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Thermophysical property measurements at high temperatures for liquid metal alloys and Gd$_2$O$_3$-doped UO$_2$ samples

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Rice University, 1993
RICE UNIVERSITY

Thermophysical Property Measurements At High Temperatures For Liquid Metal Alloys and Gd₂O₃-doped UO₂ Samples

by

Pou-Yung Lee

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Master of Arts

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ABSTRACT

Thermophysical Property Measurements At High Temperatures For Liquid Metal Alloys and Gd$_2$O$_3$-doped UO$_2$ Samples

by

Pou-Yung Lee

New techniques for obtaining various thermophysical properties, i.e., densities and incremental enthalpies of selected materials at high temperatures have been developed with emphasis on the utilization of levitation technique and drop calorimetry. The density of liquid copper has been evaluated at 1550K. The incremental enthalpies of various Gd$_2$O$_3$-doped UO$_2$ nuclear fuel pellets have been obtained at temperatures between 1700 and 2100K. Determinations of incremental enthalpies, the heat of fusion and specific heats for a liquid Ni-based superalloy have been carried out using levitation drop calorimetry. Contact angle studies between liquid titanium and selected ceramic materials have also been performed.
Acknowledgement

Sincere gratitude would I like to extend to Dr. John L. Margrave under whose generous and considerate advisorship would I be supported and allowed to cultivate and demonstrate research capability through these projects, and whose broadly encompassing understanding of subjects maintained the spirit that was the inspiration to the early scientists in their pilgrimages for Knowledge and Truth.

Appreciative thankfulness would I like to express to Dr. Robert H. Hauge from whose hand-on in-situ elucidation and rectification of malfunctioning laboratory apparatus and insightful suggestions in apparatus design and theories have I acquired fundamental practical knowledge of scientific research.

To my colleagues in the group, I am in debt for the much comity they have furnished and the presentational skills they have manifested in the numerous group sessions for my personal erudition.

To my sister Chi-wei whose support in the culinary aspect of life has been tremendous, no words expressed here can justify her deeds.

To God be my gratefulness for His mercy and love.

Philippians 4: 6,7.
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Chapter One

Liquid Metal Densities & Surface Tensions

1.1 Introduction

One version of acquiring liquid metal sample profiles, particularly those of liquid copper, at high temperature through emissive light photography has been tested. Orthogonal cross-sections of samples were collected concurrently and later analyzed for calculation of first volume, then density information. Results were compared with literature values. Meaningful relationships between density and surface tension at high temperature will be sought. History of past endeavors in the study of surface tensions for liquid metal drops will also be presented for broader perspective. Paraphernalia that are under deliberation for fine control with the goal of establishment of symmetry in the sample shapes will also be discussed.

1.2 Background Information

1.2.1 History

1.2.1.1 Importance

Densities of metals at high temperature, i.e., in the liquid state, as a function of temperature, are of essential importance for both scholars of fundamental science and engineers for industrial applications. The studies of liquid metals require density values for calculations of other secondary properties like structure factors and radial distribution functions. Density data also allow the calculation of thermal expansion coefficient of metals and alloys for use in important commercial processes like casting. In our experimental set-up,
drops of metals or alloys in the liquid state with volumes smaller than one cubic centimeter have been studied. Concomitantly, we are also interested in the surface tensions of liquid metals and alloys because understanding of the surface tension phenomenon can offer us insights about the shapes, and thus indirectly, the volumes, of drops at high temperature. While density data for low-melting metals and alloys at ambient temperature abound, relatively few works of acceptable reliability have been reported in the literature relating to densities of metals and alloys in liquid state at high temperatures, attesting to the inherent experimental difficulties in such researches caused by contamination, etc. Similarly, surface tensions of drops in general have been extensively studied only at low temperatures. Swiatecki succinctly explained such interests by noting that the analysis of drops in rotation while maintaining globular shapes by means of surface tension is

‘a special case of a single mathematical structure... which embraces in a unified manner the equilibrium of rotating masses representing at one extreme idealized atomic nuclei, at the other idealized heavenly bodies, and covering in between engineering applications in weightless space laboratories.’

