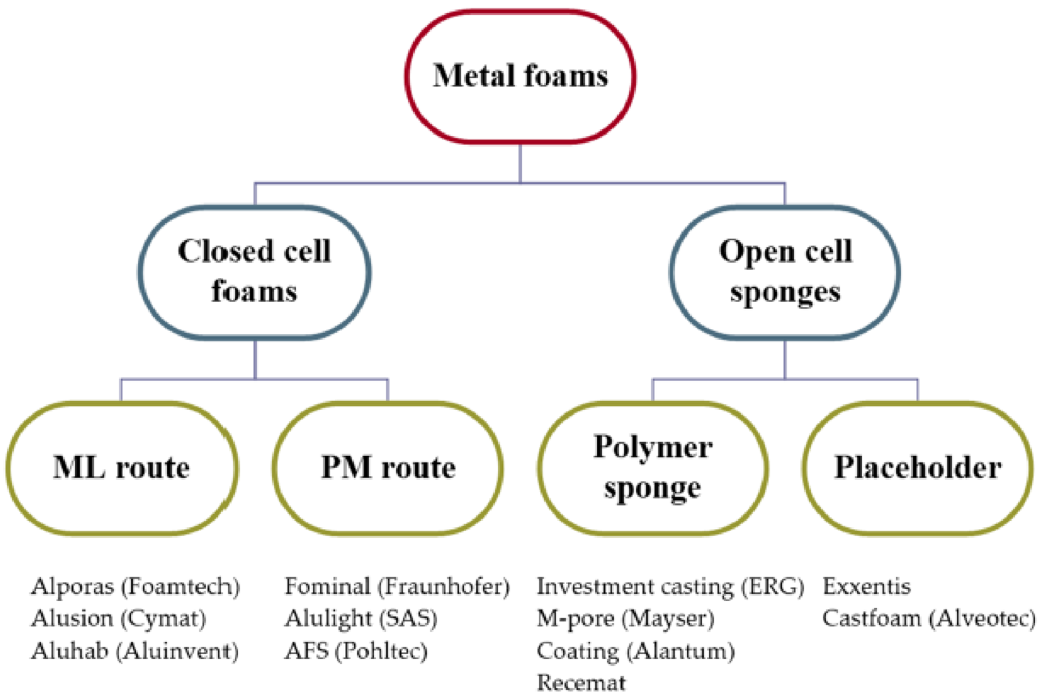
From the above link, one can get to lists of experiments by clicking on any one of the specific major categories: biology and biotechnology, earth and space science, educational activities, human research, physical sciences, and technology. Experiment titles are not especially helpful in determining what materials, for example, are being investigated. Additional information for each experiment can be obtained by clicking on the specific experiment.

Challenges of Microgravity

- Lack of buoyancy effects "renders highly efficient antifoam practically useless."[1]
  - Particles can't move from one interface to the next.

[1]P. Yazhgur et al., "How Antifoams Act: A Microgravity Study," *NPJ Microgravity* 1 (15004): 1–2.

Metal Foams: Terrestrial Manufacturing



Source: Francisco García-Moreno, "Commercial Applications of Metal Foams: Their Properties and Production," *Materials* 9 (85): 1–27.

