Investigating Thermophysical Properties Under Microgravity: A Review

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The advancement of metallic alloys is generally driven by alloy development, but furthermore requires the development of suitable production and processing routines. Almost all metallic products are formed through the solidification processing from the liquid phase. Although the solid-state is not influenced by gravitational effects, the processing of liquids is strongly impacted by earth’s gravity—this influences interface phenomena, momentum, heat, and mass transport and, consequently, the solidification events. Experiments on liquid metallic alloys in microgravity avoid these influences and therefore allow benchmark experiments. This allows, for example, to obtain reliable thermophysical properties, improve the understanding of nucleation, phase selection, crystal growth, and other basic features of the liquid phase and the liquid–solid transition. The basic methodology, as well as a number of recent results obtained in the long-duration microgravity environment on board the international space station, are presented and discussed.

1. Introduction

Materials science is strongly focused on investigations of the relationship between the structure of materials and their various physical and chemical properties. These fundamental and applied research activities are thus concerned with the synthesis, atomic structure, chemical element distribution, and the desired properties of materials and components. Originally, the focus of investigations was on the final products, i.e., the solid-state of materials and its microstructure, mechanical and thermal properties. In the last two decades, based on new experimental techniques, the importance of the liquid phase was recognized.\(^1\,\text{[1,2]}\)

Hence, it is important to improve the understanding of the liquid phase, which is still the least well understood state of matter.\(^2\) Liquids are known to lack long-range order, but in most (metallic) liquid alloys, a chemical short-range order can be found.\(^3\) This chemical short-range ordering has an important impact on the thermophysical properties. Processing the liquid phase is often one of the first forming steps in the processing route of materials, and almost all metallic products are produced through the solidification and casting from the liquid phase. A set of dimensionless numbers can be used to describe the transport phenomena in a fluid. These dimensionless numbers (Reynolds number, Pécelt number, Prandtl number, Schmidt number, Lewis number) are based on thermophysical properties of the liquid, such as its viscosity, mass density, thermal conductivity, and heat capacity. Solidification leaves its microstructural fingerprints in the final products, and therefore it is essential to understand a materials liquid state and to optimize the processing route to control the solidification pathway to the desired crystalline or glassy state.\(^4\,\text{[4,5]}\)

The development of new materials, processes, and products are the backbone of industries worldwide. Advanced simulation tools are used to support the optimization and development of fabrication processes. This approach must be based on an understanding of the physical phenomena involved, from alloy thermodynamics, heat and mass transfer, to solid–liquid interface dynamics, and microstructure formation including defects. Successful process simulations require not only the correct model for the relevant physical phenomena themselves but also accurate thermophysical property data as input parameters for modeling solidification.\(^3\) The involved length scales span from the macroscopic level (fluid flow, the spacing of dendrite arms, grain sizes) down to the atomic scale (crystalline defects, attachment of atoms). The inevitable presence of convection is a challenge for the description of the fluids’ physical properties, governed by the Navier–Stokes equation. The high temperatures involved for metallic materials lead to experimental difficulties, most importantly, the melt’s high chemical reactivity with its environment, which renders most container materials unsuitable.

Conventional methods can measure some of the necessary thermophysical data, especially for the solid phase. However, high-precision measurements on chemically reactive melts require nonconventional, container-less processing techniques together with noncontact measurement methods.

Elimination of the contact between melt and container walls allows control over surface nucleation and ensures samples that are free of surface contaminations.

To satisfy the condition of containerless processing, several levitation methods have been developed, such as aerodynamic...
levitation,\cite{6,7} electrostatic levitation,\cite{8,9} and electromagnetic levitation.\cite{5,10,11} Levitation in ground-based equipment are facing the challenge that the positioning force must overcome the gravitational force. For techniques such as aerodynamic and electrostatic levitation, this becomes increasingly challenging for samples with a higher density. Electromagnetic levitation is limited to electrically conducting samples, whereas its advantage over the electrostatic levitation is an intrinsic self-stabilization of the sample position.\cite{10} In addition, the possibility to use large samples of typically 6–8 mm diameter reduces the influence of evaporation losses on the results. In contrast, electrostatic levitation requires a fast feedback mechanism to stabilize the sample position.\cite{12} The high voltages applied in electrostatic levitation restrict in most cases the atmospheric conditions to vacuum, whereas for electromagnetic levitation also gas atmospheres, such as argon or helium are suitable.

The surface tension and density of levitated droplets might principally also be obtained using ground-based levitators. For measurements of viscosity, the requirement of laminar fluid flow and the absence of turbulent surface flows are a necessary condition. In ground-based electromagnetic levitation, the large positioning forces usually lead to turbulent flows, whereas inhomogeneous heating or cooling of the sample in electrostatic and aerodynamic levitation can lead to temperature gradients on the sample surface and hence to tangential surface flows.

Under reduced gravity, only small positioning forces are necessary, which allows the processing of perfectly spherical samples, that only contain laminar fluid flows in a large parameter range. A perfectly spherical sample shape is also important for the optical and inductive measurement of the sample density, as well as the inductive measurement of the samples electrical resistivity.

