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Challenges in Measuring of Physical Properties of Liquid Phases for Material and Process Optimisation**

By *Semiramis Akbari* and *Bernd Friedrich**

The exact knowledge of thermo-physical properties of molten phases is crucial to modern metallurgy. It leads to optimized process windows including better metal/slag separation, suitable slag selection or reduced slag/refractory wetting. The most important properties are melting and boiling point, electrical- and thermal conductivity, melting and transition enthalpies, wetting angle, density, viscosity and surface tension. The aim of this paper is to present opportunities, methods and uncertainties of characterization of this kind of materials. This will be examplified by measuring three physical properties (density, viscosity and surface tension).

Relevance for Advanced Engineering Materials

Modern high-performance materials undergo a series of different melting and remelting steps to reach their chemical and microstructural quality. In electroslag remelting (ESR), vacuum arc remelting (VAR) or vacuum induction melting (VIM), just to name a few, the knowledge of physical properties of the melts treated is crucial for optimisation of these processes. In e.g. electroslag remelting, where a resistance-heated slag is used to melt a consumable electrode, the metallurgical engineer deals with the interaction of two liquid phases. The kinetics of chemical reactions between the two phases, phase separation, heat and mass transfer phenomena, convection within the melts, heating efficiencies and solidification effects are all depended on the physical properties of the melts that have to be taken into consideration in order to improve process parameters. In VIM-melting of reactive materials, a property like the wetting of crucible has tremendous effects on the kinetic slow-down of thermodynamically feasible, but unwanted metal-refractory reactions.

Physical properties of liquid phases are also required in alloy synthesis or metal coating via high temperature molten salt electrolysis, for example Platinum, Titanium or Tantalum materials. In this process the electrolyte is the significant active element determine the efficiency of the electrochemical reactor.For optimum process performance the knowledge of the salt's physical properties is crucial. One required electrolyte property is a high electrical conductivity to assure a fast transport of the charge carrier and thus a high current flow. A second important point is electrolyte and cathode density if both are liquid, in order to allow an optimal separation in the reactor. Other relevant process parameters are the melting point of the electrolyte enriched with the metal salt, its vapour pressure to minimize losses through evaporation and its viscosity to optimize the kinetics of the process.

Viscosity Measurement

Generally speaking, viscosity represents the resistance of a fluid against shear stress. The principle of measurement present at IME Process Metallurgy and Metal Recycling is based on the so called "Vibration or Amplitude Method", which can be used for liquids with viscosities up to 10 Pa s; but giving best results for lower viscosities. In Figure 1 the measuring principle is schematically illustrated. The equipment consists of a measuring probe, which is normally a thin plate or a hollow cylinder. The probe is fixed on a rod, that is suspended by a spring system in such a way, that it can freely move in vertical direction between an exciting coil, generating the vibration in the probe and an exploring coil. The vibration characteristic changes after immersing in the fluid which can be measured as a change in current induced in the exploring coil.[3,4] The electrical effect of the immersion is logged on a data logging device, using the LabView® Software for further evaluation. A vibration is generally characterised by its amplitude, frequency and the phase shift be-

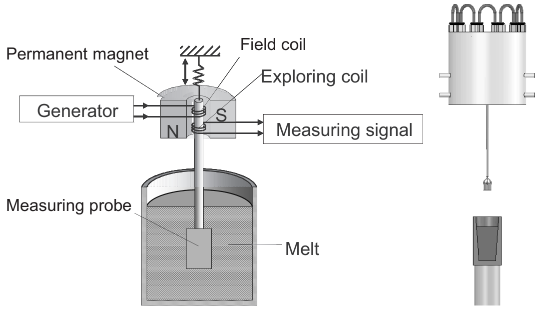

Fig. 1. Scheme of the vibration viscosity measurement at IME, Aachen.

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tween current and voltage. The mathematical model used for evaluation of the signals results in

$$\sqrt{\rho.\eta}$$

in which A represents the amplitude of vibration, ρ the density and η the viscosity of fluid as well as C_1 and C_2 the constant parameters related to the actually used measuring system.

$$\sqrt{\rho \bullet \eta} = \frac{C_1}{A} + C_2 \tag{1}$$

In order to determine the systems constant parameters C1 and C_2, the instrument must be calibrated, e.g. whenever the measuring probe (new material or new dimensions) is changed. Typically solutions with well defined viscosity and density (e.g. water, water-glycerine or NaCl-water solutions with different concentrations) are used for calibration. Table 1 shows exemplary polynomial coefficients ($A\ T_2$+$B\ T$+C) of density and viscosity for water and a 20 % NaCl-water solution.

