International Journal of Thermophysics, Vol. 19, No. 3, 1998

Measurement of Density and Structural Short-Range Order of Levitated Liquid Metals[1]

G. Jacobs,[2,3] I. Egry,[2] E. Gorges,[2] and M. Langen[2]

The determination of thermophysical properties and structure of undercooled metallic melts must be accomplished by contactless methods due to the high reactivity of the material. It has been shown that electromagnetic levitation provides high-purity conditions to allow deep undercooling. The density and thermal expansion of a levitated drop can be derived from volume measurements using a charge-coupled device (CCD) camera and a digital image processing system. Combining levitation with extended x-ray absorption fine structure (EXAFS) spectroscopy leads to the possibility of studying the local structure of the liquid in a wide temperature range including the deeply undercooled regime.

KEY WORDS: density; EXAFS; levitation; liquid metals; local structure; thermal expansion; undercooled melt.

1. INTRODUCTION

Information about thermophysical properties of liquid metals is important for materials science as well as for industrial processes and, in combination with knowledge about the structure of the melt, can help to understand the nature of the liquid state.

Due to their high temperature and reactivity, liquid metals are quite difficult to handle by conventional techniques. For this type of material, electromagnetic levitation is an elegant method, which allows containerless processing and, due to the high-purity environment, a deep undercooling of the melt. This nonequilibrium, metastable state is of interest for many reasons: first, a liquid is more quiescent in the undercooled region than it

[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

[2] Institut für Raumsimulation, Deutsches Zentrum für Luft- und Raumfahrt, D-51170 Köln, Germany.

[3] To whom correspondence should be addressed.

0195-928X/98/0500-0895$15.00/0

is in equilibrium, because the temperature is lower by several hundreds of degrees, and consequently, thermal fluctuations are greatly reduced. This quiescence makes an undercooled liquid suitable for structural studies. In addition, an undercooled liquid is not in equilibrium and new metastable phases, normally excluded by the phase diagram, may form. For studies on undercooled samples, electromagnetic levitation has to be complemented by non-contact diagnostic tools. With an advanced optical method using a videocamera and a digital image processing system, we are able to measure several thermodynamic properties [1, 2], e.g., the density and thermal expansion of the liquid. The short-range structure can be investigated by combining levitation and extended x-ray absorption fine structure spectroscopy (EXAFS). EXAFS is an established tool for the analysis of structural parameters such as the coordination number, the nearest-neighbor distance, and its variance.

2. EXPERIMENTAL PROCEDURE

2.1. Electromagnetic Levitation

Levitation of electrically conducting samples can be achieved by placing the sample into a high-frequency alternating inhomogeneous electromagnetic field, produced by a specially designed levitation coil. This field B induces eddy currents in the sample, which interact with the field. Levitation is caused by the Lorentz force F, which is, to lowest order in a multipole expansion, proportional to the gradient of the square of the field,

$$F \propto \nabla B^2 \tag{1}$$

Simultaneously, the material is heated due to ohmic losses of the induced currents. The power P absorbed by the sample is proportional to the square of the field,

$$P \propto B^2 \tag{2}$$

The levitated sample is positioned in a potential well generated by the electromagnetic field and performs oscillations about its equilibrium position, with a frequency of the order of 2–5 Hz. At the same time liquid samples display free surface oscillations, whose restoring force is the surface tension. Using samples with a typical mass of about 1 g, the frequency of these oscillations is of the order of 40–50 Hz.

A sketch of the levitation facility is shown in Fig. 1. The sample is processed inside of an UHV chamber in a levitation coil which is connected to

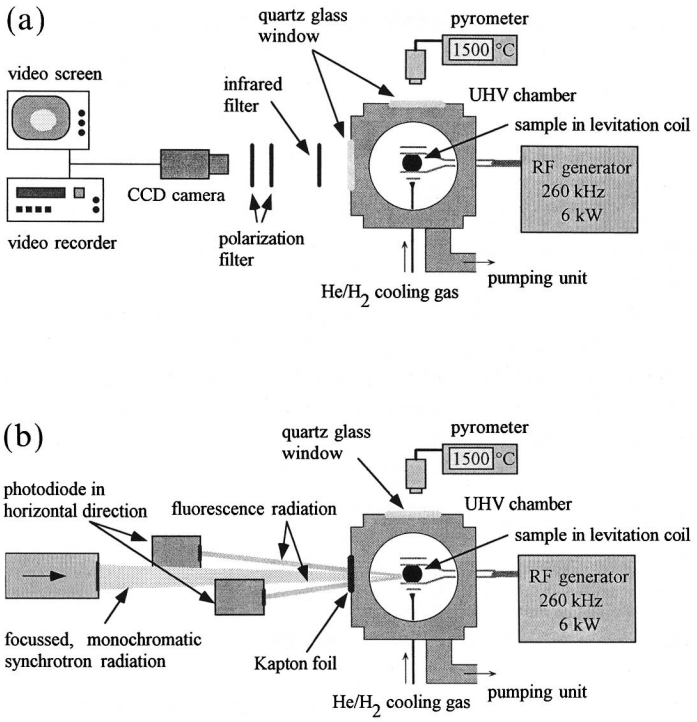

Fig. 1. Experimental setup for levitation experiments: (a) optical system for density measurements; (b) fluorescence radiation detection for EXAFS.

