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Structure and properties of undercooled liquid metals

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Abstract. Electromagnetic levitation is a useful tool to process high-temperature and highly reactive melts without a container. It provides a pure environment and contamination of the melt is reduced to a minimum. With the application of non-contact measurement techniques, structures and properties of pure samples can be investigated. One major advantage of this approach is that it allows one access to the metastable state of the undercooled melt. This paper reports on measurements of thermophysical properties of undercooled liquid metals and recent investigations of their structure. We have performed measurements of the surface tension, electrical conductivity, density and thermal expansion of a number of pure metals and alloys. Some experiments were performed under microgravity conditions which reduce the strength of the required electromagnetic fields by orders of magnitude and lead to a much higher precision. We have recently used electromagnetic levitation in combination with synchrotron radiation to obtain EXAFS spectra of an undercooled Co–Pd alloy.

1. Introduction

In contrast to solids and gases, liquids remain poorly understood phases of matter. Liquid metals are considered simple liquids in theory, but in practice most are difficult to handle, due to the high temperatures involved. Obviously, more experimental information on liquid metal properties and structure is needed, in order to test recent theories of the liquid state.

For metallic melts, electromagnetic levitation is an elegant method which allows containerless melting and solidification. It provides high-purity conditions and, consequently, also undercooling of the melt. This non-equilibrium, metastable state is of interest for many reasons. First, a liquid is more quiescent in the undercooled region than it is in equilibrium, because the temperature is lower by several hundreds of kelvins and, consequently, thermal fluctuations are greatly reduced. In addition, an undercooled liquid is not in equilibrium and new, metastable, phases, normally excluded by the phase diagram, may form upon solidification.

In order to investigate the structure and properties of undercooled melts, electromagnetic levitation must be complemented by non-contact diagnostic tools. We have developed and applied optical methods for the measurement of surface tension and density, and an inductive method for the measurement of electrical conductivity. We have also performed EXAFS studies on levitated undercooled samples which yield information about the number and distance of nearest neighbours. The synopsis of the experimental results should give us insight into ordering effects and transport properties in liquid metals.

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2. The surface tension

The surface tension of a liquid sample can be measured by the oscillating drop technique. This is a non-contact method which makes use of the fact that the frequency of surface (capillary) oscillations is related to the surface tension γ. For a drop of mass M, free of external forces, the fundamental frequency is given by [1]

$$\omega_R^2 = \frac{32\pi}{3}\frac{\gamma}{M}. \tag{1}$$

In terrestrial levitation experiments, corrections to this simple formula have to be made to account for the Lorentz force and the gravitational force. These forces result in a distortion of the otherwise spherical sample, leading to a splitting of the fundamental frequency into up to five frequencies (due to the broken symmetry) and a shift of the frequencies (due to a magnetic pressure effect). Cummings and Blackburn [2] have derived an (approximate) correction formula which reads

$$\omega_R^2 = \bar{\Omega}_2^2 - 1.9\omega_{tr}^2 - 0.3\omega_{tr}^{-2}(g/R)^2. \tag{2}$$

In this formula, $\bar{\Omega}_2^2$ is the mean of the split frequencies due to surface oscillations, ω_{tr}^2 is the mean of the frequencies of the translational oscillations, g is the gravitational acceleration and R is the radius of the sample.

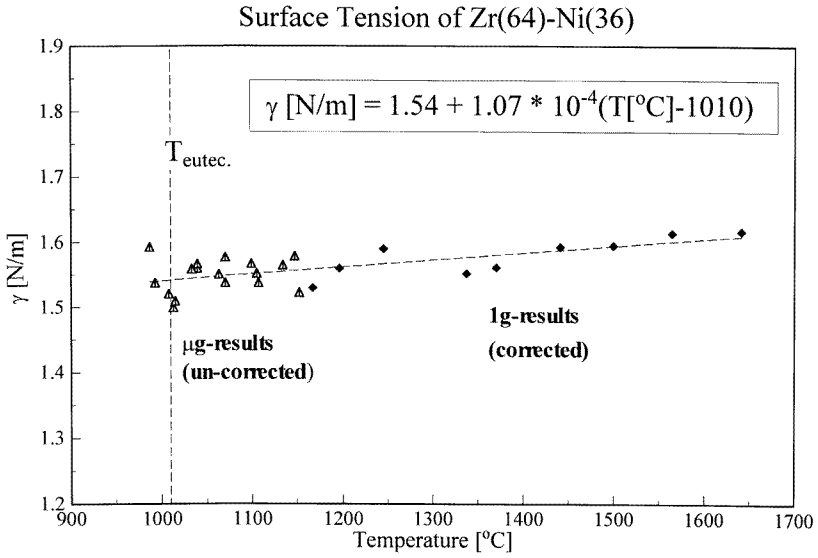

Figure 1. The surface tension of $Zr_{64}Ni_{36}$. Microgravity data points (triangles) are compared to terrestrial data (diamonds) corrected according to equation (2).