Using such coefficients together with measured Amplitude data of calibrating solutions (see Tab. 2), it is possible to draw diagrams of ((Formula 1)) against A_{Air} / A (inverse of Amplitude). The regression line with the best fit (see Fig. 2) delivers the values of C_1 and C_2 to be used for determination of the viscosity of melts. Figure 2 illustrates the LabView® response related to a viscosity calibration measurement. After calibration, the viscosity instrument is ready to be used for unknown melts (metal, slag, salt, aqueous or organic solution). The amplitudes are measured at different temperatures and the viscosity is calculated using the exact value of the fluids density and constant parameters C_1 and C_2 (Tab. 3), i.e. the density must be either measured previously (see Chapter 4) or calculated theoretically using again published polynomial coefficients (2) as a function of temperature, in which a and b are constants for each media:

$$\rho = a - \left(\frac{b}{1000}\right) T \tag{2}$$

Table 2. *Example of amplitude measurement data for different calibration solutions, including water, 20 %NaCl-water, 30 %NaCl-water and 50 %NaCl-water.*

Temp. [°C]	Amplitude [mV]	Medium	Viscosity [mPa]	Density [g/cm^3]	R oot [$\sqrt{\rho\eta}$]	A_{air}/A
23.2	540.1	Water	0.9276	0.9975	30.42	1.0716
23.2	528.8	Water	0.9276	0.9975	30.42	1.0200
23.2	538.4	Water	0.9276	0.9975	30.42	1.0208
23.5	530.4	20%	1.5953	1.0458	40.85	1.0249
23.5	530.5	20%	1.5953	1.0458	40.85	1.0247
23.0	530.8	20%	1.6172	1.0459	41.13	1.0241
22.5	525.8	30%	2.3047	1.0717	49.76	1.0302
22.5	526.3	30%	2.3047	1.0717	49.76	1.0293
22.5	525.9	30%	2.3047	1.0717	49.76	1.0300
21.0	495.2	50%	5.7750	1.1258	80.64	1.0447
21.0	507.8	50%	5.7750	1.1258	80.64	1.0447
21.8	507.4	50%	5.8191	1.1259	80.95	1.0455

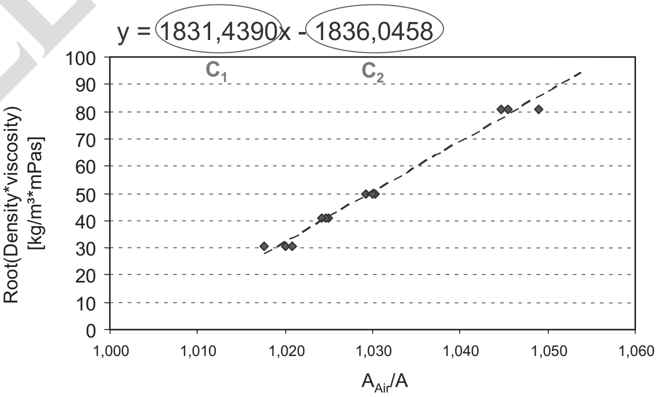


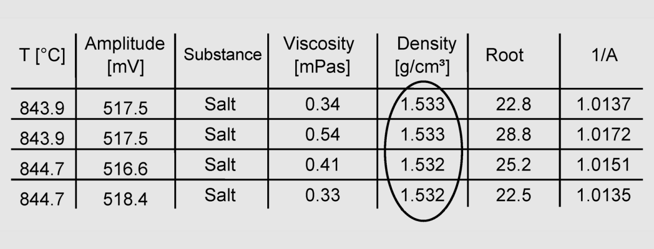
Fig. 2. *Graphical assessment of calibration results serving the system constants C_1 and C_2.*

The ratio of existing phases typically changes when the raw materials join during melting and sometimes even during measurement due to evaporation or crucible reactions. For theoretical density calculation it is very important to model the melt composition e.g. via FactSage® (a commercial thermochemical Software), showing new components with their contents after melting. So the density of the expected composition shall be calculated (see Tab. 4); however, such calculations are done often without consideration of the interaction effects (activities) due to missing data and therefore have to be based on ideal mixing models. Nevertheless a sample has to be taken before and after measurement to prove

Table 1. *Polynomial coefficients of water and a 20 %NaCl-water-solution.*[1]

	Viscosity [mPa]			Density [g/cm^3]		
Water	T^2	T	c	T^2	T	c
Polanomal Coeff.	0.0008997	-0.05279048	1.7513786	-7.8154E-06	5.8106E-05	0.999858789
20% NaCl Water	T^2	T	c	T^2	T	c
Polanomal Coeff.	0.00312	-0.139959	3.374429	-0.00000129	-0.000421	1.15672

Table 3. Example of a viscosity measurement (molten salt for Mg-alloy-synthesis).



