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Measurements of Thermophysical Properties of Liquid Metals by Noncontact Techniques[1]

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With the advent of containerless processing techniques such as electromagnetic levitation, it is now possible to study the properties of high-temperature liquid metals *in situ* by applying sophisticated noncontact diagnostics, such as pyrometry and high-speed videography. Thermophysical properties of interest are, e.g., specific heat, thermal conductivity, and viscosity. Applying containerless processing, it is also possible to undercool the melt because of the lack of container-induced nucleation sites. This gives access to a metastable region of the phase diagram. The knowledge of thermophysical data in this region is very important, because undercooling plays a major role in any solidification process. The degree of undercooling not only determines the growth velocity, but also is crucial in selecting the eventually obtained metastable solid phase. In this paper, some recent developments are surveyed relating to the noncontact measurements of emissivity, specific heat, electrical conductivity, density, surface tension, and viscosity, as well as a discussion of possible experiments in microgravity.

KEY WORDS: density; electrical conductivity; electromagnetic levitation; emissivity; liquid metals; microgravity; specific heat; surface tension; undercooling; viscosity.

1. INTRODUCTION

1.1. Objectives

The measurement of thermophysical properties at high temperatures is an important, but difficult, task. This is particularly true for high-temperature melts such as liquid metals. The importance lies not only in the technologi-

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cal relevance of having precise and reliable data for materials processing, but also in advancing our understanding of the fundamental physical phenomena that determine the thermophysical properties.

The difficulties can be avoided partly by using transient, subsecond techniques, where the liquid state is created for such a short period that the shape of the sample is preserved and collapsing is prevented. This method is applicable to temperatures slightly above the melting point and gives reliable data, e.g., for the emissivity and thermal expansion. Undercooling is not possible by this technique.

An alternative approach is to establish a liquid sample in a steady state for an extended period of time. This can be accomplished by electromagnetic levitation for electrically conducting melts, where the sample is suspended by high-frequency electromagnetic fields. Being a containerless technique, electromagnetic levitation assures minimum chemical contamination of the sample. Through the elimination of container induced nucleation, undercooling of the sample by several hundred degrees for virtually unlimited time becomes possible. This gives access to the metastable state of the undercooled melt and opens the door to an entire new field of research: thermodynamics of metastable states.

In addition to noncontact positioning and heating, also noncontact measurement techniques must be developed. In the following sections, we discuss how they can be used to measure thermophysical properties of liquid metals.

2. LEVITATION AND MICROGRAVITY

2.1. Levitation

The principle of levitation melting can be formulated following Okress et al. [1] as follows. An inhomogeneous, alternating electromagnetic field has two effects on a conducting, diamagnetic body; first, it induces eddy currents within the material, which, due to ohmic losses, eventually heat up the sample (inductive heating); and second, it exerts a force on the body pushing it toward regions of lower field strength (Lorentz force). The latter effect can be used to compensate the gravitational force acting on the body.

The fundamental parameter of levitation theory is

$$q = R_S/\delta \tag{1}$$

Here R_S is the radius of the sample, and δ is the skin depth, given by

$$\delta = \sqrt{\frac{2}{\omega\sigma\mu_0}} \tag{2}$$

where σ is the electrical conductivity of the sample, ω is the angular frequency of the electromagnetic field, and μ_0 is the magnetic permeability. For frequencies in the megahertz range, the skin depth is ≈ 0.1 mm for many metals, whereas usually $R_S \approx 3$–5 mm.

More explicitly, the time-averaged absorbed power by a sample of volume V is given by

$$P = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \int_V \frac{\vec{j}_{\text{ind}}^{\,2}}{\sigma} \, dV \, dt \tag{3}$$

where $\vec{j}_{\text{ind}}$ is the induced current density.