Higher strength-to-weight-ratio, longer lifetimes, better corrosion resistance, faster and more cost-efficient development, lower energy consumption, environmental compatibility, and recyclability are only some of the increasing demands on current engineering materials.

Continuous research and development efforts are needed to improve the current materials and manufacturing processes. Quantitative numerical simulations of solidification processes have become a common tool to simulate solidification processes in industrial fabrication. Such process simulations are a cost-efficient way to reduce the development time for optimized microstructures and high-quality products.\cite{13}

Figure 1 shows the simulation of a high-quality casting, illustrating the temperature distribution during casting and illustrates the complexity of the involved interplay of the occurring phenomena. Precise knowledge of the processed material’s thermophysical property data in the liquid and solid phase is needed to improve the accuracy of the model predictions.

The most important thermophysical properties needed for modeling and simulation of solidification processes can be divided into properties affecting heat transport and properties affecting mass transport. Using the international space station-electromagnetic levitator (ISS-EML) on board the international space station, the following surface- and volume-dependent thermophysical properties can be directly measured in the temperature range between 700 °C and 2200 °C as given in Table 1.

2. Scientific Challenges

For high-precision castings and, e.g., for the fast and highly nonequilibrium solidification processes of additive manufacturing, the control of material structure is of the highest importance in quality control and for the design of advanced materials with improved properties.

| Fluid flow (forced and natural) | Changing thermophysical properties |
|---------------------------------|-----------------------------------|
| Chemical reactions with mould and oxygen | Thermal contraction |
| Heat transfer | Nucleation |
| Diffusion and solute distribution | Movements of grains |
| | Latent heat evolution |
| | Solidification shrinkage |

Figure 1. Wide range of fundamental processes taking place during the casting of complex components. Here is shown the temperature distribution during the casting of several turbine blades (Image courtesy of David Furrer, Pratt&Witney).
have been developed for bulk metallic glasses.\cite{26} Thermoplastic forming can be used to surface pattern bulk metallic glasses with much higher precision than crystalline metallic materials.\cite{27} The use of new additive manufacturing methods has been demonstrated to allow the fabrication of metallic glass structures of dimensions much larger than the critical casting thickness.\cite{28}

3. Microgravity Platforms and Facilities

The absence of a container, as well as the absence of gravitationally driven convection are preconditions to perform precise measurements in the stable and undercooled liquid state.

3.1. Parabolic Flights

Parabolic flights can offer about 20 s of microgravity. To position and process samples on board a parabolic flight by means of electromagnetic levitation, the German Aerospace Center (Deutsches Zentrum für Luft- und Raumfahrt, DLR) has developed the successful TEMPUS facility (‘Tiegelfreies elektromagnetisches Prozessieren unter Schwerelosigkeit’, engl. ‘Containerless electromagnetic processing under weightlessness’).\cite{29}

For typical experiments in the liquid phase of metallic alloys, 20 s are a relatively short time. During this time, the sample is heated, molten, heated to the stable liquid phase, and cooled down until solidification. During the cooling phase, surface oscillations can be excited and recorded using high-speed cameras. This allows the analysis of surface tension and viscosity. As most metallic materials of interest melt in a temperature range between 1000 and 2000 °C, the sample needs to be processed in a gas atmosphere under convective cooling conditions. This does not allow for measurements in thermal equilibrium. However, parabolic flight experiments serve as important precursor experiments for long-duration microgravity experiments on board the ISS.

3.2. Long-Duration Microgravity Experiments on ISS

The electromagnetic processing facility ISS-EML is located in the European science module “Columbus” on board the ISS. Figure 2 shows an image of the ISS-EML facility.

The core of the device, developed and built by Airbus Defence and Space, is a coil system,\cite{30} which allows the independent positioning and heating of electrically conductive samples. The sample positioning is realized by a weak electromagnetic RF field, applied by the coil system, which, by creating eddy currents in the sample, leads to the generation of the relevant positioning forces onto the sample. As the necessary positioning forces are small, compared to electromagnetic levitation in 1 g, the sample does generally not heat up notably. Hence, the electromagnetic RF heating field is able to heat the sample independently from the positioning system. The samples typically have a diameter between 6 and 8 mm, and they reside inside an exchangeable sample chamber while they are not processed. Each sample chamber can contain 18 different samples. The ISS-EML exhibits a number of analytical tools, that enable the intended investigations. In the axial direction, a pyrometer is pointing toward the sample, allowing the precise measurement of the sample temperature. Two high-speed cameras (one in axial, one in the radial
direction) are installed to observe the sample oscillations. The axial camera is typically operated at a frame rate of 150 Hz, whereas the radial camera is typically operated at 200 or 400 Hz for the measurements of surface tension and viscosity. To track crystal nucleation and growth, the radial camera can also be operated at frame rates as high as 30 kHz.[31] A so-called sample coupling electronics (SCE) can be used to measure the impedance of the resonance circuit built by the coil and an external capacitor, to derive the specific electrical resistivity and radius of the sample.[32] For further technical information on the ISS-EML, the reader is referred to the literature.[30,31,33,34]

