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FUNDAMENTAL MATERIALS RESEARCH
THERMOPHYSICAL AND THERMOCHEMICAL PROPERTIES
THE BASIS FOR ALL ADVANCED MATERIALS RESEARCH

Submitted by

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1 Introduction :

Long-term habitation in Space will necessitate transformational improvements in advanced manufacturing, thermal control, and life support processes[1][2][3]. Advanced manufacturing processes include additive manufacturing of metals and metallic alloys, soft matter, directed energy deposition of metals, and crystal production among others[4]. Thermal control processes include managing heat release from electronics, space-based nuclear reactors, batteries, and life support systems. These processes will be important, for example, on the ISS, in the habitation on the Lunar surface, and for all space programs that involve NASA's Science Mission Directorate (SMD) and Human Explorations[5].

With limited access to hardware and space modules deployed in orbit, or on the Lunar surface, there is very little or no margin for error in the design and development of systems. The time between iterations necessitates incorporation of simulations based on sound theoretical models or machine learning algorithms. As Space programs reach increasingly farther into the solar system, it becomes increasingly important to know a priori how materials and systems will behave. Knowledge of system behavior, especially in the extreme environments of space, is necessary to make the most of program budgets, minimize risk of loss of human life, and enable the next few generations of advancement. Proper design and control of these processes and systems requires accurate knowledge of system parameters and material thermophysical properties to allow for the development of simulations and ultimately the design and development of the actual systems.

The understanding of thermophysical and chemical properties are incorporated into process algorithms that allow for optimized operation and thus minimize the repeated use of precious energy resources developed for in-space habitats. The foundation of this understanding resides in the accurate determination of thermophysical properties. Key thermophysical properties are those that pertain to fluid processes such as density, viscosity, surface tension, and elasticity. Other significant thermophysical properties include thermal conductivity and mass transfer properties such as diffusion coefficients. Thermodynamic or thermochemical properties such as specific heats, heats of formation, heats of fusion, surface energy and chemical potential, characterize phase diagrams in phase transition and having accurate values for these properties is key to understanding the science of a material's structure, as well as thermal control related to phase-change processes. Additive manufacturing and other related processes provide new challenges for using and understanding non-equilibrium processes. The extreme temperatures and stress gradients introduced by these processes require the study of "far-from-equilibrium" events and the properties and metastable states of the materials they produce. In other examples where there is an accurate need of physical and chemical properties we include microgravity growth of large crystals of inorganic materials required for opto-electronics and organic or protein crystals for biological applications.

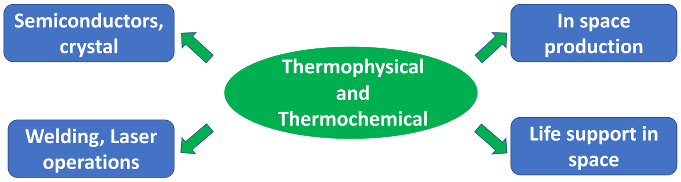

Figure 1: Connecting Space Applications to Property Measurements.

Although researchers are getting more experienced in using far-from-equilibrium processing, which also includes semiconductors and additive manufacturing, the underlying science is missing. “The need for a deeper understanding of nonequilibrium phenomena is nowhere greater than in materials science” [Frontiers Decadal 2019 [6]]. Accurate process algorithms are necessary for advanced manufacturing and life support systems such as thermal management systems and also for enabling operations such as space based selective laser melting and welding. These processes rely on deterministic models and, increasingly, on machine learning schemes. The foundation stone on which any simulation for predictive processing and control resides, is a reliable data bank of thermophysical and chemical properties. Figure 1 shows the satellite connections to the topic of this Decadal white paper. This document identifies the key areas of science research that are central to property measurement. These areas are divided into two major parts: a) Fluid and thermal property measurement and b) thermo-chemical property measurement.

2 Research on Fluid Dynamical and Thermal Properties: Key material properties connected to the fluid dynamics of materials processing are viscosity and surface tension. An example where they play a role can be seen from Figure 2, a depiction of Directed Energy Deposition (DED) where a metallic wire is melted via an EBeam on a moving platform, leading to layered manufacture of a desired product. During processing the molten pool is subject to disturbances that cause sustained ripples unless the pulling speed is optimally controlled. The DED process also involves solidification with latent heat release, during which undesirable morphological patterned structures at the solid liquid front may form and destroy the integrity of the product.

