

Coarsening in Solid-Liquid Mixtures-2: A Materials Science Experiment for the ISS

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Abstract—A materials science experiment¹ has been developed and readied for operation aboard the International Space Station (ISS). Components of this experiment are on-board ISS and are awaiting the flight of science samples. The goal of the experiment is to understand the dynamics of Ostwald ripening, also known as coarsening, a process that occurs in nearly any two-phase mixture found in nature. Attempts to obtain experimental data in ground-based laboratories are hindered due to the presence of gravity, which introduces material transport modes other than that of the coarsening phenomenon. This introduces adjustable parameters in the formulation of theory.

The original Coarsening in Solid-Liquid Mixtures (CSLM) mission, which flew on the Space Shuttle in 1997, produced data from a coarsened eutectic alloy. Unfortunately, both the science matrix and the hardware, while nominally functional, did not account adequately for operations in microgravity. A significantly redesigned follow-on experiment, CSLM-2 has been developed to redress the inadequacies of the original experiment. This paper reviews the CSLM-2 project: its history, science goals, flight hardware implementation, and planned operations and analysis.

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1. ACRONYMS

CSLM-2	Coarsening in Solid-Liquid Mixtures-2
ECU	Electronics Control Unit
ESA	European Space Agency
g-LIMIT	Glovebox Integrated Microgravity Isolation Technology
GRC	Glenn Research Center
MELFI	Minus Eighty-degree Laboratory Freezer for ISS
MSFC	Marshall Space Flight Center
MSG	Microgravity Science Glovebox
MSL	Microgravity Science Laboratory
NASA	National Aeronautics and Space Administration
NRA	NASA Research Announcement
PSD	Particle Size Distribution
SPU	Sample Processing Unit
VES	Vacuum Exhaust System

2. INTRODUCTION

To understand coarsening dynamics, the CSLM-2 experiment has been designed to obtain data on the coarsening behavior of a particular eutectic alloy in microgravity. Coarsening, as realized for this experiment, is the growth of larger tin particles in a tin-rich lead-tin eutectic at the expense of smaller tin particles. By performing the experiment on-board ISS, coarsening data can be produced which can be compared directly to theory with no adjustable parameters, particularly convection and buoyancy, both effects of gravity. By eliminating these effects, a greater understanding of the factors controlling the morphology of solid-liquid mixtures during coarsening will be obtained. In addition, the long duration microgravity environment of ISS permits long processing times allowing the investigation of the steady-state regime of Ostwald ripening.

To perform the microgravity experiment, the NASA Glenn Research Center has, with ZIN Technology, Inc., developed a suite of flight hardware that will precisely process a series of eutectic samples, accelerating the coarsening process.

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The original CSLM experiment flew on the STS-83 and STS-94 Microgravity Science Laboratory (MSL-1) mission. These experiments demonstrated the importance of isothermal conditions across the samples. The CSLM-2 hardware, while based on the original hardware solution, has redesigned and added to certain elements and furnace subsystems so as to create extremely small gradients in the sample holder. Chief among these changes are the shape and type of heaters, the quench system, and the design of the chamber to hold a high quality vacuum.

To provide an adequate science matrix that will allow the university science team to compare data to theory, 48 samples of various volume fractions will be processed for one of six processing times. Four samples can be processed in a single furnace, thus twelve furnaces or Sample Processing Units (SPUs) have been readied for flight. In order to allow for adjustments between experimental runs and because of resource limitations on ISS, it is planned that the twelve SPUs will be sent to the ISS over three flights or stages, four SPUs per stage. To slow any further growth of the microstructure grains, the samples are refrigerated after processing. The samples continue in cold preservation until transferred to the next Shuttle orbiter for return to ground. Other resources necessary for proper processing of the samples are the Microgravity Science Glovebox (MSG), the Vacuum Exhaust System (VES), and the Glovebox Integrated Microgravity Isolation Technology (g-LIMIT). The applications of these resources are detailed below.