4. Alloy Selection

For different production methods, such as casting, spray-coating, injection molding, gas atomization, additive manufacturing, and for a wide range of new industrial products, solidification from the melt is of utmost importance. On this basis, several alloy classes and corresponding fields of applications are identified. A number of examples are: 1) Turbine blades for land-based power plants and for aircraft engines, able to sustain high temperatures and stress levels to enable improved efficiency and reduced environmental impact. 2) Biocompatible medical implants. 3) Low-emission energy-efficient engines for cars and aerospace. 4) Improved functional materials with enhanced performance (electronic transport, soft/hard magnetic materials, catalysts, hydrogen storage materials, thermoelectrics). 5) Bulk metallic glasses and metallic glass matrix composites, e.g., thin sheets for electronic/magnetic components, or for structural elements with ultimate strength to weight ratio. 6) New low-weight and high-strength materials for space exploration and future space vehicles.

The material classes that have been studied by the ThermoLab/ThermoProp project can be categorized as high-temperature materials (Ni-based superalloys, Zr-alloys, and titanium-aluminides), modern steels, and bulk metallic glasses. Advanced Ni-based superalloys are a class of complex metallic alloys with exceptionally high-temperature strength, creep resistance, and toughness typically used in turbine components of aircraft and for power generation in land-based turbines.[35,36] Their γ/γ′ microstructure is characterized by precipitates of an ordered cubic γ′ phase in the disordered cubic γ matrix phase.[37–40] Current alloy developments are focused on increased temperature for increased energy efficiency and exhaust reduction. The production of turbine parts is commonly a complex casting process, such as directional solidification casting.[41] By this route, different polycrystalline, as well as single-crystalline turbine parts, can be produced.[42] Commonly, also a heat treatment after the casting is normally used to reach the desired final microstructure.[47,49,43]

The geometries of turbine parts are becoming more and more complex, including internal thin-walled structures for advanced cooling techniques. The challenges arising from the demand for higher operating temperatures and more demanding geometries require simulations of the production process, including the simulation of liquid metal filling of mold cavities and defect formation.[44–47] Container-less methods, such as electromagnetic levitation, are used to supply benchmark data for advanced Ni-based superalloys in the liquid state.

Thermophysical properties of several complex advanced Ni-based superalloys have been measured in the solid phase using conventional equipment and in the liquid phase by microgravity-based measurement equipment.[48–51]

Titanium alloys such as the widely studied γ-Ti-Al alloys and α–β Ti-Alloys are important for high-temperature applications in the aerospace industry as well as for a large range of medical applications. A continuous development of the γ-Ti-Al alloys by the addition of refractory elements such as tungsten, rhenium, and zirconium has taken place, which improves the high-temperature properties of the material and increases the liquidus temperature even further (beyond 1700 °C). [52] Thermophysical property measurements by conventional container-based methods are not possible in this temperature range. New high-strength Ti-aluminide alloys have been explored recently, where solidification and phase selection,[53] grain refinement,[54] casting simulations,[55] and the measurements of thermophysical properties[52,56–58] have been in focus. This allows the production of advanced turbine blades for jet engines and other functional machinery parts reaching high strength levels at low density.

The industrially widely applied alloy Ti64 was also investigated in the ISS-EML due to its importance for biomedical implants, for automotive and for the aerospace industries.[59] Even though the alloy is known for long time, the high chemical reactivity in the liquid phase makes the precise determination of all its thermophysical properties reliant on container-less methods, such as
pulse heating,\textsuperscript{[60]} electrostatic,\textsuperscript{[61]} or electromagnetic levitation,\textsuperscript{[56]} where a number of thermophysical quantities can only be precisely measured under long-duration microgravity.\textsuperscript{[59]}

Modern steels are used in a large variety of applications. To develop and improve existing casting models, thermophysical property data needs to be collected. In several parabolic flight campaigns, the surface tension, viscosity, and density of a variety of steel grades were investigated,\textsuperscript{[49,62,63]} together with ground-based measurements for thermophysical properties in the solid-state.\textsuperscript{[63]} Stainless steels based on the Fe-Cr-Ni alloy system primarily in the solid-state.\textsuperscript{[63]} These steel alloys show primary metastable ferritic phases. These steel alloys also show primary metastable ferritic solidification, rapidly followed by a transformation to the stable austenite.\textsuperscript{[64–66]} This transformation has been shown to be significantly influenced by liquid convection.\textsuperscript{[66–68]} Maintaining microstructural control requires the development of casting models, which include these effects.

Similar steel alloys are also tested for additive manufacturing of complex shapes.\textsuperscript{[69–73]} The simulation of such production processes requires precise knowledge of thermophysical properties in the solid and liquid phase.