Chemistry in Space—Follow-on Research

Jessica Swallow

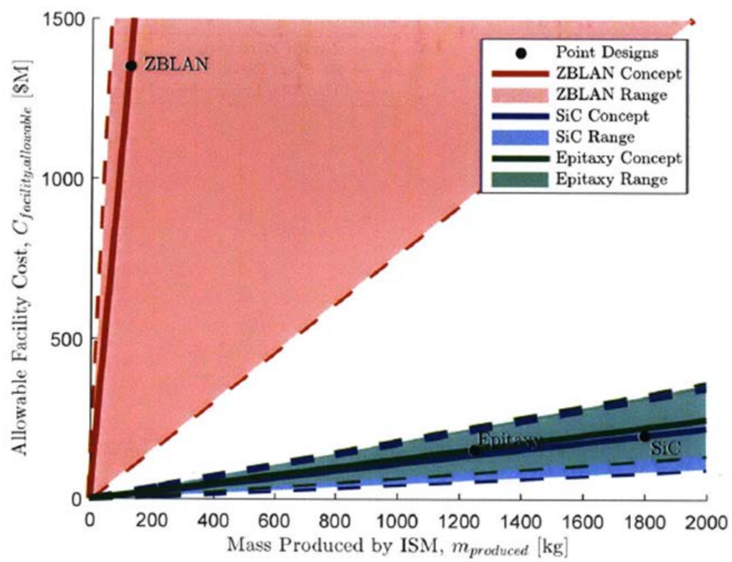
Martian and Lunar Temperature Cycles

- Martian temperature can swing by ~60 °C in a single Martian day
  - –89 to –31 °C at the Viking 1 lander site
- Lunar temperature can swing by ~300 °C in a single lunar day (which is equivalent to about 27 Earth days)
  - –178 to 117 °C at the moon equator
- Sources: NASA Fact Sheets
  - https://nssdc.gsfc.nasa.gov/planetary/factsheet/marsfact.html
  - https://nssdc.gsfc.nasa.gov/planetary/factsheet/moonfact.html
- Articles on temperature on Mars and the moon
  - https://www.space.com/16907-what-is-the-temperature-of-mars.html
  - https://www.space.com/18175-moon-temperature.html
  - https://www-k12.atmos.washington.edu/k12/resources/mars_data-information/temperature_overview.html

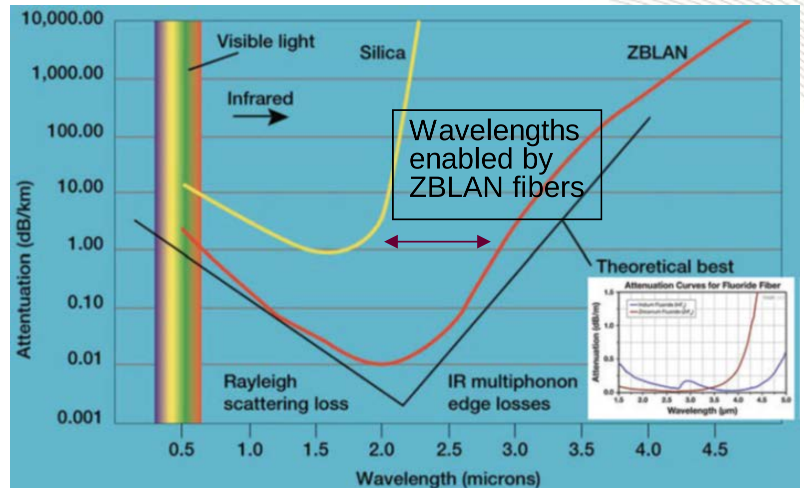
39

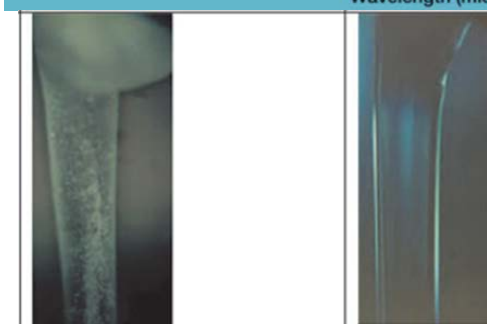
ZBLAN Fibers—Best Business Case to Date

ZBLAN optical fibers fabricated in microgravity can have substantially decreased attenuation compared with SiO_2 fibers and expand the range of wavelengths available.



Moraguez, “Technology Development Targets for Commercial In-Space Manufacturing.”





Note crystals in the preform melt.

Fiber pulling in 20 seconds of microgravity. No crystals are present.

Cozmuta and Rasky, “Exotic Optical Fibers and Glasses.”

IDA | Optical Fibers: Cost

- From Department of Transportation estimates of fiber optic installation costs:[1]
    - 2011 estimated installation cost, VA: $2.50–$3.30 / foot
    - 2017 estimated installation cost, CO: $10,000–$100,000 per mile depending on the fiber count
- “Exotic fiber” cost estimates:[2]
    - Low-quality ZBLAN fiber sells at $150/m today
    - High-end custom optical fibers sell for $300–$3000/m
    - Microgravity-manufactured ZBLAN should be comparable to or better than high-end custom fibers
    - 1 kg of ZBLAN feedstock = 3–7 km of fiber in 1 hour of microgravity processing “under optimized conditions”

This machine, which is slightly larger than a microwave, is intended for production of more than 100 m of optical fiber on the ISS

Figure from: https://www.space.com/39039-made-in-space-off-earth-manufacturing-test.html

[1] https://www.itscosts.its.dot.gov/its/benecost.nsf/DisplayRUCByUnitCostElementUnadjusted?ReadForm&UnitCostElement=Fiber+Optic+Cable+Installation+&Subsystem=Roadside+Telecommunications

[2] Cozmuta and Rasky, “Exotic Optical Fibers and Glasses.”