T [°C]	Amplitude [mV]	Substance	Viscosity [mPas]	Density [g/cm³]	Root	1/A
843.9	517.5	Salt	0.34	1.533	22.8	1.0137
843.9	517.5	Salt	0.54	1.533	28.8	1.0172
844.7	516.6	Salt	0.41	1.532	25.2	1.0151
844.7	518.4	Salt	0.33	1.532	22.5	1.0135

the composition of the melt during the test that must be constant.

Based on the above calculation of the melt-phase composition, the theoretical density of the melt can be estimated, using the model of mechanical mixing to build a weighted average of the densities of the pure components. This theoretical value for the density of the melt serves as reliable value for comparison with the experimental measurement, assuming that mixing effects on molar volume are relatively small.

Density Measurement

Generally, the density is defined as the relation between the weight and the volume of a sample and showed as the well-known Equation 3:

$$\rho = \frac{m}{V} \tag{3}$$

The knowledge of density is necessary to analyse physical- and physicochemical processes and properties respectively, e.g. liquid-liquid and liquid-solid phase separation, viscosity and surface tension or thermal expansion (α: linear thermal expansion coefficient, γ: thermal expansion coefficient of volume) of fluids. The latter can be expressed as

$$\rho = \frac{\rho_0}{1 + \gamma \Delta T} \text{ with } \gamma \cong 3\alpha \tag{4}$$

The measurement principle of the density instrument at IME is based on the traditional "Archimedes" method, whose mathematical equation is made up as follows:

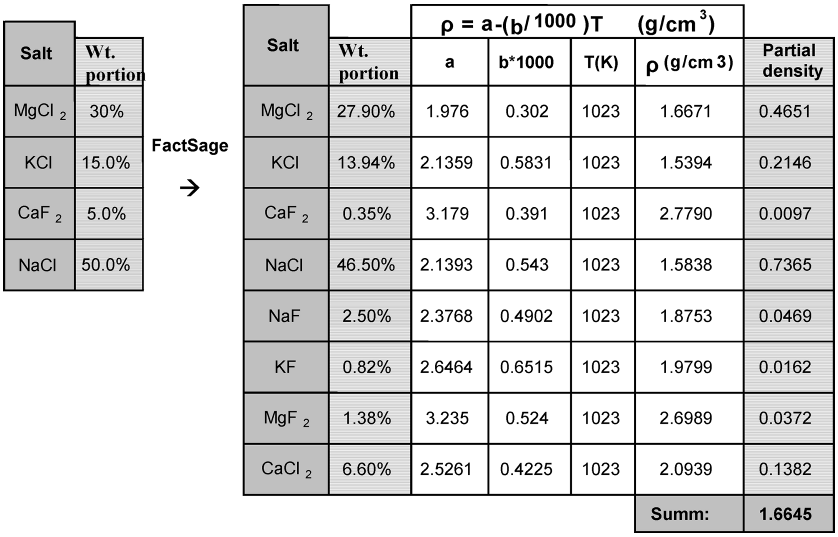
$$\rho_m - \rho_a = \frac{m_a - m_m}{V} \tag{5}$$

where ρ_m and ρ_a are the densities of melt and air, ma and mm the weight of the measuring probe in air resp. in melt and V is the volume of measuring probe. The instrument consists of a hydrostatic balance and a free hanging probe. The weight of this probe is weighed firstly in air, and afterwards in the melt.[4] In Figure 3 the principle of the method has been illustrated schematically. Figure 4 illustrates schematically the current position of two instruments; density and viscosity measurement. There is only one conductive heated furnace for both of them. A shifting system serves for the precise position of the furnace, which can be relocated and pulled easily from one sensor to the other.