Bulk metallic glasses represent a new and promising development in materials science. In the beginning, glass-forming alloys containing metals, metalloids, and nonmetals were investigated.\textsuperscript{[18,19,74]} The next generation of metallic glasses was based on the early and late transition metals,\textsuperscript{[75]} followed by more complex alloys with low critical cooling rates, such as Vit1.\textsuperscript{[20]} In recent years, new, lightweight compositions have been developed.\textsuperscript{[21]} The development of metallic glass matrix composites\textsuperscript{[23,76]} opens the door to materials with higher toughness than other engineering production.

Also, alternative production methods for metallic glass structures were developed that can grant a higher degree of freedom to obtain large glassy structures than casting with rapid quenching. These new techniques, which are also already commercially used, are injection molding\textsuperscript{[26]} and 3D-printing.\textsuperscript{[28,77–79]} To enable proper process simulations and to develop further improved bulk metallic glasses, thermophysical properties in the solid and liquid phase are needed to gain a thorough understanding of the kinetic and thermodynamic properties affecting nucleation and phase formation.

### 5. Measurement Methods

The container- and contactless processing of liquid metallic materials requires suitable measurement methods to gather thermophysical property data. The following gives an overview over the common methods developed and applied for the measurement of thermophysical properties by electromagnetic levitation in microgravity.

#### 5.1. Specific Heat

The AC modulation technique, invented by Corbino 1910 for measurements in the solid-state,\textsuperscript{[80]} found its first application in low-temperature heat capacity measurements.\textsuperscript{[81,82]} In the AC calorimetry method, the heating power of the heater is modulated, leading to a modulated sample temperature.\textsuperscript{[83]} For this method, the time constants needed to reach thermal equilibrium can be quite small, which makes it feasible for noncontact calorimetry.\textsuperscript{[83]} In electromagnetic levitation processing, the sample heating is done inductively, by an electromagnetic heater field, that dissipates a power $P_{\text{Hi}}$ in the sample (Figure 3).

The best way to modulate the heating power is in the form

$$P(t) = P_{\text{Hi}} + \Delta P_{av} + \Delta P_{\text{mod}} \sin(\omega_{\text{mod}} t + \varphi_0)$$

which requires a coil current of the following form\textsuperscript{[84–86]}

$$I_{\text{coil}}(t) = \sqrt{\frac{P_{\text{Hi}}^2 + \Delta I_{\text{mod}}^2}{\tan^2(\omega_{\text{mod}} t + \varphi_0)}}$$

The temperature response for a sinusoidal power modulation as given in Equation (2) is\textsuperscript{[85]}

$$T(t) = T_0 + \Delta T_{av} \left[1 - \exp\left(-\frac{1}{\tau_{T,1}}\right)\right] + \Delta T_{\text{mod}} \sin(\omega_{\text{mod}} t + \varphi_1)$$

where the temperature response $\Delta T_{av} \left[1 - \exp\left(-\frac{1}{\tau_{T,1}}\right)\right]$ is the consequence of a stepwise rise of the average heating power $P_{\text{Hi}}$ by $\Delta P_{av}$ and the last term is the response to the sinusoidal power modulation. That way, the samples heat capacity can be calculated by

$$C_p = \frac{\Delta P_{\text{mod}}}{\omega_{\text{mod}} \Delta T_{\text{mod}}} \int f(\omega_{\text{mod}} t, \tau_{T,1}, \tau_{T,2})$$

where $f$ is a correction function that accounts for internal and external relaxation times.

The external relaxation time $\tau_{T,1}$ is given by

$$\tau_{T,1} = \frac{C_p \cdot \Delta T_{av}}{\Delta P_{av}}$$

where $C_p$ is the heat capacity of the sample. For radiative heat loss, the external relaxation time is given as

![Figure 3. Typical modulation calorimetry cycle, showing melting, overheating, and subsequent cooling with heater modulations at two different frequencies. The inset shows a zoom-in on the temperature response on one power step.](image-url)
\[
\tau_{T,1} = \frac{C_p}{4\pi k_{\text{tot}} \sigma_B} \tau^3
\]

(7)

where \(\varepsilon_{\text{tot}}\) is the total hemispherical emissivity and \(\sigma_B\) the Stefan-Boltzmann constant. The thermal relaxation time \(\tau_{T,2}\) characterizes a time constant of internal heat transport in the sample. It can be described as

\[
\tau_{T,2} = \frac{3C_p}{4\pi k_a}\alpha
\]

(8)

where \(\alpha\) is the effective thermal conductivity of the sample.[83,91]

For metallic samples, internal heat transport is typically much faster than external heat loss.[87] Hence, using proper parameters for sample sizes, modulation frequency, etc., the correction term for sample sizes, modulation frequency, etc., the correction term will be small.[83]

5.2. Inductive Measurement of Electrical Resistivity and Density

If an electrically conductive spherical sample is positioned inside the electromagnetic field of a circular coil that carries a periodically varying current, the impedance of the coil is changed. This is a consequence of the field induced by the eddy currents in the sample that is generated by the periodic current in the coil. In addition, this field also induces a current in the primary coil.[88,89] From the external circuit, the sample can be viewed as an additional complex impedance.[88,89] For the case of a coil geometry that leads to a homogeneous field around a spherical sample, the sample impedance \(Z_s\) can be expressed as[88,90]

\[
Z_s(\omega_{i1}, a, \rho) = c_i\omega_{i1}a^3 \left(\frac{1}{q} - \frac{1}{q^2} + i \left(\frac{1}{q} - \frac{2}{3}\right)\right)
\]