a 6-kW RF generator with a frequency of about 260 kHz. The temperature of the sample can be controlled by convective cooling using He/H_2 gas, and is measured with a pyrometer.

2.2. The Density

There are a number of techniques to measure the density of liquid systems; however, none of them is a noncontact method and applicable to undercooled liquids. This can be achieved by using a videographic method. Averaging over approximately 100 pictures of the sample allows a fit of its equilibrium shape by a series expansion in Legendre polynomials [3],

$$r(u) = \sum_{l} \varepsilon_l P^l(u) \tag{3}$$

where $u = \cos \vartheta$. Provided that the equilibrium shape of the liquid sample has a rotational symmetry, the volume is then given by

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

and, finally, the density is obtained from

$$\rho = \frac{M}{V} \tag{5}$$

where M is the mass of the sample.

For the measurement of the density an infrared and two polarization filters are placed in front of the chamber as shown in Fig. 1a, and a CCD camera takes video sequences of the sample, which are stored on a videotape. The filter arrangement is used to maintain the intensity on the CCD camera; the sample's brightness is a function of temperature. By controlling the angle between two polarization filters, the intensity of the picture is kept constant. Since the polarization filters work only in the visible range, we use an infrared filter with a very low transmission rate in the infrared wavelength regime.

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 nonrotationally symmetric surface oscillations [4].

2.3. EXAFS

The absorption coefficient of an atom in condensed matter is known to oscillate at energies of approximately 50–1000 eV above the absorption edge. This structure is called EXAFS and reflects the scattering of the emitted photoelectron by the surrounding atoms [5]. The EXAFS signal is defined as the normalized difference between the actual absorption $\alpha(k)$ and the absorption of an isolated atom $\alpha_0(k)$:

$$\chi(k) = \frac{\alpha(k) - \alpha_0(k)}{\alpha_0(k)} \tag{6}$$

where k is the wave vector of the emitted photoelectron.

In the case of a purely Gaussian pair distribution function, the expression for $\chi(k)$ is given by [6]

$$\chi(k) = -\sum_j \frac{N_j}{R_j^2 k} |f_j(\pi, k)|\, e^{-2\sigma_j^2 k^2} e^{-2R_j/\lambda(k)} \sin[2kR_j + \phi_j(k)] \tag{7}$$

where N_j is the number of atoms in the jth shell, R_j is the mean distance between the absorber and the jth scatterer, σ_j^2 is the corresponding mean square displacement of the Gaussian pair correlation function, $|f_j(\pi, k)|$ is the absolute value of the scattering amplitude, $\phi(k)$ is the total phase shift of the electron wave function, and $\lambda(k)$ is the electron mean free path.

For the EXAFS measurements the chamber is equipped with a Kapton window to allow the incident synchrotron beam to reach the sample (Fig. 1b). Since it is not possible to measure the absorption of the sample directly in transmission, due to the thickness of the sample (about 5 mm in diameter), we detect the secondary fluorescence by two photodiodes which are placed opposite to the direction of the incident beam.

Two serious problems affect the measurements as well as the data evaluation: first, the absorption of a levitating liquid, performing translational and surface oscillations, has to be detected with sufficient precision; and secondly, the thermal vibrations of the atoms together with the absence of a crystalline order lead to huge damping of the EXAFS oscillations, due to the Debye–Waller factor in Eq. (7), which makes it difficult to obtain sharply peaked spectra.

3. RESULTS

3.1. Density

Figure 2 shows the shape of a levitated droplet. The full line was produced by fitting a series expansion in Legendre polynomials up to the order of $\ell = 4$. The agreement of the fit with the data points is obvious and allows a determination of the density and thermal expansion of liquids with an uncertainty of 5%.

The result of the density measurements on liquid $Cu_{20}Ni_{80}$ is shown in Fig. 3. The solid line represents a least squares fit to the data points, whereas the dashed line shows the results of Watanabe and Saito [7]. It was possible to measure the density over a temperature range of more than 300°C, including an undercooling of about 230°C.