The weight data are continuously recorded by the LabView Software. Figure 5 shows an example of a density measurement curve of a liquid (CaF_2+5 mol% La_2O_3) at ca. 1600 °C. Each position of this curve demonstrates different situations in the density measurement as described. Generally, the weight stays constant after complete immersion of the probe in the melt. If the weight decreases dramatically, as shown on the right wing in Figure 5, the holding wire has been broken by oxidation/ corrosion/reaction and the probe has been fallen into the melt. This occasionally happens at very high temperature due to the presence of oxygen in a semi-open-system (despite of inserting Ar on top of the melt). If so, the measurement is conducted in a fully evacuated and Ar-flushed device. For flux or slag measurements the probe, wire and clasp is either Mo or W-10Rh, but the suitable probe material selection in physical properties measurement is a great challenge. Thicker wires resp. clasps lead to higher errors in calculation while thinner wires will give more accurate results, comprise a higher risk of failure.

In order to calculate the density of a liquid, the exact volume of the measuring probe is required. Sometimes (especially after some usage), the probes do not have easy geometrical dimensions and therefore it is difficult to determine their exact volume. Volume measurement through water displacement is not accurate enough, because via glass cans, using here, the volume of probe can be measured with the accuracy of only ± 0.1 cm^3. Instead, the volume shall be

Table 4. Calculation of existing phases in four base salt melts using the thermochemical software FactSage®.



Salt	Wt. portion
$MgCl_2$	30%
KCl	15.0%
CaF_2	5.0%
NaCl	50.0%

FactSage
→

Salt	Wt. portion	ρ = a-(b/1000)T (g/cm^3)				Partial density
		a	b*1000	T(K)	ρ (g/cm 3)	
$MgCl_2$	27.90%	1.976	0.302	1023	1.6671	0.4651
KCl	13.94%	2.1359	0.5831	1023	1.5394	0.2146
CaF_2	0.35%	3.179	0.391	1023	2.7790	0.0097
NaCl	46.50%	2.1393	0.543	1023	1.5838	0.7365
NaF	2.50%	2.3768	0.4902	1023	1.8753	0.0469
KF	0.82%	2.6464	0.6515	1023	1.9799	0.0162
MgF_2	1.38%	3.235	0.524	1023	2.6989	0.0372
$CaCl_2$	6.60%	2.5261	0.4225	1023	2.0939	0.1382
					Summ:	1.6645

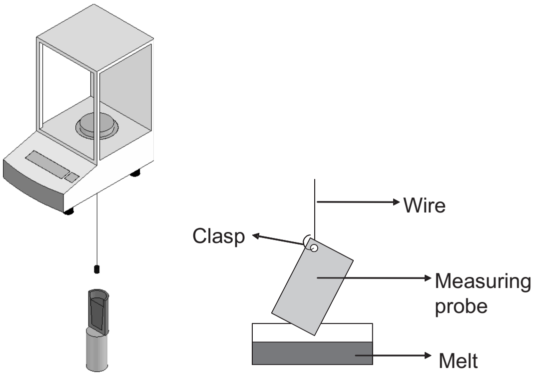


Fig. 3. Scheme of the "Archimedes" density measurement device at IME, Aachen.

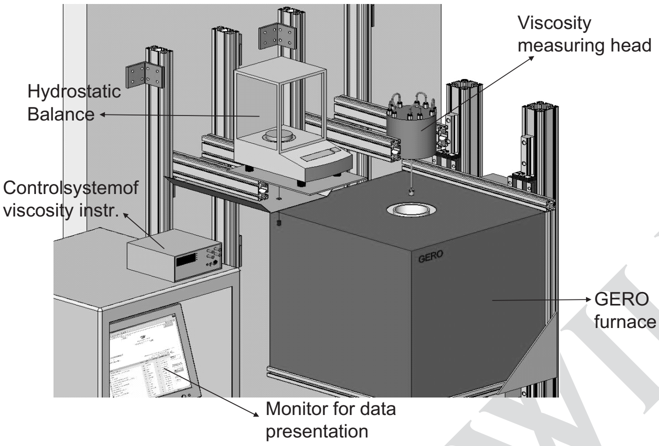


Fig. 4. Density and viscosity instruments beside each other on the wall and GERO furnace used for the both.

converted to the weight divided by density of material, which can be found from the literature as a function of temperature. For instance, the polynomial coefficient of Mo density is as the following equation:[2]

$$\rho_{Mo} = -3.66E - 08T^2 - 0.000157T + 10.27 \tag{6}$$

As an example, different ESR-slag mixtures were investigated. The density values of pure CaF_2 and in mixtures with compounds like CaO, MgO, SrO, La_2O_3 at 1600 °C are illustrated in Table 5 together with the corresponding standard and median deviation. Due to the complexity of material selection for the probe especially for ESR-Slags, these trials were of great challenges, as the both used Mo as well as W-Rh wires burned and had to be renewed very often during the tests.