(9)

where

\[
q(\omega, a, \rho) = \frac{a}{\delta} = a \sqrt{\frac{\mu_0 \omega_{i1}}{2 \rho}}
\]

(10)

with the skin depth \(\delta = \sqrt{2\rho/(\mu_0 \omega_{i1})}\), where \(\mu_0\) is the magnetic vacuum permeability, \(a\) the sample radius, and \(\omega_{i1}\) denotes the frequency of the coil current oscillation. This expression is an approximation, which is true under the circumstances realized in the ISS-EML and TEMPUS facilities, where \(a/\delta \geq 3\).

Figure 4 shows a typical temperature–time diagram of an oscillating drop cycle performed on sample LM105, b) relative oscillation amplitude as a function of time, together with a fit of decay time constant.

5.3. Surface Tension and Viscosity

Surface tension and viscosity can be determined by the oscillating drop method.[91] In this method, surface oscillations are excited in the levitating droplet by an external electromagnetic force field, e.g., a short pulse by the heater field. The surface oscillation frequency is determined by the samples surface tension, whereas the damping is determined by the viscosity of the liquid.[92]

Using high-speed camera recordings, combined with appropriate algorithms,[93] the shape oscillations can be recorded and analyzed. The surface oscillation frequency \(\omega_2\) is usually obtained by Fourier transformation.

Figure 4a shows a typical temperature–time diagram of an oscillating drop cycle. Figure 4b shows the relative surface oscillation amplitude \(\delta/R_0\) obtained from the analysis of the high-speed camera. In addition, a time-domain fitting of the data is shown.

Rayleigh[94] derived for infinitely small amplitude oscillations \(\delta\) the surface tension \(\gamma\) of a droplet as
\[ \omega_{lm}^2 = l(l+2)/(l-1) \frac{4\pi \gamma}{3M} \]  
(12)

with the sample mass \( M \), and \( l \) denoting the oscillation mode. Lamb derived a relationship between damping time constant \( \tau_{lm} \) and viscosity \( \eta \) of a droplet as

\[ \frac{1}{\tau_{lm}} = (2l+1)(l-1) \frac{4\pi R_0 \eta}{3M} \]  
(13)

Under microgravity, the \( l = 2 \) mode does not split up, but only consists of one frequency. Furthermore, the geometrical similarity of the oscillation in the \( l = 2 \) mode and the elongation of the sample by the heater pulse leads predominantly to oscillations in the \( l = 2 \) mode only.

The Equation (12) and (13) have been derived under assumptions which are strictly not holding in practical applications. The exceptional conditions of the long-term microgravity platform ISS allowed the description of a nonlinear effect, that leads to the shift of the surface oscillation frequency for large oscillation amplitudes.\(^{[96]} \) Strong rotations of the sample droplet can also lead to a frequency shift. Also it was shown that this can be corrected if, e.g., the shape deformation is used to obtain the rotation frequency.\(^{[97]} \) The Equation (13) was derived for small viscosities and hence, for samples of large viscosity, the results deviate systematically from the real viscosity. Lohöfer gives an improved equation, which gives more accurate results for the case of large viscosities.\(^{[98]} \)

6. Recent Results

Several alloys were processed in their liquid phase, using the ISS-EML on board the ISS. The investigated temperature range was from around 700 to 2200 °C, only limited by the design constraints of the ISS-EML.

Three alloy compositions were in the focus of the investigations on Ni-based superalloys. These were LEK94, CMSX-10, and MC2. LEK94 is a rhenium-containing single-crystal superalloy with a low density between 8.1 and 8.3 g cm\(^{-3} \), developed by MTU Aero Engines, München, Germany.\(^{[99,100]} \) It was first used in the series production of the low-pressure part of the GP7000 turbine for the Airbus A380.\(^{[101]} \) The third-generation single-crystal alloy CMSX-10 was developed by Cannon Muskegon for the temperature range of 850–950 °C.\(^{[102,103]} \) It can be found, e.g., in the Rolls Royce engine TRENT 800.\(^{[104]} \) The second-generation alloy MC2, developed by ONERA in the late 1980s is rhenium-free alloy used in the high-pressure turbine blades of engines of Safran Helicopter Engines.\(^{[105]} \) Table 2 shows the chemical composition of the three Ni-based superalloys.