3.2. EXAFS

The first EXAFS measurements on levitated metallic melts were performed using liquid $Co_{80}Pd_{20}$ samples. These measurements, performed at DESY, Hamburg, showed the possibility of obtaining reasonable EXAFS spectra of levitating melts [8]. Figure 4 shows two EXAFS spectra of an overheated and an undercooled liquid sample obtained during recent measurements at the European Synchrotron Radiation Facility (ESRF

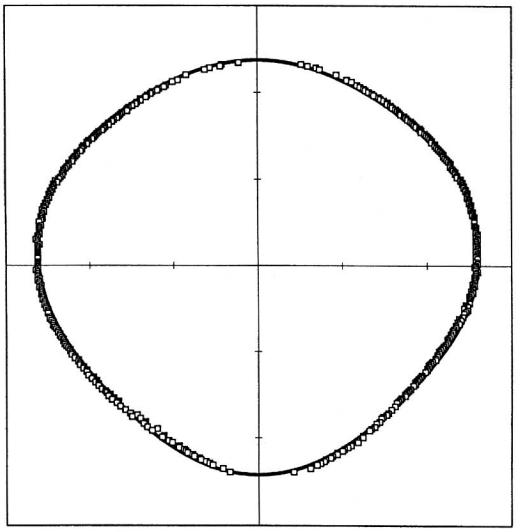

Fig. 2. Shape of a levitated droplet: the solid line represents a fit to the data points.

Grenoble/France) using a focused x-ray beam. By using the GNXAS method [9, 10], which allows a decomposition of the measured x-ray absorption structure (XAS) into contributions of n-body pair distribution functions (GN) $g_n(r)$, it was possible to evaluate the mean distance of the cobalt atoms to each other, $R_{\mathrm{Co-Co}}$ as well as of the cobalt atoms to the

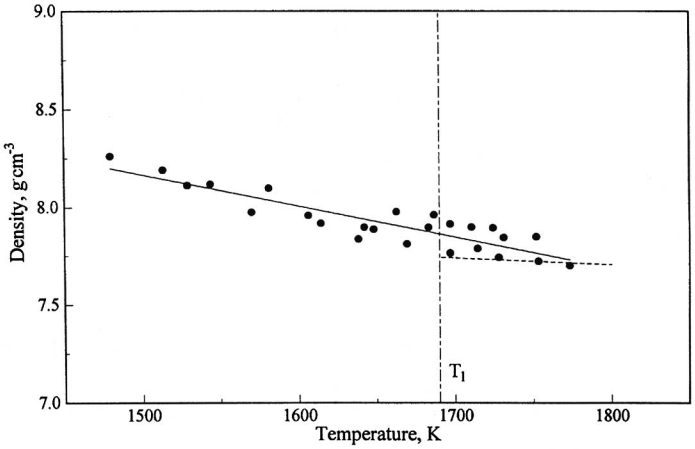

Fig. 3. Density of liquid $Cu_{20}Ni_{80}$. The solid line represents a least-squares fit to the data points and the dashed line represents the literature value.

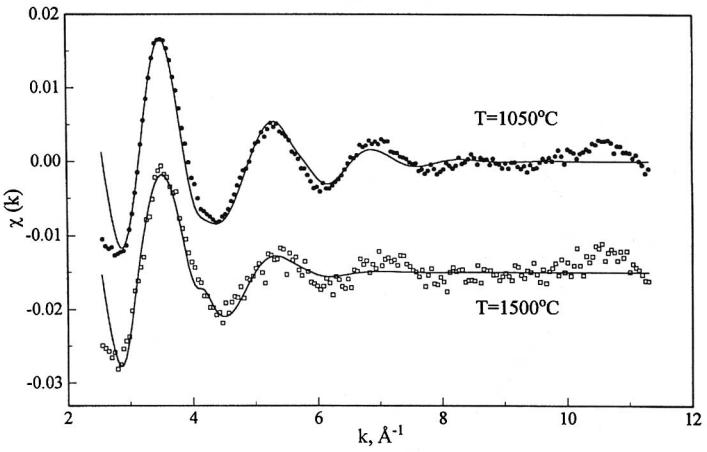

Fig. 4. EXAFS spectra of liquid $Co_{80}Pd_{20}$ obtained at an overheating of about 110 °C and an undercooling of about 290 °C. The solid lines represent least-squares fits to the data points. For reasons of clarity both curves are shifted against each other.

palladium atoms, R_{Co-Pd} (Fig. 5) and the corresponding Debye–Waller factors σ^2_{Co-Co} and σ^2_{Co-Pd} (Fig. 6) over a temperature range of 420 °C including an undercooling of more than 310 °C. In the harmonic approximation, Eq. (7), the increase of nearest-neighbor distances and Debye–Waller factors indicates a positive thermal expansion coefficient.