Surface Tension

Due to the surface tension 7 of a liquid, the specific surface will be minimized, therefore, an "Energy" is required to extend the surface.

$$\sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P} \tag{7}$$

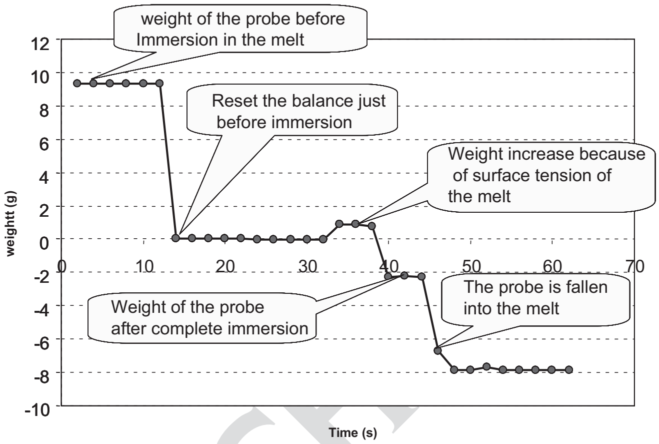


Fig. 5. Example of a weight-time curve during density measurement of slag CaF_2 + 5 mol% La_2O_3 at 1600 °C.

The measurement principle at IME is based on the determination of the "maximum pressure", which is essential to create and release a gas bubble from a capillary submerged in a fluid. One or two capillaries are used for insertion of inert gas into the melt (see Fig. 6). The gas pressure in the capillary must be increased as long as a bubble grows to a critical size, than the pressure relieves again until the bubble disconnects to the capillary. This maximum pressure, which slightly differs from bubble to bubble, is recorded and the average of all maxima in a time interval will be taken as the "maximum bubble pressure". The mathematical model of the surface tension has been exhibited as the following Equation 8:

$$P_{\max} = \rho g h + \frac{2\sigma}{r} \tag{8}$$

in which Pmax is the maximum pressure in the bubble, h the immersion depth, r the capillary radius, ρ the density of the liquid, g the acceleration of gravity and σ the surface tension of the liquid.[5–9]

Also in this method, selection of materials (here the capillaries) is of great importance. In an unreal situation, i.e. using a capillary with either excellent or "zero" wettability, only a single maximum of the bubble pressure will be formed, related to the interior or in outer diameter of the capillary (Fig. 7). But in reality, two maxima often occur as the bubble

Table 5. Density of pure CaF_2 and in combination with different oxides at 1600 °C, showing also the median and standard deviation.

Measurement error sources	Solutions methods
Capillary Diameter	Determination using a light optical microscope with 0.01 mm accuracy
Immersion depth of capilary	Usage of two capillaries with different diameters
Density of melt	Firstly density measurement; or, usage of two capillaries with different immersion depth

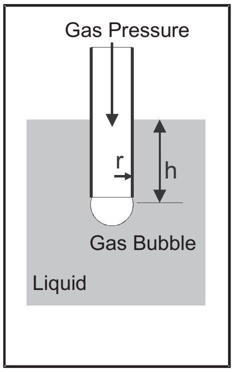


Fig. 6. Principle of surface tension measurement at IME, Aachen.

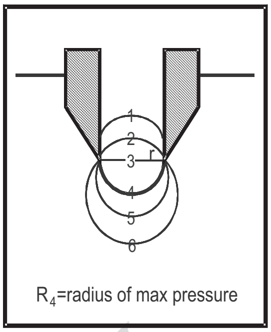


Fig. 8. Sharpened capillary for real solutions to ensure only one maximum during bubble pressure measurement.

"jumps" from the inner to the outer side of the tube. In order to avoid this effect, an extreme thin-walled capillary should be utilized. Practically, a sharpened ceramic capillary is used (Fig. 8). However, it has been seen from many experiments, that in spite of sharp edge of the capillary, sometimes more than one maximum can be noticed. By any means, the thinner the capillary tip, the smaller the error.