As precursor experiments, measurements on Ni-based superalloys (LEK94 and CMSX-10) have been performed using the TEMPUS facility on board a parabolic flight.\(^{[106]} \) Figure 5a shows a typical process cycle of CMSX-10 from a parabolic flight campaign, Figure 5b shows the processing of the same material on board the ISS. The longer available μg-time allowed the processing of the sample in the gas atmosphere of choice (He, Ar, or vacuum), rather than only in He, which allows the sample to cool slower. The strong noise on the temperature signal, typical for experiments in parabolic flights and apparent in Figure 5a, is caused by the relatively large sample movements caused by the lesser μg-quality and the challenge to obtain a stable sample positioning at the very beginning of the μg-phase of the parabola. The extended μg-time available on board the ISS improves the initial sample positioning capability and allows in general considerably longer and more precise experimental conditions. The longer available μg-times on board the ISS proved to increase the accuracy of the results due to the reduced noise level. In addition, it allows measurements under steady-state thermodynamic equilibrium conditions, for example, for the specific heat and total hemispherical emissivity, which is accessible within the short μg-times (≈10 s in the liquid state) of the parabolic flight.

For the three Ni-based superalloys LEK94, MC2, and CMSX-10, a large set of thermophysical properties were determined. This includes the surface tension, viscosity, heat capacity, total hemispherical emissivity, specific resistivity, and mass density as a function of temperature.\(^{[107]} \) The obtained surface tension and viscosity of the three samples LEK94, MC2, and CMSX-10 are shown in Figure 6. The obtained temperature-dependent surface tension of LEK94, MC2, and CMSX-10 in a temperature range of 1550–1850 K are shown in Figure 6a-c, whereas the viscosities are shown in Figure 6d-f. The obtained surface tension values support the description of Ni-based superalloys surface tension by the compound formation model, using the binary Ni-Al system as an approximation.\(^{[107,108]} \)

It is worth noting that the measurements do confirm that simple model-approaches, such as the Kopp–Neumann rule for the specific heat capacity are not accurate. Also the empirical rule for the viscosities by Mills et al.\(^{[109]} \) generally underestimated the obtained temperature-dependent viscosity (see Figure 6d–f).\(^{[106]} \) This highlights the necessity of precise measurements for model refinements and improvements in industrial process simulations.

Further investigations were concerned with the nonlinear effects of the oscillation of the liquid droplet. It was shown that for large oscillation amplitudes, a shift in the oscillation frequency occurs,\(^{[96]} \) but no measurable effect for the observed damping time constant was shown.\(^{[110]} \) This result is at variance with several modeling predictions from different authors based on

| Table 2. Nominal compositions of the three investigated Ni-based superalloys. |
|-----------------|-----------------|-----------------|
| Compositions in wt% | LEK94 | CMSX-10 | MC2 |
| Ni              | bal.   | bal.   | bal. |
| Al              | 7.1    | 5.7    | 5.0  |
| Cr              | 6.1    | 2.0    | 8.0  |
| Co              | 7.5    | 3.0    | 5.0  |
| Mo              | 2.3    | 0.4    | 2.2  |
| W               | 4.4    | 5.0    | 8.0  |
| Ti              | 1.0    | 0.2    | 1.5  |
| Re              | 2.9    | 6.0    | –    |
| Ta              | 2.8    | 8.0    | 6.0  |
| Hf              | 0.6    | 0.03   | –    |
| Nb              | –      | 0.1    | –    |
magnetohydrodynamic (MHD) modeling. Hence, further refinement and improvements in current MHD models are encouraged. The experiments performed on the Ni-based superalloys on board the ISS also supported the development and verification of an evaporation model that could predict compositional shifts, especially important for additive manufacturing with Ni-based superalloys.[111]

Two different titanium–aluminum alloys were investigated using the ISS-EML, one of them being the alloy with composition Ti-47.5Al-2Cr-2Nb in at%. It is a technical γ-titanium-aluminide alloy, qualified for use in the low-pressure stage of commercial jet engine turbines with a roughly 100 K increased liquidus temperature than most Ni-based superalloys. The complex solidification behavior of different alloys of this class was intensely investigated, e.g., in the European FP6 project IMPRESS.[52,56] Cast Ti-Al alloys typically require post-processing steps, such as hot-isostatic pressing, hot working and other heat treatments,[112,113] to achieve the desired microstructure and material properties. However, casting itself is challenging[113] and is usually guided by casting simulations.[65,114,115] The numerical simulations rely on precise thermophysical property data in the solid and especially in the liquid phase, which is typically not available due to the high melt reactivity of liquid titanium. Similar to all Ti-alloys, the titanium-aluminide is highly reactive in the

Figure 5. a) CMSX-10, typical cycle on a parabolic flight, ≈10 s in the liquid phase, b) a typical process of CMSX-10 in the ISS-EML on board the ISS, about 30 s. in the liquid phase.

Figure 6. Surface tension of a) LEK94, b) MC2, c) CMSX-10 and the viscosity of d) LEK94, e) MC2, f) CMSX-10. Dashed–dotted lines in (d), (e), (f) are model-curves after ref. [101]. Reproduced under the terms of the CC BY 4.0 license.[100] Copyright 2020, Wiley.
liquid phase. Several thermophysical property measurements on γ-Ti-Al alloys were obtained on parabolic flights, and as such, these alloys are predestined for processing with the ISS-EML for thermophysical property measurements in the liquid phase. The Ti-47.5Al-2Cr-2Nb alloy was processed successfully on board the ISS. On free cooling, the alloy repeatedly exhibited an undercooling of about 230 K. Figure 7 shows a temperature–time diagram of a measurement cycle for the AC calorimetry. In the shown cycle, the sample was kept in the undercooled liquid phase for about 8 min.