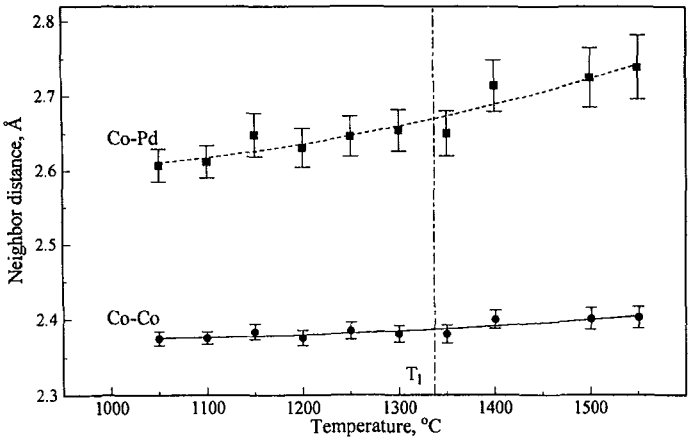

Fig. 5. Mean value of the nearest-neighbor distances R_{Co-Co} and R_{Co-Pd} in liquid $Co_{80}Pd_{20}$. The liquidus temperature is 1337 °C.

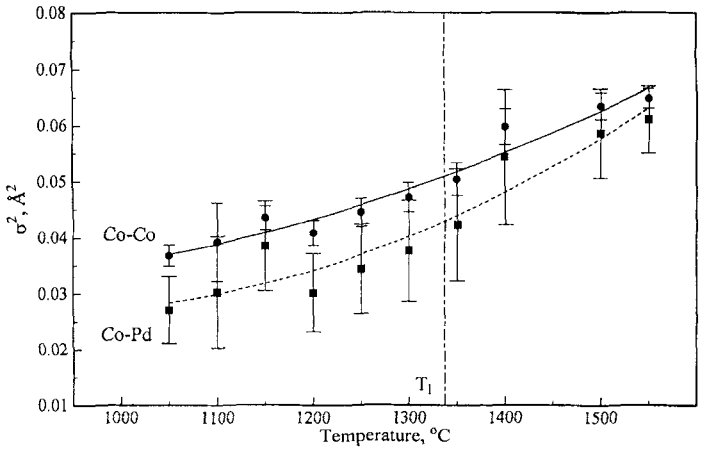

Fig. 6. Debye–Waller factors $\sigma^2_{Co\,Co}$ and $\sigma^2_{Co\,Pd}$ in liquid $Co_{80}Pd_{20}$. The liquidus temperature is 1337°C.

3.3. Summary and Outlook

As we have shown, electromagnetic levitation opens the way to structural and thermophysical investigations of undercooled liquid metals. We plan to perform density measurements on CoPd. Combining the results of density measurements with knowledge about the short-range order in the liquid could lead to interesting insights into the origin of thermal expansion in liquids.

ACKNOWLEDGMENT

Two of the authors (I. E. and G. J.) want to acknowledge A. Filipponi (BL 18, ESRF) for his help during the EXAFS measurements and the introduction to the GNXAS method.

REFERENCES

1. I. Egry, S. Sauerland, and G. Jacobs, *High Temp. High Press.* **26**:217 (1994).
2. I. Egry, G. Lohöfer, E. Gorges, and G. Jacobs, *J. Phys. Condens. Matter* **8**:9363 (1996).
3. L. M. Racz and I. Egry, *Rev. Sci. Instrum.* **66**:4254 (1995).
4. E. Gorges, L. M. Racz, A. Schillings, and I. Egry, *Int. J. Thermophys.* **17**:1163 (1996).
5. B. K. Teo, in *EXAFS Spectroscopy*, B. K. Teo and D. C. Joy, eds. (Plenum, New York, 1981), p. 13.
6. P. Lagarde, in *Amorphous Solids and the Liquid State*, N. H. March, R. A. Street, and M. Tosi, eds. (Plenum, New York, 1985), p. 365.

7. S. Watanabe and A. Saito, *Nippon Kinzoku Gakkaishi* **35**:554 (1971).
8. G. Jacobs, I. Egry, K. Maier, D. Platzek, J. Reske, and R. Frahm, *Rev. Sci. Instrum.* **67**:3683 (1996).
9. A. Filipponi, A. Di Cicco, and C. R. Natoli, *Phys. Rev. B* **52**:15122 (1995).
10. A. Filipponi and A. Di Cicco, *Phys. Rev. B* **52**:15135 (1995).