In surface tension measurement like in all other thermophysical property measurements, a variety of measurement potential error sources exist, including capillary diameter, immersion depth of the capillary (sometimes even not constant), density of the melt, etc. In Table 5, some solutions are suggested to overcome some of those error sources:

The amounts of bubble pressures are recorded by the software as pulses, which are repeated frequently. The gas flow rate must be so adjusted that about one bubble per second is formed. The capillary is then placed at different depths and the average of the maximum bubble pressures for each immersion depth will be fixed (see Tab. 6, measuring Number 1–6). The surface tension is then calculated using Equation 8. Table 7 shows only as an example the surface tension calculation for distilled water. Again the exact value of the density is required, which should be either measured previously or calculated theoretically. The bubble diameter is considered as the same diameter as of the capillary opening.

It must be expected to reach the same values of surface tension in different immersion depths, but as shown in Table 7 different values are calculated e.g. due to minor changes in temperature or not accurate measured immersion depths. Therefore, the average of these values will be considered as the amount of surface tension.

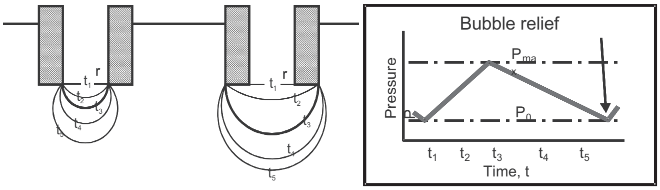


Fig. 7. Theoretical gas bubble formation on a capillary with excellent (left) and zero (right) wettability and the curve of maximum bubble pressure.[6]

Conclusion and Outlook

Besides the presented methods the IME-lab is equipped with a surface angle measuring device (liquid drop on solid surface) and electrical conductivity, using a four electrode sensor at high frequencies for impedance investigation. All the mentioned methods are of high complexity, especially the material selection takes a long time. Before each test, ade-

Table 6. Different bubble pressure related to different immersion depth in water.

	Measurement Nr.					
Max. Pressure (mbar)	1	2	3	4	5	6
	1.912	2.414	2.912	3.403	3.893	4.387
	1.907	2.42	2.908	3.404	3.89	4.392
	1.909	2.418	2.909	3.405	3.892	4.388
	1.913	2.42	2.91	3.404	3.894	4.389
	1.918	2.42	2.907	3.402	3.889	4.385
Average	1.989	2.478	2.959	3.431	3.911	4.403
Water density	T^2	T	C		: Literature	
Polynom. Coeff.	-0-0078154	0.05810633	999.8587891			

Table 7. Surface tension calculation exemplary for water based on data of Table 6.

Water	Nr. 1	2	3	4	5	6
Pressure [Pa]	198.9	247.8	295.9	343.1	391.1	440.3
Bubble diameter [mm]	0.72	0.72	0.72	0.72	0.72	0.72
Density [kg/m^3]	997.6	997.9	998.0	998.0	998.0	998.0
Temperature [°C]	22.8	21.5	21.2	21.1	21.0	20.9
g [m/s^2]	9.811	9.811	9.811	9.811	9.811	9.811
Immersion depth [m]	0.000	0.005	0.010	0.015	0.020	0.025
Surface tension [N/m]	0.0699	0.0699	0.0696	0.0689	0.0686	0.0687

quate materials for the crucible, wire, clasp, measuring probes and capillary must be carefully selected and depending on the liquid be tested.

There are also different sources of errors in each method that have to be carefully considered, starting with geometric values like probe volumes, capillary diameters, immersions depths etc., physical data like temperature, systematic aspects like wire thickness, immersion depth, etc. up to chemical issues like sample evaporation or reactions with crucible/materials. Sometimes they interfere like sample loss due to evaporation and immersion depth. In such a case the chemical composition will change and the measured property data may be useless. In all cases the melt composition has to be controlled at the beginning and at the end of the measurement.

The physical properties measurement instruments at IME allows a relatively “quick” analysis under air or shrouded cover gas as well as under vacuum or 100 % inert gas like Argon in a special equipment with conductive heated crucibles. They allow also the measurement of different properties in the same melt/heat just changing the sensors. Nevertheless this lab demands still a variety of activities, which are done frequently to further improve the precision. The success of this device area strongly depends on the experience of the experts working here, who accumulate the necessary knowledge from many kinds of investigations in the past.

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The exact knowledge of thermo-physical properties of molten phases is crucial to modern metallurgy. It leads to optimized process windows including better metal/slag separation, suitable slag selection or reduced slag/refractory wetting. The most important properties are melting and boiling point, electrical- and thermal conductivity, melting and transition enthalpies, wetting angle, density, viscosity and surface tension. The aim of this paper is to present opportunities, methods and uncertainties of characterization of this kind of materials. This will be examplified by measuring three physical properties (density, viscosity and surface tension).

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