The titanium alloy Ti64 is an alloy widely applied in aerospace and biomedicine. Measurement of thermophysical properties using conventional container-based methods is fraught with error due to the high reactivity of liquid Ti. Ground-based experiments could contribute some surface tension data, whereas parabolic flight campaigns yielded some initial data for surface tension and viscosity. However, only with the longer μg times on board the ISS, benchmark measurements of the full set of thermophysical properties were possible.

For this sample, the complete set of thermophysical properties was obtained, including the electrical resistivity, surface tension, viscosity, mass density, specific heat, and also total hemispherical emissivity. The molar specific heat capacity and the total hemispherical emissivity of Ti64 is shown in Figure 8. The literature values for the mass density in the liquid phase given in a handbook differ by about 30% from the values obtained by us and by Li. The results for the thermal conductivity in the liquid phase, obtained by Boivineau et al. using pulse heating experiments, are in agreement with our values, but differ from the literature data obtained by thermal diffusivity measurements.

A generic stainless-steel alloy Fe-21Cr-19Ni was investigated in the framework of the international ThermoLab-ISS project. One aspect of the measurements has been the thermophysical properties of the alloy, such as its surface tension, viscosity, and specific heat capacity. In combination with the data that will be obtained on other Fe-Cr-Ni alloys in the future, the obtained data is used for a general description of the Fe-Cr-Ni system. Figure 9 shows the molar heat capacity of the investigated Fe-21Cr-19Ni alloy.

Furthermore, the sample was also part of a study to establish a model connecting undercooling, shear flow rate, and resulting phase selection. It was shown that the free energy driving the transformation from primary ferrite to austenite phase is associated with the undercooling, as well as with an additional contribution that is retained in the metastable solid. The retained free energy hence originate from the primary phase undercooling and the melt shear. This investigation was only possible, as under microgravity, the melt shear can be controlled in a wide range by the heater field and can be estimated by MHD simulations. The thermophysical properties, together with the improved understanding of phase selection and defect generation during solidification can greatly improve models for casting and welding of Fe-Cr-Ni stainless steels.

Two Zirconium samples were successfully processed for different calibration measurements, facility check-out procedures, and also for scientific purposes. The electrical resistivity of Zr, known from the literature at the α → β transformation, and the electrical resistivity measurements performed on the Zr samples were used to calibrate the electrical conductivity measurements. Further calibration measurements in the solid-state were performed for the optical determination of the sample density.
The comparison of cooling curves in vacuum and in argon was used to verify a new description of heat loss in gas, which adds the ability to determine the total hemispherical emissivity not only under vacuum conditions but also under Ar gas conditions.\[59\]

With regard to Zr-based alloys—e.g., Zr-based BMGs and industrial Zr-based alloys—the thermophysical properties of pure zirconium are also of general interest for comparison and modeling approaches. Figure 10a shows a typical melt cycle used to perform surface tension and viscosity measurements that demonstrates the accurate temperature control of the ISS-EML.

It can be seen that the sample is molten, overheated to about 2200 °C and subsequently cooled down. Figure 10b shows the obtained viscosity of the Zr sample containing about 1.2 ± 0.5 at% oxygen, together with viscosity data obtained by MD simulations of pure Zr. The comparison of the viscosity data with MD simulations of pure Zr revealed that the viscosity of liquid Zr is increased by the addition of oxygen.\[124\] Furthermore, the MD simulations showed that a crossover in the nearest neighbor coordination exists in the undercooled liquid state. A decrease in mobile atoms increases the number of high-coordinated clusters during cooling, which results in increased local stability and increases viscosity in liquid Zr.\[124\]

In general, a reduced glass-forming ability is found for a higher oxygen concentration in the melt of Zr-based metallic glass formers.\[125\] Only recently, Mizuno et al. showed by synchrotron X-ray diffraction, that a small amount of oxygen in binary Cu-Zr could improve the glass-forming ability, which was explainable by an increased viscosity due to oxygen.\[126\] Containerless benchmark measurements of the viscosity of Cu50Zr50 in the ISS-EML showed good agreement with MD simulations.\[97\]

Further simulations show that the temperature-dependent viscosity of Cu50Zr50 is related to the atomic packing evolution in the melt.\[127\] This shows that the study of thermophysical properties in combination with MD simulations and synchrotron diffraction measurements has the potential to provide deeper insights into nucleation, solidification, and glass formation processes.

Among the beryllium-free Zr-based metallic glass formers, the alloy Vit106a (Zr58.5–15.6Cu–12.8Ni–10.3Al–2.8Nb) has one of the best glass-forming abilities, with a critical casting thickness of more than 1.5 cm.\[128\] The heat capacity in the liquid phase plays an important role, e.g., for process simulations, but also for the calculation of thermodynamic functions.