For a homogeneous magnetic field $\vec{B}$, an approximate analytical expression can be given for a spherical metal sample by

$$P = \frac{3\pi R_S}{\sigma \mu_0^2} H(q) \, B^2 \tag{4}$$

where

$$H(q) = q \frac{\sinh(2q) + \sin(2q)}{\cosh(2q) - \cos(2q)} - 1 \tag{5}$$

The time-averaged force acting on a spherical sample can be calculated from

$$\vec{F} = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \int_V \vec{j}_{\text{ind}} \times \vec{B} \, dV \, dt \tag{6}$$

For a weakly nonhomogeneous magnetic field, the following expression can be derived:

$$\vec{F} = -\frac{\pi R_S^3}{\mu_0} G(q) \, \nabla B^2 \tag{7}$$

where

$$G(q) = 1 - \frac{3}{2q} \frac{\sinh(2q) - \sin(2q)}{\cosh(2q) - \cos(2q)} \tag{8}$$

Equations (4) and (7) are the (approximate) working relations of electromagnetic levitation.

Forces acting on a liquid sample inevitably deform its shape. This is true for both the gravitational and the electromagnetic forces. Analytical calculations on the equilibrium shape have been performed by Cummings and Blackburn [2]; numerical results are published in Ref. 3.

2.2. Microgravity

On earth, strong magnetic fields are needed to compensate the 1-*g* gravitational force. The microgravity environment offers the unique possibility to minimize the magnetic positioning fields. Therefore, after melting, in the cooling phase, only negligible forces act on the sample. There is now practically no deformation of the sample, the spherical shape is maintained. This is important for measurements of, e.g., electrical conductivity and surface tension which assume a spherical sample.

Furthermore, there will be no turbulent flow in the melt, and no additional damping of oscillations due to magnetic fields occurs in the sample. This is essential for viscosity measurements.

Heat is induced in the sample only by the small positioning field, which allows for cooling by radiation only; hence processing in ultrahigh vacuum becomes possible, which is a prerequisite for the proposed specific heat measurements.

Finally, due to the strong electromagnetic fields needed on earth, terrestrial levitation experiments are essentially restricted to refractory metals and good conductors. In space, low-melting point materials, such as many glass-forming alloys can be undercooled. It may even be possible to levitate semiconductors such as Si and Ge.

3. THERMOPHYSICAL PROPERTIES

3.1. Emissivity

The spectral normal emissivity $\varepsilon(\lambda, T)$ is defined as

$$I_\varepsilon(\lambda, T) = \varepsilon(\lambda, T)\, I_b(\lambda, T) \tag{9}$$

where I_ε and I_b are the spectral radiance of the real and blackbody, respectively.

For solid metals, the accepted standard technique uses a heated tube with a small hole drilled into its wall [4]. The hole acts as a source for blackbody radiation and has the same temperature as the tube. Therefore, by comparing the radiation emitted from the tube's surface to that from the hole, one obtains the emissivity of the tube material.

Obviously, this technique cannot be applied to liquid specimens and alternative methods must be employed. A promising approach is to combine electromagnetic levitation with ellipsometry [5]. Levitation provides a liquid sample with a smooth, specularly reflecting surface, and ellipsometry can be used to determine the complex, spectral refractive index $\tilde{n}$,

$$\tilde{n} = n - ik \tag{10}$$

The spectral reflectivity $r(\lambda, T)$ is obtained from

$$r(\lambda, T) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{11}$$

With the help of Kirchhoff's law

$$r(\lambda, T) + \varepsilon(\lambda, T) = 1 \tag{12}$$

the spectral emissivity can finally be derived. Using this technique, Hansen et al. [5] have measured the emissivities of a number of liquid metals as functions of temperature and wavelength. As an example, their results on Co, Ag, Au, Ni, Pd, and Pt are shown in Fig. 1.

3.2. Specific Heat

The specific heat of liquid, even undercooled, metals can be determined using drop calorimetry. In this technique, the liquid sample is electromagnetically levitated. If the desired temperature is reached, the

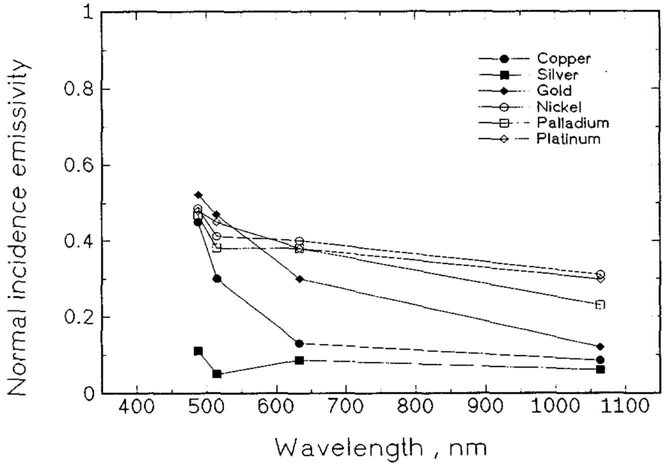

Fig. 1. Spectral emissivity of several liquid metals for temperatures 100–200 K above the melting point as a function of wavelength. After Ref. 5.