After return to ground, the science team will retrieve the samples and return them to Northwestern University. Once there, the samples will be refrigerated to -80°C to halt all modes of material transport. The samples will be sectioned and photographed. Computer imaging will be able to reconstruct the sample in a three-dimensional model. From the samples, the particle size distribution (PSD) rate constant will be determined as a function of the sample volume fraction, and agreement of the proposed theory with experimental measurements will be ascertained.

Science Background

Ostwald ripening, otherwise known as coarsening, is a natural phenomenon that occurs in the late stages of virtually all two-phase mixtures as they separate from one another [1]. Examples of this can be found in nature, such as in the mixtures of two solid-state crystals and in raindrops as they form from clouds. An example from commercial industry includes the degradation of mechanical properties of jet-turbine blades as they experience extremes in temperature.

Classical theory of the coarsening process is given by Lifshitz, and Slyosov[2] and Wagner[3] (LSW). This theory attempts to describe the collective behavior of an ensemble of coarsening spherical particles. The theory predicts that the cube of the average particle radius should grow linearly with time and that the particle size distribution

(PSD) should assume a unique time-independent form under the scaling of the average particle radius.

There is, however, widely reported disagreement between theory and experiment, and recent theories have dismissed some of the assumptions of the LSW theory. It has been found, for example, that the PSD rate constant is a function of the volume fraction. Further, no measured PSD agrees with those given by theory. Dr. Peter Voorhees, the Principal Investigator for CSLM-2, has predicted that scaled PSD's are broader and more symmetric than those given by LSW.

The standard method of investigating coarsening theory has been to heat a tin enriched lead-tin eutectic to its eutectic melting point and allow it to remain in a two-phase mixture for a period of time. During this heat soak period small tin particles dissolve and transport their mass by material diffusion due to a concentration gradient in the particle-matrix interface. Particles that are smaller than average size have a higher concentration at the interface than larger particles. Thus, large particles tend to grow at the expense of small particles, the average PSD increases, and the total number of particles decreases with time.

Measuring PSD's in a ground-based laboratory, however, is complicated by sedimentation of solid particles and buoyancy-driven convection of the liquid matrix. Free or adjustable parameters need to be employed to ensure agreement of theory with experimental measurements. However, by eliminating adjustable parameters, the implications of the theory should be thoroughly definitive and should, therefore, provide an unambiguous test of whether the theory is correct or not. As sedimentation and convection are both effects of gravity, performing coarsening experiments in the reduced gravity of space would eliminate the adjustable parameters and decidedly address the validity of the proposed theory.

Figure 1 shows the efficacy of performing this experiment in the microgravity environment of the ISS. Ground-based samples experience gravity gradients that cause the tin particles within the liquid matrix to float to the top of the sample. The microgravity environment of the ISS is ideal for negating gravity-based material transport modes, leaving diffusion as the only form of material transport.

Previous Work

Prof. Voorhees proposed an experiment in 1991 through the NASA Materials Science NRA that would obtain coarsening data that can be compared to theory without adjustable parameters. The Coarsening in Solid-Liquid Mixtures (CSLM) experiment was selected and developed for flight on-board the Space Shuttle. In April of 1997, CSLM flew on STS-83 in MSL-1, and again on STS-94 in MSL-1R in July 1997. This experiment was somewhat successful. A large amount of data was obtained, including the creation of approximately 25,000 micrographs.

Moreover, CSLM was the first unambiguous observation of transient Ostwald ripening, and showed excellent agreement between experiment and simulations of transient Ostwald ripening from theory. In addition, the experiment was very useful in showing that Pb-Sn solid-liquid mixtures, along with the microgravity environment, can be used to obtain unique data on the coarsening behavior of two-phase systems. Of note was the successful accumulation of data at the 10% volume fraction of solid at all but the longest processing times. Most theories for Ostwald ripening make predictions at the 10% volume fraction.