Most of the fluids that are familiar to us display Newtonian viscosity: the flow is dissipative with the stress being linear in strain rate. Thus, stellar and nuclear systems, having a dissipative and radiative nature, can be modeled by bubbles and drops of Newtonian fluids. Bohr and Wheeler first used uniformly charged liquid drops under strong surface tensions as models in picturing atomic nuclei. Classical Newtonian hydrodynamics and Maxwellian electrostatics have also been applied in calculation of nuclear oscillation, or in construction of simulations. At the other end of the spectrum, self-gravitating blobs have long been used as models for stars. This is because a
close analogy can be established between volume change and surface tension when a drop is under dominating effects produced by its internal gravity or surface tension. An inverse-distance dependence is observed in the energy of self-gravitation and also in the electrostatic energy. Nuclear physics and astrophysics are thus linked in the study of drops\textsuperscript{3,4}. Between these two subjects, are other studies in fields some of which are related to ours, i.e., the study of chemistry and physics at alkali metal liquid/solid interfaces. In situations not unlike what we have often found ourselves to be in, Barker\textsuperscript{5} who has done researches in the aforementioned area, noted that often like scientist/engineers in industry, he found usually only a general background in theory existed, with no good explanation available for specific experimental puzzlement.

1.2.1.2 Contact methods

Density data for liquid metals can be acquired by the following methods: Archimedean, Pycnometric, Dilatometric, Maximum Bubble Pressure, Manometric, Sessile Drop, Gamma Radiation Attenuation and Levitation Melting methods. Please consult references \textsuperscript{6} and \textsuperscript{7} for in-depth discussions of these methods. A comparison of their essential features is listed in the following page\textsuperscript{8}. All but the first and last methods suffered reliability problems caused by the extreme reactivity of liquid metals and alloys with the container materials, resulting in contamination.
<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Levitation Melting Method</td>
<td>*non-contact technique, no contamination from crucible or holder</td>
<td>*instabilities due to rotation, vibration and oscillation</td>
</tr>
<tr>
<td></td>
<td>*can be used in vacuum, or in any special atmosphere</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*no correction for thermal expansivity and volume change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*fast attainment of high temperatures</td>
<td></td>
</tr>
<tr>
<td>Archimedean Methods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(direct and indirect)</td>
<td>*very simple</td>
<td>*contamination from crucible, suspension wire, and sinking vessel</td>
</tr>
<tr>
<td></td>
<td>*continuous density measurement</td>
<td>*contact angle correction needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*large volume of liquid sample needed</td>
</tr>
<tr>
<td>Pycnometric Method</td>
<td>*absolute density measurement is possible</td>
<td>*contamination</td>
</tr>
<tr>
<td></td>
<td>*simple</td>
<td>*thermal expansion corrections</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*good only for low-melting metals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*unsuitable for continuous measurements.</td>
</tr>
<tr>
<td>Dilatometric and Manometric</td>
<td>*small amount of liquid sample</td>
<td>*contamination</td>
</tr>
<tr>
<td>Methods</td>
<td>*continuous measurement</td>
<td>*vessel calibration necessary</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*liquid meniscus correction</td>
</tr>
<tr>
<td>Maximum Bubble Pressure Method</td>
<td>*high temperature measurement is possible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*can be used for reactive metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*contamination</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*thermal expansion correction needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*not accurate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*large volume of liquid metal needed</td>
</tr>
<tr>
<td>Sessile Drop Method</td>
<td>*can be used for reactive metals</td>
<td>*contamination from the substrate material</td>
</tr>
<tr>
<td></td>
<td>*accurate</td>
<td>*symmetric shape is needed</td>
</tr>
<tr>
<td></td>
<td>*wide range of temperature</td>
<td></td>
</tr>
<tr>
<td>Gamma Radiation Attenuation</td>
<td></td>
<td>*sensitive radiation counter needed</td>
</tr>
<tr>
<td>Method</td>
<td>*accurate</td>
<td>*only for low melting point metals and alloys.</td>
</tr>
<tr>
<td></td>
<td>*no contamination since x-ray beam penetrates the bulk</td>
<td></td>
</tr>
<tr>
<td></td>
<td>*no correction necessary</td>
<td></td>
</tr>
</tbody>
</table>