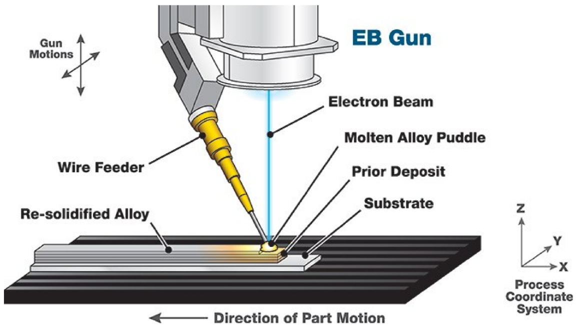

Figure 2: Directed Energy Deposition-from Scialy Inc

To control product quality, ripple formation must be avoided and to do this simulations of morphological structures, heat transfer dynamics, and fluid flow must take place. These simulations depend on input values of dimensionless groups such as the Weber number (ratio of kinetic to surface energy) and the Reynolds number (ratio of inertial force to viscous force) [7]. These groups depend on length scales and time scales governed by the the thermophysical properties. Accurate measurements of viscosity, surface tension between liquid and ambient, surface energy between liquid and solid as also thermal properties are therefore imperative to control the process. Doing this, in turn, will lead to a transformative way to process materials via accurate process algorithms and machine learning. We address, in brief, the science and technical challenges that must be addressed in obtaining accurate measurements of these fundamental properties.

The measurement of viscosity and surface tension for high temperature materials such as metals, alloys, molten oxides, and semiconductors rely on containerless drop levitation techniques performed on electrostatic or magnetic levitators such as those at NASA, JAXA or at ESA[8],[9],[10],[11][12]. These, in turn, restrict materials to small sizes on account of gravitational effects or to vacuum ambients so as to reduce the possibility of electric arcing during (electrostatic) levitation. In addition they do not easily allow the measurement of interfacial tension between two fluids, a property required for encapsulated processing such as crystal growth of compound semi-conductors. To alleviate these problems, creative methods that overcome these deficiencies are needed. Some possible ideas include microgravity testing using instruments such as the JAXA electrostatic furnace on KIBO where high speed cameras and larger sample holders need to be installed. Other possible means include the employment of fluid resonance via electrostatic or magnetic forcing to induce flow patterns that correlate to surface tension and viscosity.

Measurement of surface energy between solids and liquids is also key to determination of microstructure patterns in processed materials. Available data are based on guesses and extrapolation from liquid/gas measurements. Possible new avenues to explore are surface energy measurements via morphological pattern development in solidification or during electrodeposition and correlation of the patterns to surface energy via theoretical models.

In addition to key fluid properties, other important thermophysical properties encompass thermal and mass transport related properties i.e., thermal conductivity and diffusion coefficients. These are particularly of importance for high temperature materials in space enabling processes. Like viscosity these are *kinetic* properties, having to do with transport processes. Their measurement has to do with time constants that can be adjusted by measurement length scales. Long time constants afford accurate measurements on account of the long measurement times but also require longer duration microgravity platforms. Current measurement techniques for thermal conductivity measurements include the use of Fourier's law via coaxial cylinder temperature gradients or transient heated wire measurements. Challenges include the elimination or accounting of temperature gradient flows such as Marangoni flows if free surfaces are present and accounting for "g-jitter". Diffusion coefficients of species in liquid metals including atomic species such as oxygen in liquid metals are also of fundamental importance for earth and space metallurgy. Their values are known to be strongly affected by convection and vary by as much as two orders of magnitude. Microgravity experiments are crucial to eliminate solutal driven buoyancy flows and are important for both fundamental science and applications.

3 Research on Thermo-chemical Properties In addition to thermophysical data, thermochemical properties are an integral component for computational modeling for a variety NASA related interests, including but not limited to: (i) Advanced Manufacturing processes for space related manufacturing, (ii) Design of ultra-high temperature materials for next generation hypersonic and re-entry vehicles and (iii) Exoplanet formation modelling to better understand what materials could exist on a planet's surface. These data are not readily available for many material systems of interest (metallic and ceramic) at temperatures close to and above the melting point. When not experimentally available, property data is obtained from semi-empirical extrapolations derived from free energies and may significantly differ from true values [13]. The experimental extraction of thermochemical properties as a function of temperature and composition can lead to an improved materials characterization and design process relative to high-temperature and liquid metals. Levitation techniques such as Electrostatic Levitation (ESL) and/or Acoustic Aerodynamic Levitation (AAL) coupled with laser heating, provide the stability to maintain constant sample temperatures while in a levitated state. This allows the conversion of equilibrium vapor pressure data, generated through mass loss experiments, into thermochemical properties as a function of composition.