We have performed surface tension measurements in microgravity on gold, a congruently melting Au–Cu alloy and a eutectic Zr–Ni alloy [3]. The results were compared with our ground-based experiments to test the validity of this correction formula. We found perfect agreement when we used the Rayleigh formula for the microgravity data and the Cummings–Blackburn formula for the terrestrial data. This is shown in figure 1 for $Zr_{64}Ni_{34}$.

3. The density

There are a number of techniques to measure the density of liquid systems; however, none of them is a non-contact method and applicable to undercooled liquids. We used a videographic method in combination with electromagnetic levitation. The mass M of the sample is determined before and after levitation to account for evaporation losses. The volume is determined from a fit to the visible lateral cross section of the sample, assuming rotational symmetry of the equilibrium shape.

The fit is performed using a series expansion in Legendre polynomials P_n yielding the radius R as a function of angle θ:

$$R(u) = \sum_n a_n P_n(u) \qquad u = \cos(\theta). \tag{3}$$

The volume is then given as

$$V = \frac{2\pi}{3} \int_{-1}^{1} R^3(u)\,\mathrm{d}u \tag{4}$$

and, finally, the density is obtained from

$$\rho = M/V. \tag{5}$$

The major experimental difficulties lie in the high spatial resolution required to resolve volume changes of the order of $\Delta V/V \approx 10^{-4}$ and in the elimination of the non-rotationally symmetric surface oscillations.

We have measured the density of the Cu–Ni alloy system over the entire concentration range and over a wide temperature range, including the undercooled regime [4]. For the pure elements Cu and Ni, our results agree well with published data [5, 6]. The concentration-dependence of the density of the Cu–Ni system at constant temperature is shown in figure 2; our data indicate a nonlinear concentration-dependence which may be explained by clustering effects.

4. The electrical conductivity

The non-contact measurement of the electrical conductivity of a material, liquid or solid, can be based on electromagnetic induction. The sample is placed inside a coil carrying a RF current. By virtue of the presence of the sample, the impedance of the coil changes. The impedance can be easily determined by measuring the current and voltage through the coil simultaneously. Therefore, if the impedance can be expressed in terms of the conductivity of the sample, this method can be used to measure electrical conductivities in a non-contact manner. The relation between impedance and conductivity for spherical samples has been given in [7]. If the coil is part of an oscillatory circuit of high frequency and low damping, the sample conductivity can be derived from the following approximate formula:

$$\delta = \frac{R}{2}\{1 - \{1 - 4[A_0 I/U - B_0]\}^{\frac{1}{2}}\} \tag{6}$$

where δ, the skin depth, is defined as

$$\delta = \left(\frac{2}{\omega\sigma\mu_0}\right)^{1/2} \tag{7}$$

has to be small, $\delta < R/3$. Here, ω is the frequency of the oscillatory circuit, σ is the sample's conductivity and μ_0 is the magnetic permeability. The ratio I/U of the amplitudes

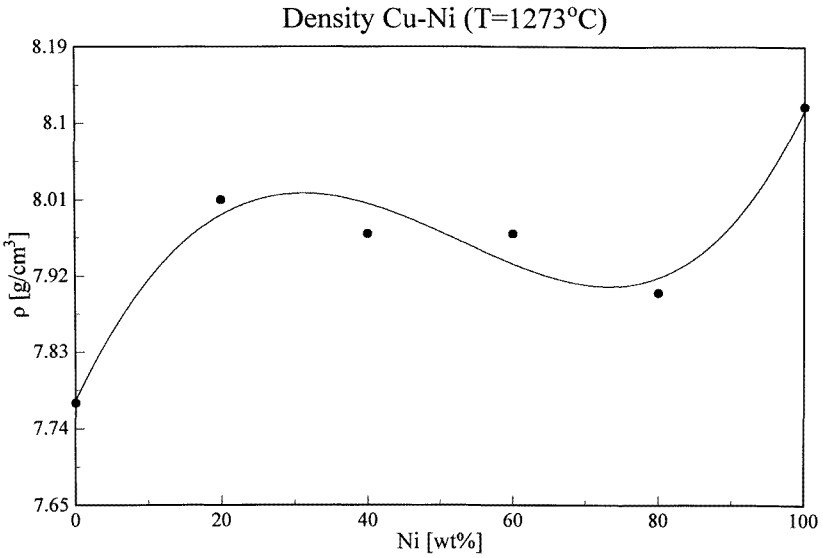

Figure 2. The density of Cu–Ni alloys as a function of concentration at $T = 1273\,^{\circ}$C.