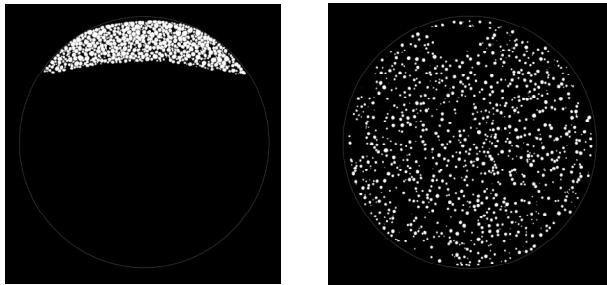


Figure 1 – Ground-based coarsening sample (left) compared to space-based sample from STS-83 (right)

However, the full objectives of the CSLM experiment were not achieved. The transient coarsening process in microgravity, without gravity driven convection, is a slower process than was originally anticipated, based upon ground experience with high volume fraction solid-growth based experiments. Therefore, the longest processing times intended to reach steady state were insufficient and, as a result, steady-state theories remain untested. Moreover, micrographs of some of the samples, particularly those of the longest processing times and those on the perimeter of the sample holder showed elongation of particles indicating material transport due to thermal gradients. The thermal gradients were due in large part to the design of the sample holder as well as heat loss due to air conduction within the furnace chamber. These gradients caused material transport via fluid convection currents and resulted in malformation of the sample microstructures. A significant fraction of the samples taken on CSLM, particularly the lowest volume fractions and longest experiment run times, were therefore not viable for comparison to theory.

Thus, much of the CSLM data was insufficient to determine accurately the manner in which the ripening kinetics, particle size distribution, and microstructure varies with the volume fraction of the coarsening phase. It was determined that a reflight was necessary to achieve the original objectives.

The purpose and significance of CSLM-2

In October 1998, an Investigation Continuation Review (ICR) was held at NASA Glenn Research Center where science and engineering panels were briefed on the purpose and feasibility of completing the science objectives of

CSLM.³ At that time, the convened science panel “agree[d] unanimously that the proposed experiment has potential significant and important impact on the materials science research community.” The engineering panel raised concerns regarding budget, schedule, and interfaces. Subsequent reviews were held to discuss technical and budgetary concerns, and the experiment was approved to proceed to flight in June 2000. In that time, thermal modeling was performed and an engineering unit constructed based on the results of the thermal modeling and analysis.

Keys to the new design were efforts to reduce the thermal gradients across the samples as compared to the furnace used in CSLM-1. This was accomplished by redesigning several components. The first component was the sample holder. Altered were the number of samples in the heater cartridge, the size and shape of the cartridge, the type of temperature detectors, and the heater unit itself. In addition to the sample holder, the water quench subsystem was redesigned to reduce heat radiation from the sample holder. And finally, the furnace chamber itself was designed to hold a vacuum to reduce or eliminate heat transfer by air conduction. These design changes are addressed in more detail in the following section.

In addition to redesigning the flight hardware, the science matrix was altered to allow for more coarsening experiments at longer times. These longer times are anticipated to assess the validity of steady-state coarsening theory.

3. FLIGHT HARDWARE IMPLEMENTATION

The flight hardware for the CSLM-2 experiment consists of two modules: the sample processing unit (SPU) module and the electronic control unit (ECU) module. The furnace chamber, heaters, and quench system were modified from the original design to improve performance and to allow for longer processing times that will extend to the steady state coarsening regime. CSLM-2 will process 48 samples in 12 furnace chambers over three flights. Figure 2 shows a photograph of CSLM-2 flight hardware on-board the ISS and within the MSG.

SPU

The SPU consists of a heating unit, quenching unit, sample holder, water chamber, solenoid isolation valve, humidity sensor, and pressurized air. The heater, sample holder, and humidity sensor are contained in a sealed furnace chamber. The quench water reservoir is in a second sealed chamber. The SPU heats material samples up to 185 °C in less than

³ The purpose of an ICR is threefold: 1) To show that the science requirements are complete, 2) To show that the hardware design is known well enough to show that the science requirements can be met, and 3) To show that the budget is adequate to accomplish the science objectives.

9.5 minutes, soaks for various periods of time at $185^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$, and then quenches the samples to room temperature in less than one minute. The SPU sample holder can house four lead-tin samples of 12 mm in diameter by 6 mm high, which are heated concurrently. A photograph of the prototype SPU sample holder is shown in Figure 3.