Sample area variation in time can be accurately measured for a given temperatures and since the sample evaporates isotropically, the effusion Knudsen method [14, 10] can be utilized assuming that the effective area of effusion is the surface of the sample at a given time. Therefore, vapor pressure can be found using the measured rate of elemental evaporation, the effective surface area, the sample temperature, and the molecular weight of the material. The relative vapor pressures of the constituent material can be used to determine chemical activities and free energies of multi-component systems as a function of temperature and composition. The impact of being able to accurately measure chemical activities at ultra-high temperatures cannot be understated. Currently, the highest temperature operating effusion Knudsen cell in the USA is operated at NASA Glenn. This facility can measure activities up to temperatures of 2000 C. The main limitation of this current technique is sample-container compatibility. Levitation methods are key to overcoming this fundamental roadblock, which could extend the technique up to temperatures of 4000 C. This would have a major impact on ultra-high temperature materials development for hypersonic flight and re-entry vehicles along with planetary sciences. A phenomenological and semi-empirical approach to computational thermodynamics, CALPHAD (CALculation of PHAse Diagrams), aims at coupling phase diagrams with thermochemistry by computational techniques. The well-established computational methods are based on the theory of deriving the thermodynamic functions of a system from experimental databases on a theoretical framework [15, 16]. The parametric thermodynamic models of Gibbs free energy functions are expressed as polynomials of temperature and chemical composition. The polynomial parameters are obtained by optimizing the available experimental data. The experimentally optimized coefficients model the Gibbs energy of a phase including descriptions of melting and other transformation temperatures, solubilities, and other thermodynamic properties including heat capacities, enthalpies of formation, and chemical potentials. The combination of theoretical and stochastic techniques results in potential deviations from physical processes, especially as multi-component materials are investigated. Additionally, CALPHAD does not currently provide a reliable methodology for the generation of undercooled properties. Experimental methods for processing reactive materials at high temperatures to extract these important data are not readily available. This calls for a container-less experimental technique such as levitation -greatly improved and facilitated in micro-gravity - to be employed to support the numerical modeling methods. Preliminary experimental results derived from ESL measurements at Marshall Space Flight Center (MSFC) have shown the potential to aid in the generation of Gibbs free energies that can be used to validate CALPHAD databases. Since the CALPHAD approach utilizes empirical as well as a phenomenological approach to extrapolating free energies, the empirical data generated can be employed to update the database where hard to measure properties were estimated. In this way, the binary and ternary phase diagram generation can be made more complete and reliable, such as the Extensible Self-optimizing Phase Equilibria Infrastructure (ESPEI) datasets which operates using PyCalphad, a package developed in collaboration with Penn State and NASA Jet Propulsion Laboratory (available online [17]). Improvement in CALPHAD databases, in turn, aids in new material design as the CALPHAD technique is often used as a first pass materials screening method. The modeling techniques and experimental analysis have the potential to be integrated to produce a more holistic generation of material property data, particularly at high temperatures.

Research issues of importance whose resolution will benefit from the use of microgravity platforms

- Measurement of fluid properties such as viscosity and surface tension for high temperature materials such as metals, oxides, alloys, and regolith must be obtained without the influence of gravity driven flows. Levitated drop techniques in microgravity would provide such data with nominal modifications of the current equipment on the ISS. Self consistent benchmarked methods that do not require different samples should also be tested on such platforms.

- Surface energy measurements between liquids and solids would benefit from low gravity experimentation as such measurements typically use correlation of morphological patterns with this key property and pattern development is strongly affected by gravitational fields even at small length scales. Apparatus such as potentiostats and low gradient furnaces will be needed on the ISS or other platforms. Experimentation on Parabolic flights or LEO platforms such as Blue Origin or also possible.

- Interfacial property measurement, again, for high temperature materials have not been done to date in microgravity and can be proposed using novel means where otherwise gravity fields would interfere in the measurement by becoming a dominant force field.

- Shear modulus data for soft materials benefit from acoustic levitation and microgravity. Such experiments have not been tested in low gravity platforms.

- Bulk and surface property measurements will be required for large crystal growth in microgravity for Inorganic and Organic (Proteins,say). These have applications in opto-electronics and pharmaceuticals.

- Vapor pressure measurement in containerless systems at high temperatures would benefit from experimentation in microgravity platforms to allow for uniform temperatures in liquid samples of spherical shape.

4 Summary Transformational advances and rapid deployment of advanced materials manufacturing and processing require predictive simulations based on sound theoretical models or machine learning algorithms. In all cases the availability of accurate and precise thermophysical and thermochemical properties is imperative. This topical paper identifies the critical need for experimental research programs that use microgravity platforms and ground-based facilities to address the needs of advanced manufacturing for space and earth benefit.

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