Due to the relatively low liquidus temperature of Vit106a (Tliq = 832 °C), almost all AC calorimetry measurements were performed in the stable liquid phase in the ISS-EML. Gallino et al.\[129\] has measured the molar heat capacity of Vit106a in the crystalline, as well as in the glassy and undercooled liquid state by means of differential scanning calorimetry. Bendert et al.,\[140\] as well as Stolpe et al.\[131\] measured c_p/c_v of Vit106a in the stable and undercooled liquid phase by an electrostatic levitator. As in the ESL calorimetry technique, the total hemispherical emissivity and specific heat cannot be obtained separately, Stolpe et al.\[131\] chose c_tot = 0.22 to achieve a reasonable agreement with the DSC data in the undercooled liquid of ref. [129]. Within the measurement uncertainty, the proposed value for c_tot in ref. [131] is in agreement with our measured value for c_tot of 0.20 ± 0.02. Figure 11a shows the molar heat capacity of Vit106a measured in the stable liquid phase by the ISS-EML and by ESL\[131\] in the undercooled liquid, glassy, and crystalline phase by DSC.\[129\]
Furthermore, the viscosity of Vit106a was obtained in the stable liquid phase, as shown in Figure 11b. The data confirms the viscosity measurements and predictions from structural data in the high-temperature, stable liquid phase of Vit106a, shown in ref. [131].

Another Zr-based metallic glass, which was investigated using the ISS-EML, is the alloy LM105 (Zr52.5Cu17.9Ni14.6Al10Ti5). The alloy was produced and provided by Liquidmetal Technologies Inc., CA. The cooling rate ($\approx 8 \text{ K s}^{-1}$) of the 6.5 mm diameter sphere in He gas atmosphere was slightly lower than the reported critical cooling rate of $\approx 10 \text{ K s}^{-1}$.[132] Consequently, complete vitrification of the sample under microgravity was achieved in several subsequent cycles.[133] Figure 12 shows temperature–time profiles of cooling in vacuum, argon, and helium.

As compared with the cooling curves obtained in vacuum and argon, the cooling curve in He does not show any sign of a temperature increase in the continuous cooling, indicating the full glassy solidification. In addition to the surface tension, viscosity,
and specific heat capacity in the stable and undercooled liquid phase, also the electrical resistivity was measured during cooling.

Figure 13 shows the temperature–time diagrams and the electrical resistivity for the cooling in He, both for the case when the sample is vitrified (a),(b), as well as for the case when the sample crystallized (c),(d). The electrical resistivity of liquid LM105 is increasing with decreasing temperature, which is a feature often found for disordered metals.\[134\] The continuity of the electrical resistivity in Figure 13b also underpins that the sample vitrified, whereas the discontinuity between the undercooled liquid and the solid phase in Figure 13d, which appears at the same time when the recalescence occurs, is expected for the case of crystallization.

The vitrification of the LM105 sphere shows that the ISS-EML presents container-less, clean process conditions. MHD modeling allows to predict the fluid flow situation inside the levitated samples. In the case of LM105, the Reynolds number was estimated to have been below $Re = 15$ during the cooling to vitrification.\[133\] This also indicates, that future experiments could address also the questions to which extent the fluid flow conditions inside a sample influence the crystal nucleation or glass formation.

### 7. Conclusion

Precise thermophysical property data of a number of metallic alloys was obtained using the ISS-EML on board the ISS. The excellent long-duration microgravity conditions allowed measurements with a precision not possible on Earth. Thermophysical property data for high-temperature materials, modern steel materials, as well as for bulk metallic glasses, was gathered. The precise thermophysical property data obtained for the Ni-based superalloys, titanium-alloys, stainless steel, and Zr-based metallic glasses can be benchmark data for future process simulations. These data can be used to set up proper material models for advanced numerical simulations of industrial manufacturing processes, such as casting, welding, and additive manufacturing. The measurements performed on the Ni-based superalloys\[106\] supported also the development of a new evaporation model, to predict evaporation losses and composition shifts, which is important especially for additive manufacturing of such alloys.\[111\] A new nucleation model of stainless steel, describing the austenite to ferrite metastable transformation with convection was developed, which is applicable to numerical process simulations of steel casting on Earth, for example in continuous casting processes.\[66–68\] For metallic glasses, the measurement of viscosity and specific heat capacity in the liquid phase supports investigations on the kinetic and thermodynamic driving forces involved in glass formation. The successful vitrification of a Zr-based metallic glass proves the clean process conditions.

The availability of the long microgravity duration on board the ISS enables experiments with higher precision than on board...
parabolic flights. A number of experiments, such as the AC calorimetry, are only possible due to the long-duration microgravity conditions on board the ISS. The ISS-EML has shown to be a reliable tool to get better insights into the physics of stable and undercooled liquid metals. The combination of experimental benchmark results of thermophysical properties with simulations (e.g., MD simulations) and advanced synchrotron-based diffraction data in the future will increase the insight into the properties of stable and undercooled liquid metallic melts.

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Conflict of Interest

The authors declare no conflict of interest.

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