Figure 2 – CSLM-2 Flight Hardware showing SPU (left) and ECU (right) within the MSG Work Volume

The original CSLM-1 experiment found that the samples while processing were very sensitive to thermal gradients. One of the design changes made in CSLM-2 was to eliminate thermal loss due to air conduction. To do this, the furnace chamber was designed to hold a vacuum. If the vacuum within the furnace chamber is lost, air conduction becomes a factor raising the power (by a factor of 2 to 3) required to sustain the soak temperature. Gradients would form and the microstructures likely become unacceptable. This corresponds to observed theory in heat power required to maintain eutectic melting point temperature. Nitrile o-rings (2-240 N552-90) were employed to help seal the furnace chamber and hold a high quality vacuum.

Thermal conductivity of air drops precipitously at approximately 10^{-3} to 10^{-4} Torr. The science requirement is for the furnace chamber to hold at least a 200-millitorr vacuum for the length of the experiments. To better ensure the quality of the vacuum within the furnace chamber, the SPU to be run will be evacuated using the Vacuum Exhaust System (VES) for 24 hours prior to operations. This will provide an initial vacuum of 10^{-3} Torr or better.

Another method of creating isothermal conditions across the samples was to change the shape of the sample holder. The CSLM-1 sample holder was a square with rounded corners. By redesigning the holder to be a circular disk, temperatures could be controlled in a radially uniform manner by the heating unit.

The heating unit is composed of several sets of thermofoil heaters that are integrated into the sample holder assembly.

There are two heaters for the top and bottom of the aluminum sample holder disk and two semicircular ring heaters to provide radial thermal control. The thermofoil heaters are thin kapton heater sandwiches that provide uniform heating density via a 0.0001-inch separation between heating elements. The kapton sandwich is composed of layers in the order of kapton, adhesive, CuNi heating elements, adhesive, and kapton. The thermofoil heaters are space qualified and can operate up to 200°C .

The CSLM-1 sample holder held 9 samples each. The change in the shape of the disk would not permit that number of samples, however, it was deemed as an improvement to have fewer samples placed radially and away from the center of the holder for improved thermal control. This would require more processing units, however, than the previous experiment.

In another approach to decreasing thermal gradients, the furnace chamber quench nozzles were moved away from the sample holder clamping plate from a distance of 0.30 inches in the CSLM-1 design to a distance of 0.85 inches. This will reduce heat transfer to nozzles by radiation.

The final designed thermal gradient control uses platinum resistance-temperature detectors (RTDs) control the temperature within the heater. The RTDs are secured into milled holes within the sample holder using a silicone sealant. Because RTDs are a linear device, they are simple to calibrate, requiring only one temperature point (185°C , in this case). RTDs are reliable up to 600°C , well above the operating temperature of the heating unit. RTDs have good dynamic range: 100Ω at 0°C and 170Ω at 185°C . In addition, RTDs have long temperature stability over time.

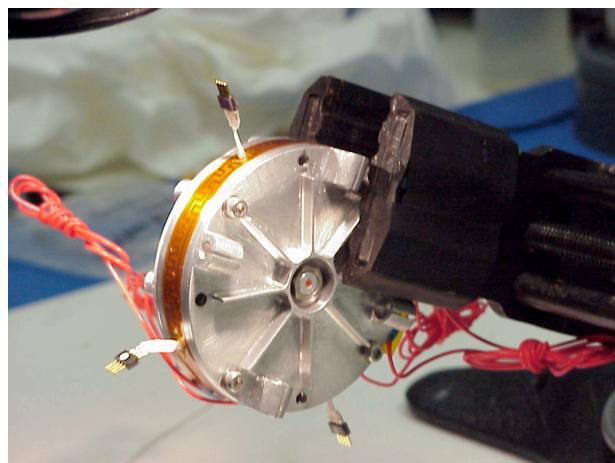


Figure 3 – Prototype CSLM-2 Sample Holder

During initial ground verification testing it was noted that sample microstructure was elongated, indicating that despite the extensive effort to create isothermal conditions across the samples that a small thermal gradient still existed. Analysis showed that heat transport occurred through the

face of the cylindrical samples and out the sides. To more evenly distribute the heat load, the sample slugs were shortened slightly and aluminum disks were placed over the top and bottom of the slugs within the heater disk. This method effectively spread the heat over the samples and reduced the thermal gradients to within the science requirement of 0.02 °C per centimeter.