Table 1-1 Density Measurement Methods Comparison Table
Surface tensions for liquid drops have been measured using one of the following methods: Balanced columns\textsuperscript{9}, Pycnometer\textsuperscript{10}, Immersed-sinker\textsuperscript{11}, Maximum bubble pressure\textsuperscript{12,13}, Inert refractory plaque\textsuperscript{14}. For more discussions and references, please see footnote \textsuperscript{15}. Urbain has provided an excellent discussion on difficulties related to these methods\textsuperscript{16}. Shapes of bubbles and drops can become more complex when surface tension is not the only dominating force. Normally, gravity needs to be taken into consideration. Pendant and sessile drops are axisymmetric forms of bubbles and drops that have long been used in the study of surface tension. Again, the interaction of samples with supporting apparatus presented a major obstacle. This was especially true when liquid metals were studied. The only accurately known surface tension of a liquid metal so far, is that of mercury. For the other metals, values reported by different parties tended to diverse than converge\textsuperscript{17}. Experimental studies on the surface tensions of liquid metals have been reviewed by Kozakevitch\textsuperscript{18,19}, Semenchenko\textsuperscript{20}, Wilson\textsuperscript{21} and Allen\textsuperscript{22}. A table of surface properties of liquid metals at the melting point has been prepared\textsuperscript{23}. Evans and Kumaravadivel have established the surface tension and ion density profile of a liquid metal\textsuperscript{24}.

1.2.1.3 Non-contact method

El-Mehairy and Ward were the first to take advantage of the non-contact nature of the levitation method for density studies of liquid metals\textsuperscript{25,26}. High-speed 35-mm emitted-light photography was utilized on levitating samples. With an exposure time of 1/200 second, samples were "frozen" to eliminate errors introduced by vibration, rotation and oscillation. Other advantages were that no impurity corrections were necessary in vacuum or special gas
atmosphere environment. The two views of sample drops acquired were from the top and from the side. The top profile was for determination of circular symmetry of the drops. The side profile view was used also for symmetry determination, and allowed calculation of the volumes of the drops once symmetry was ascertained. Volume calculation was done by numerical integration (Note 1). A formula for the density of copper between 1000 and 1800 °C is:

\[
D \text{ (g/cm}^3\text{)} = 9.370 - 9.442 \times 10^{-4} \times T \text{ (°K)} \pm 0.026 \quad \text{Eq. I-1}
\]

which gives generally good agreement with experimental data. Molar volume and thermal coefficients of expansion were also calculated for copper. In liquid state, copper was found to expand 3.34 pct. In the case of nickel, it was commented that extensive supercooling was frequently observed. Densities of liquid metal both in the superheated and supercooled liquid states were thus measurable.

Sakuma and Saito utilized a similar set-up for density determinations of Ti, V, Cr, Mn, Fe, Co and Ni between 1800 ~ 2200 °C and presented an insightful discussion on experimental problems like oxygen contamination\textsuperscript{27}.

1.2.2 Theory

1.2.2.1 On Surface Tensions and Densities

An interface existing between two (fluid) media will apply a shear stress on the adjoining bulk fluids with a surface tension gradient resulting. Viscosity of the bulk propagates the effect of this gradient into the bulk. It has an intrinsic tendency to resist any movement resulted from any other causes\textsuperscript{28}. 
In other words, "motion within a drop or around a bubble brings inertial and viscous forces into play, and these by their action on the interface recruit surface tension as well."\textsuperscript{29}

Lord Rayleigh\textsuperscript{30} has derived the oscillation frequency of a conducting charged liquid drop, with charges $Q$, under the restoring force of its own surface tension:

$$\omega = [8\sigma (1 - Q^2 / 16 \pi R^3 \sigma) / R^3 \rho]^{1/2}. \quad \text{Eq. 1-2}$$

where $\sigma$ and $\rho$ are the surface tension and the density of the liquid, and $R$ is the drop radius. If $Q_R = (16 \pi R^3 \sigma)^{1/2}$ is the Rayleigh critical charge\textsuperscript{31}, then also

$$\left(\frac{\omega}{\omega_0}\right)^2 = 1 - \frac{Q}{Q_R}. \quad \text{Eq. 1-3}$$