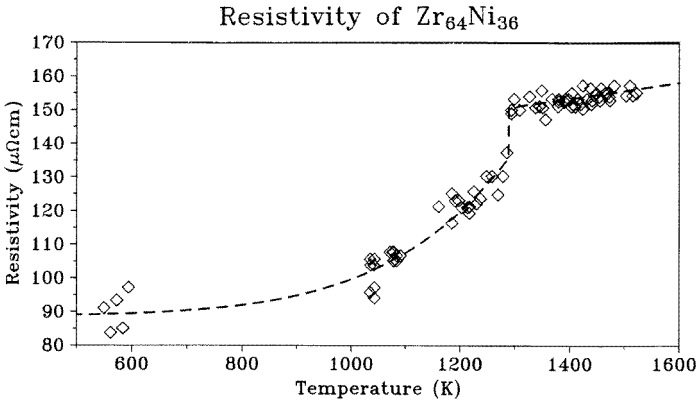

Figure 3. The electrical resistivity of $Zr_{64}Ni_{36}$ measured in microgravity.

of the AC coil current and voltage can be measured directly. The constants A_0 and B_0 are characteristic of the coil and the oscillatory circuit and have to be determined beforehand via calibration experiments with test samples of known conductivities.

The principle of this measurement can be combined with electromagnetic levitation, in which the levitation coil is part of an oscillatory circuit and can be simultaneously used as the probing coil. If the experiment is performed under microgravity conditions, the liquid sample remains spherical and the formula outlined above is applicable. In our microgravity experiment, we have measured the electrical conductivity of the eutectic $Zr_{64}Ni_{34}$ alloy mentioned before, both in the solid and in the liquid state [8]. The result is shown in figure 3; the change in resistivity at the melting point is clearly visible.

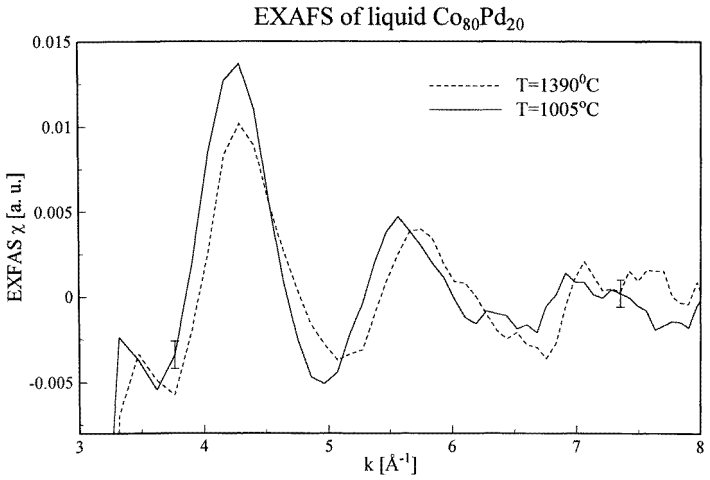

Figure 4. EXAFS spectra of levitated liquid $Co_{80}Pd_{20}$ at 1390 °C (dotted line) and 1005 °C (full line).

5. EXAFS

The EXAFS signal $\chi(k)$, due to an atom embedded in condensed matter and excited by synchrotron radiation, is defined as the difference between the actual absorption $\alpha(k)$, and the absorption of an isolated atom, $\alpha_0(k)$, normalized with respect to $\alpha_0(k)$:

$$\chi(k) = \frac{\alpha(k) - \alpha_0(k)}{\alpha_0(k)}. \tag{8}$$

The function $\chi(k)$ contains information about the short-range order in the vicinity of the absorbing atom, namely the distances and numbers of the nearest neighbours. In k-space, $\chi(k)$ is a superposition of oscillating functions, such that its amplitude is determined by the number of neighbours in a given shell and its frequency is related to the distance of the absorbing atom from that shell:

$$\chi(k) = \sum_j A_j(k) \sin(2kR_j + \psi_j). \tag{9}$$

For the determination of the nearest-neighbour distances R_j, the phase shift $\psi_j(k)$ and in particular its k-dependence must be known. For highly disordered systems, like high-temperature metallic melts, this is a serious problem in the interpretation of EXAFS spectra [9].

To test the compatibility of EXAFS and electromagnetic levitation we have performed preliminary experiments at HASYLAB of DESY, Hamburg [10]. Due to the strong absorbtion of synchrotron radiation by metals and due to the large size of the levitated sample ($R = 3$ mm), absorption spectra could not be recorded and hence fluorescence spectra were used instead. We observed EXAFS spectra of a levitated liquid $Co_{80}Pd_{20}$ (liquidus temperature $T_l = 1333$ °C) sample in the temperature range from 1390 down to 1005 °C, which means an overheating of the sample of about 55 °C and a maximum undercooling of about 325 °C. Figure 4 shows the spectra at sample temperatures of $T = 1390$ and 1005 °C. The EXAFS oscillations are clearly visible in the k-range up to about 6.5–7.0 Å^{-1} for both temperatures, whereas, in the higher k-range, the oscillations can no longer be distinguished from the noise.

6. Conclusions

Electromagnetic levitation is a useful method for the study of metallic melts. As we have shown, it can be combined with a number of non-contact diagnostic tools to measure such quantities as surface tension, density and electrical conductivity. Electromagnetic levitation is also compatible with synchrotron radiation sources and EXAFS spectra can be obtained. We are now focusing on refining the experimental techniques and developing new non-contact methods, for example for measuring the viscosity of undercooled melts. Or goal for the future is to be able to perform systematic studies of interesting physical phenomena and systems.

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