ECU

The ECU consists of a hard-drive, a central processing unit, an RS-422 interface, an LCD display, an analog and digital I/O board, an RTD signal conditioning board, multi-purpose I/O board, a heater/solenoid driver, DC-DC power converters, and an EMI filter. The hard-drive board is a STD-80 bus board with an IDE interface and a 2.5-inch disk format. Flight firmware and experiment data are stored on the hard-drive. The central processing unit board is a STD-80 bus, 8 MHz, 8-bit single board computer. It uses an NEC V40 microprocessor that is 8088/8086-code compatible. The LCD display provides current experiment status. An RS-422 connection to the MSG will provide real-time (if available) connectivity and/or archival telemetry to ground.

The analog and digital I/O board has 16 analog input channels, 16 digital I/O lines, and two analog output channels. An analog output channel will provide linear control for the SPU heaters utilizing a PID control algorithm. Digital I/O channels will transmit SPU solenoid command and status, and will communicate SPU identification. The analog input channels will carry temperature data and experimental housekeeping and health status data.

The CSLM-1 hard-drive, central processing unit, and analog and digital I/O boards were successfully flown on STS-83 and STS-94. Similar items were installed in the CSLM-2 ECUs. Lifetime issues have been addressed. Testing and verification were accomplished to assure flight readiness.

The multi-purpose board provides RS232 to RS422 conversion, power switching for the heaters and humidity sensor, and thermistor signal conditioning for fire detection, if required.

The DC-DC converters, which are new to CSLM-2, will provide isolation from the MSG input power and will include a current-limit feature.

4. PLANNED ON-ORBIT OPERATIONS

Two ECUs have been created and are currently in orbit aboard the ISS. These units are identical; ECU #1 is the primary unit, ECU#2 serves as an on-orbit spare. These ECUs were transported in November 2002 to the ISS on ISS Assembly Flight 11A (STS-113) along with auxiliary

hardware: the harnesses, baseplates, cables, etc. Also, on Flight 11A were two SPUs. Originally four SPUs were scheduled for ascent, but two units were withdrawn when problems with the ARCTIC freezers became evident just prior to the launch of STS-113.

It was hoped that one of the two ARCTIC freezers could be made functional early in the 11A stage so that the CSLM-2 samples could be cold stowed until return to ground. Unfortunately, the ARCTIC freezers could not be repaired on orbit. Further, the Columbia tragedy has grounded the Shuttle fleet and thereby postponed ascent and descent of CSLM-2 samples. CSLM-2 requires the Space Shuttle for delivery to the Space Station as the Shuttle is the only carrier that will accommodate late access for the volume and launch loads requirements of the CSLM-2 hardware. Late access ensures that the samples are fresh and that their microstructure has not begun to coarsen prior to processing.

The life of the current on-board samples has since lapsed. However, in July and August of 2003, the two SPU currently on orbit were set up for processing in the MSG. The intent was to run the SPUs to obtain engineering verification data from the hardware and software. The CSLM-2 ground operations team was unable to fully test SPU#1 as readings from the SPU's humidity sensor indicated that a possible leak from the water reservoir might have occurred. According to operational procedures, the SPU was removed and stowed for analysis on the ground. SPU#6, however, was processed and returned excellent engineering data. Had this been an actual run with fresh science samples, all indications were that exceptional samples would have been obtained. The engineering team is confident that the software and hardware functioned extremely well, and that future runs should provide outstanding results.