levitation fields are switched off, and the sample drops into a copper block. The temperature rise ΔT of the copper block is measured, and the enthalpy loss ΔH of the liquid sample is obtained:

$$\Delta H = C_p \Delta T \tag{13}$$

Here, C_p is the specific heat of the copper block. Once the enthalpy is obtained as a function of temperature, the specific heat c_p of the sample can be determined as

$$c_p = \frac{\partial H}{\partial T} \tag{14}$$

This method has been pioneered by Betz and Frohberg [6] to determine the enthalpy as well as the heat and entropy of fusion for some refractory metals. In addition, they have also measured the heat of mixing by alloying two liquid metals *in situ* during levitation and detecting the related change in temperature. More recently, Ohsaka et al. [7] have extended this work to measure the specific heat of undercooled liquids.

A very elegant way of determining the specific heat directly has been proposed by Fecht and Johnson [8]. They combine electromagnetic levitation with a modulation technique. The current through the heating coil is modulated sinusoidally, resulting in a modulated power absorption in the sample. This induces a temperature variation of the sample. The heat input into the sample can be written as

$$P_{\text{in}} = P_0 + P_\omega, \qquad P_\omega = P_{\omega 0} \cos^2(\omega t/2) \tag{15}$$

where P_0 is a constant term and P_ω is the oscillatory contribution.

Under steady-state conditions, the heat input equals the heat output:

$$P_{\text{in}} = P_{\text{out}} \tag{16}$$

In microgravity, electromagnetic levitation and undercooling are possible under vacuum conditions. In this case, heat loss is due entirely to radiation and is given by

$$P_{\text{out}} = P_{\text{rad}} \sim 4\pi R_S^2 \varepsilon T^4 \tag{17}$$

where R_S is the radius of the sample and ε is the total emissivity. If temperature and emissivity are known, this allows calibration of the power input to the sample with respect to the power input to the heating coil, the only quantity which can be measured directly.

The temperature of the sample will follow the oscillatory behavior of the heating power, subject to some internal and external relaxation mechanisms. Fecht and Johnson showed that the temperature variation is given by

$$(\Delta T)_\omega = \frac{P_{\omega 0}}{2\omega c_p}\left(1 + \left(\frac{1}{\omega \tau_1}\right)^2 + (\omega \tau_2)^2\right)^{-1/2} \tag{18}$$

Here τ_1 is an external relaxation time and τ_2 is the internal relaxation time. By choosing the appropriate modulation frequency, one can satisfy the following inequality:

$$\tau_2 \ll 1/\omega \ll \tau_1 \tag{19}$$

In this case, one obtains the specific heat from

$$c_p = \frac{P_{\omega 0}}{2\omega(\Delta T)_\omega} \tag{20}$$

3.3. Electrical Resistivity

The electrical conductivity can be measured contact-free by inductive methods. Here, the sample is placed inside a solenoid which itself is part of an oscillatory circuit. A change in the sample conductivity σ modifies the total impedance $Z(\sigma)$ of the oscillatory circuit, given by

$$Z(\sigma) = R(\sigma) + i\omega L(\sigma) \tag{21}$$

where R and L are the resistance and inductance of the solenoid, respectively.

On earth, this inductive method has already been applied to metallic melts enclosed in a cylindrical crucible [9–11]. This method can also be applied for measuring the electrical conductivity of levitated droplets by using the levitation coil simultaneously as the probing coil.