41

Optical Fibers: Applications

- Less attenuation translates to faster transmission speeds
- The mid-infrared range is available to ZBLAN and not to SiO_2
  - New capabilities in sensors, lasers, imaging, satellite tracking, spectroscopy, standoff explosive detection, direct infrared countermeasures, nondestructive evaluation, etc.
- ZBLAN can be used for "supercontinuum" sources because of its wide bandwidth

Table 1. Application Areas and Examples for Exotic Optical Fibers and Glasses

Application Area	Examples
Medical	Light guides, imaging tools, and lasers for surgery
Defense/government	IR countermeasures, stand-off detection of explosion hazards, eye-safe seekers for smart munitions, covert communications systems
Information technologies	Data transmission
Fiber lasers	Plastic and polymer processing, spectroscopy, noninvasive medical diagnosis, remote sensing
Telecommunications and networking	Connect users and servers in a variety of network settings and help increase the speed and accuracy of data transmission.
Industrial/ commercial	Imaging in hard-to-reach areas, (wiring where electromagnetic interference is an issue); sensory devices to make temperature, pressure, and other measurements; nondestructive testing

IR, infrared.

Cozmuta and Rasky, "Exotic Optical Fibers and Glasses."

42

ZBLAN Fiber Production

- Preforms are melted and drawn into a fiber
- Clean, dry environment required
- Terrestrial methods use drop towers that limit final fiber length
  - Manufacturing equipment in space can be much more compact
- Microgravity environment enables improved fiber *quality* (fewer defects), *length* (no need for drop tower), and *composition control* (clean environment and uniform composition)
  - Improved uniformity and lack of defects may also improve the strength and flexibility of the fibers
  - Some compositions of optical fibers that cannot be manufactured terrestrially may be accessible via in-space manufacturing

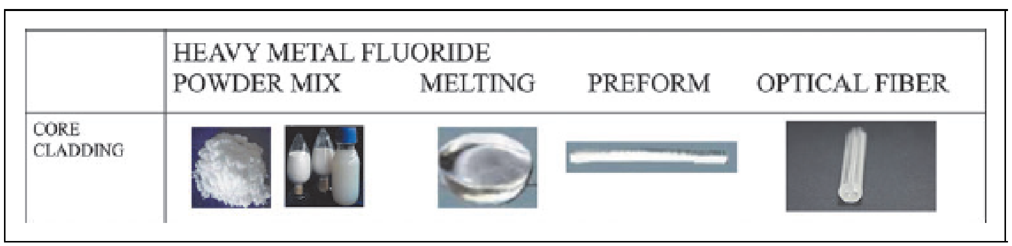


Fig. 8. Fiber optics production starts from a mix of heavy metal fluoride powders (*Table 2*) mixed together and subjected to melting (*Table 2*) into a preform. The preform is then pulled into an optical fiber. (Sources: Wikipedia, Photonics Society)

Cozmuta and Rasky, "Exotic Optical Fibers and Glasses."

43

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The Defense Advanced Research Projects Agency requested that the Institute for Defense Analyses (IDA) explore the challenges and opportunities for chemical and material processing in extraterrestrial environments such as the International Space Station (ISS), the moon, or Mars. Specifically, IDA investigated possible manufacturing methods in these environments, as well as differences in processing physics that might enable improved or novel processing methods. Some methods for preparing Martian and lunar building materials in situ have been developed. Facilities aboard the ISS include additive manufacturing systems that can prepare polymer parts on demand. Flow chemistry may be a valuable approach for molecular synthesis in microgravity. IDA also found that microgravity largely eliminates buoyancy-driven convection and enables the possibility for contactless processing. These effects, combined with low-impurity environments, produce more uniform microstructures with decreased defect densities for materials such as semiconductors, metallic foams, and glasses. Microgravity can also expand the working temperature ranges of some non-Newtonian fluids, which can be advantageous for glass formation. Microgravity also enables protein crystallization at larger scales, facilitates tissue assembly, and changes the processes of combustion and soot production. Microgravity manufacturing is limited by cost, volume, and the availability of starting materials and power sources.

15. SUBJECT TERMS

Chemistry; extraterrestrial manufacturing; material processing; microgravity

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