Future shipments of CSLM-2 samples for science results are postponed until the Space Shuttle returns to service. This is so in part as the project now requires the MELFI unit to provide cold stowage for the CSLM-2 samples. The MELFI will be able to provide better quality cold stowage at approximately -56 °C or colder. The MELFI is currently scheduled for ascent on the second Shuttle mission after Return to Flight, on Flight ULF1.1.

When the Shuttle resumes operations, CSLM-2 intends to send at least 3 groups of four SPUs to ISS. By separating the SPU shipments into three flights, we allow the PI time to check the returned samples and possibly repeat certain elements of the CSLM-2 science matrix. Also certain pieces of hardware can be refurbished and reused, such as insulated stowage containers for returning samples, and possibly even used, but high performing, SPUs.

The order of operations follows. The first step is to de-stow the CSLM-2 hardware, and install the g-LIMIT (used to isolate ISS accelerations from the experiment). An ECU and SPU are then installed within the MSG working volume and initial connections to ISS are made. The SPU is

connected to the VES to evacuate the chamber for 24 hours. Then the vacuum line is removed so as to not introduce accelerations from ISS to the SPU. Final settings are made at the ECU and the power switch is thrown. A delay circuit permits a period of time to close up the MSG and push the working volume back into the MSG rack. The ECU then controls the experiment processing until quench, at which point the power is cut. A period of time is permitted to allow the SPU to come to ambient temperature. The sample chamber is removed from the SPU and installed in cold stowage. The remaining SPU is stowed and a new SPU is installed. This repeats until all SPUs are processed, then all hardware is stowed. Just prior to return to earth, the sample chamber is removed from cold stowage and inserted into an Insulated Stowage Container (ISC). This ISC will protect the crew from the cold aluminum chamber, will delay the chamber from returning to ambient temperature, and will absorb condensate.

5. POST-FLIGHT ANALYSIS PLANS

As soon as samples return from flight, they are to be stored at -80°C to prevent their microstructures from changing. Then, each sample is to be sectioned, photographed, and analyzed to get a particle size distribution and a radial distribution function, the primary data to be used to compare experiment with theory. The science team will do standard image analysis on montages large enough to encompass an entire cross section of a sample so as to obtain statistically relevant data. Using CSLM-1 data, the science team has improved sample analysis techniques. Many programs which can make the analysis much more effective have been developed by members in the CSLM research group. It will now take much less time than for CSLM-1 to take microscopic images, do a series of image-processes to transform raw images to binary images which have only black matrix and white Sn-rich particles, and then measure all particle sizes in an entire section using these programs.

In addition, the CSLM research group will do analyses on the three dimensional geometry of the microstructures. For example the connectivity, that is, how many particles are attached per particle, will be determined using the serial cross sectioning technique [4] that has been used previously to construct three-dimensional images. Connectivity affects mechanical properties and electrical conductivities of samples that have skeletal microstructure. This will help determine how connectivity varies to volume fractions and coarsening times. Computer programs to do these three-dimensional structure analyses have also been prepared by the CSLM Science Team.

Results from CSLM-2 will be published in scientific journals, presented in conferences, and posted on a publicly available website.

6. CONCLUSIONS

In 1997, the CSLM experiment provided important, albeit incomplete data, toward understanding the dynamics of Ostwald Ripening. A follow-on experiment was designed to amend the deficiencies in hardware design and procedures. The hardware and software for this experiment has been developed and verified and has been sent to the International Space Station where engineering validation has been performed. The experiment is awaiting the return to flight of the Space Shuttle fleet and delivery of the MELFI and g-LIMIT support facilities prior to flight of science samples for processing and return. It is anticipated that the data to be returned will provide unambiguous evidence of the validity of a new theory of coarsening.

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8. BIOGRAPHY



Mark Hickman is an aerospace engineer for the NASA Glenn Research Center and Project Manager for CSLM-2. He is also currently the Project Manager for the Capillary Flow Experiments (CFE), which began experimentation on the ISS in August 2004, and for the Liquid Management Experiment (LME).



Peter Voorhees is the Frank C. Engelhart Professor, MCC Materials Science and Engineering, Northwestern University, and he is the Principal Investigator for CSLM-2.



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