For a spherical sample of radius R_S inside a high-frequency levitation coil, the skin depth $\delta \ll R_S$. In this limit, the changes in resistance and inductance are given by [12]

$$\frac{\Delta R}{\omega L_0} \sim \frac{\delta}{2R_S} \tag{22}$$

$$\frac{\Delta L}{L_0} \sim \left(\frac{\delta}{2R_S} - \frac{1}{3}\right) \tag{23}$$

where L_0 is the inductance of the solenoid without the sample. The electrical conductivity σ enters through the skin depth; see Eq. (2).

The complex impedance can be determined by different methods, e.g., through the measurement of the phase shift between current and voltage:

$$\tan\varphi = \frac{\mathrm{Im}\{Z(\sigma)\}}{\mathrm{Re}\{Z(\sigma)\}}$$

For small changes, both sides can be expanded to yield

$$\frac{2\Delta\varphi}{\sin 2\varphi_0} = \frac{\Delta L}{L_0} - \frac{\omega L_0}{R_0}\frac{\Delta R}{\omega L_0} \tag{24}$$

Inserting Eqs. (22) and (23) in Eq. (24), a relation between the phase shift $\Delta\varphi$ and the skin depth, i.e., the conductivity, is established.

The use of electromagnetic levitation on earth for measuring the electrical conductivity of liquid metals is hindered by the fact that under 1-g the sample is not spherical. The relation $Z(\sigma)$ is known only for simple geometries such as a spherical shape. Therefore, this method seems to be restricted to a microgravity environment, where it will allow to measure electrical conductivities of liquid metals in a wide temperature range.

3.4. Density and Thermal Expansion

The first measurements of density and thermal expansion using electromagnetic levitation were made by Ward et al. [13, 14] in the sixties. Their experimental setup consisted of a levitation tube surrounded by the levitation coil and an optical system (prisms) for pyrometric temperature measurement and high-speed photography. From the photographs, they measured the radius of the drop. Assuming a spherical shape, the volume V could be determined. The sample was weighed before and after the levitation process, and thus the density ρ could be calculated from

$$\rho = M/V \tag{25}$$

Repeating the measurement at different temperatures, thermal expansion

$$\beta = \frac{1}{V}\frac{\partial V}{\partial T} \tag{26}$$

can also be obtained. The result for nickel is shown in Fig. 2.

3.5. Surface Tension

The surface tension of a liquid drop can be measured by exciting surface oscillations. The angular frequency ω of the oscillations is related to the surface tension γ.

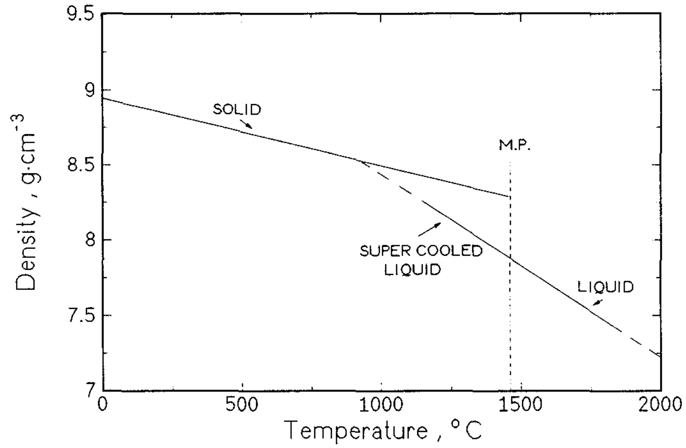

Fig. 2. Density of nickel as a function of temperature. After Ref. 14.

The radial distance between the center and the surface of an oscillating liquid sphere can be described by

$$R_n \sim R_S \cos(\omega_n t)\, P_n(\cos \vartheta) \tag{27}$$

where R_S is the radius of the undeformed sphere, n is a label for the different modes, and P_n denotes the Legendre polynomials.

The frequency ω_n is given by [15]

$$\omega_n^2 = \frac{4\pi}{3} n(n-1)(n+2) \frac{\gamma}{M} \tag{28}$$

where M is the mass of the sphere. Conventionally, the oscillations are detected as variations in the intensity of light falling onto a photodetector [16]. Using a video camera and subsequent digital image processing [17], the variations in the shape of the sample can be observed directly.

Unfortunately, Eq. (28) is valid for spherical samples only. On earth, levitated samples are always deformed and are, at best, axially symmetric. This complicates, however, the oscillation spectrum of the levitated drops. Instead of a single peak for each value of n, as in the case of spherical samples [see Eq. (28)], there are three to five peaks. This makes a quantitative evaluation of the oscillation spectra obtained on earth more difficult [2]. Recently, Sauerland et al. [17] have improved the evaluation procedure for aspherical drops by employing image processing. In principle, this new

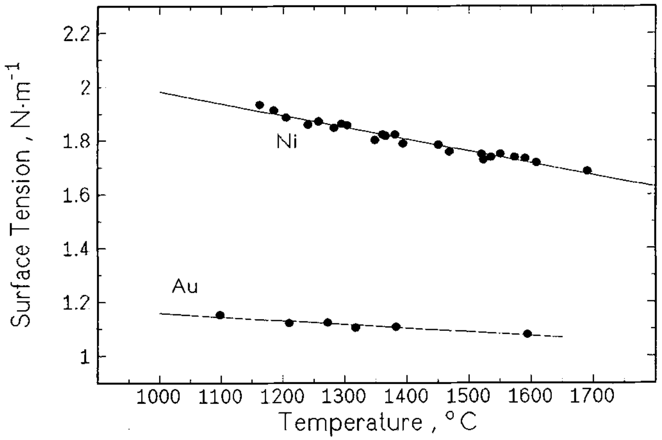

Fig. 3. Surface tension of nickel and gold as a function of temperature.

method yields surface tension values from frequency spectra of aspherical drops with the same precision as the conventional technique would yield for spherical drops. The results for gold and nickel are shown in Fig. 3.

3.6. Viscosity

Using the levitation technique, the viscosity can be measured in analogy with surface tension measurements and the undercooled regime becomes accessible.

Viscosity introduces damping into the oscillation spectrum of a sphere. Taking damping into account, we can rewrite Eq. (27);

$$R_n \sim R_S \cos(\omega_n t)\, e^{\ t/\tau_n} P_n(\cos \vartheta) \tag{29}$$

where τ_n is the damping of the nth mode. For weak damping, it is given by [18]

$$1/\tau_n = \frac{4\pi}{3}(n-1)(2n+1)\frac{\eta R_S}{M} \tag{30}$$

where R_S is the radius of the sphere and η the viscosity. As shown by Reid [18], the frequency ω remains uneffected from the viscosity in the weak damping limit. In the general case, however, one obtains a complex frequency $\Omega = \omega + i/\tau$, and frequency and damping depend on both surface tension and viscosity. The general case is not amenable to an analytical treatment, but Suryanarayana and Bayazitoglu [19] have solved the eigenvalue equation for the complex frequency numerically.

Employing the Stokes–Einstein relation,

$$D\eta = \frac{k_B T}{6\pi r} \tag{31}$$

where r is a characteristic atomic particle radius, also the diffusion coefficient D can be derived from this type of experiment. This has the advantage that viscosity measurements are not so sensitive to convection as diffusion measurements.

Viscosity measurements using levitation techniques have not been attempted so far. One reason is that under 1-g conditions the electromagnetically induced flow in the sample may be turbulent. The effect of turbulence on the apparent viscosity, however, cannot be neglected [20]. Here, again, microgravity may be the required remedy since it allows to use small magnetic fields.

4. CONCLUSIONS

Electromagnetic levitation allows containerless handling of liquid, electrically conducting, samples. It provides the possibility for *in situ* measurements on liquid and, in particular, undercooled samples. In the past, it has been used for melt refining, nucleation, and solidification studies. Recently, attention has turned to the measurements of thermophysical properties. The need for these data is obvious: in order to understand, and eventually model, the solidification from the undercooled melt and the controlled formation of metastable phases, the fluid dynamical and thermal properties of the melt must be known.

To measure these quantities, electromagnetic levitation must be complemented by noncontact diagnostic tools. In this paper, we have presented old and new concepts. Some of them are well established and results are available; some of them still have to prove their feasibility.

Since the levitating magnetic fields inevitably introduce disturbances into the sample, it is natural to try to minimize them. This becomes possible by performing the experiments in a microgravity environment. Regrettably, opportunities for microgravity experiments are scarce and expensive.

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