For a nonconducting charged drop, Wong and Tang\textsuperscript{32} arrived at the same results with the characteristic angular frequency of uncharged drop being:

$$\omega_0 = (8 \sigma / R^3 \rho)^{1/2}. \quad \text{Eq. 1-4}$$

From Eq. 4, once the oscillation frequency of the drops is measured and its density calculated, surface tension can be derived. Statistical mechanical relation, (Buff\textsuperscript{33}, Harashima\textsuperscript{34,35}) and a mechanical treatment for the anisotropy of the stress tensor in the surface region (Kirkwood and Buff\textsuperscript{36}, Green\textsuperscript{37}) are two other methods. If the liquid is of one component and at equilibrium with its own or inert vapor, the Helmholtz surface free energy per unit area is the same as the surface tension. The respective units are dyne cm\textsuperscript{-1} and ergs cm\textsuperscript{-2}, which are dimensionally equivalent.
When there is any change in temperature, electrical potential or composition, surface tension is perturbed. The Marangoni effect occurs when a surface tension gradient results from any of these perturbations, appearing along an interface, causing a flow to transpire. In addition, Carruthers noticed that in some instances, "Marangoni instability" can transform a gradient perpendicular to the interface into relatively steady convection. This could pose an insurmountable obstacle for techniques of material processing in space, in which absence of convection is desired when crystal growth and solidification are of a nonisothermal nature.  

For a one-component liquid, the surface tension should have an inverse relationship with temperature. At the critical temperature, the surface interface disappears, with surface tension becomes zero. This is stated in Eötvös' Law:

\[
\sigma_{LV} \left( \frac{M}{\rho_L} \right)^{2/3} = k \left( T_c - T \right) \quad \text{Eq. 1-5}
\]

with \( M \) the gram molecular weight, \( \rho_L \) the liquid density, and \( T_c \) the critical temperature. In non-metallic liquids, substitution of \( \rho_L \) by \( (\rho_L - \rho_V) \) in Eq. 1-5 can offer better agreement with empirical data when the density of the vapor phase \( \rho_V \) is significant. If the molecules are symmetric, dissociative and of covalent or molecular liquids, the Eötvös constant \( k \) is about 2.1. For liquid metals, its value approaches 0.64 erg K\(^{-1}\). Another equation that has been found applicable to describe temperature effects on surface tension, is the van der Waals equation:

\[
\sigma_{LV} = \sigma_0 \left[ 1 - \left( T / T_0 \right) \right]^n \quad \text{Eq. 1-6}
\]

with \( \sigma_0 \) and \( n \) being constants, and \( n \sim 1.2 \) for dissociated nonmetallic liquids.
Several theories have been developed to explain the surface tension phenomenon in liquid metals. Lattice model, Distribution function method, and Electron theory were reviewed by Shimoji\textsuperscript{41}. In the Electron theory (Frenkel\textsuperscript{42}, Breger and Zhukovitskii\textsuperscript{43}; Huang and Wyllie\textsuperscript{44}, Stratton\textsuperscript{45}, Flynn\textsuperscript{46}, Smith\textsuperscript{47}, Lang and Kohn\textsuperscript{48}), it is speculated that depletion of bulk metal electrons and an excess in the bulk vapour generates formation of a double layer at the metal-gas boundary. This could explain, besides the speculation of formation of oxide, why in our experiments, once melting starts but before complete melting takes place, a mantle of shadow can be seen forming and receding on the surface of samples.

1.2.2.2 Non-metallic impurity effect

The interactions of non-metallic elements with the surface of liquid metals and alloys demand special attention because of the strong surface-active features and ubiquity of certain non-metallic elements. For example, oxygen, sulphur, and selenium dissolve readily in liquid iron\textsuperscript{51-55} and liquid copper\textsuperscript{54,55} and drastically affect the surface tension.

Even if Henry’s Law holds true because of the small concentration of these species present for reactions, surface tensions of the sample can still be significantly affected. Studies have been done on the effect and nature of interactions between oxygen, sulfur and liquid metal surfaces. Formation of an oxide or sulfide monolayer was postulated. Kozakevitch suggested that the surface of melts such as Fe-O and Fe-S is comprised of an double layer of ionic nature, a “compound” with a structure in which the “anions” (from the electronegative atoms) resting on the top of the metal cations. At the surface, a close packed layer of anions\textsuperscript{56} is postulated to be the actual packing of
adsorbed species. This layer may be significantly looser when compared to that in the solid state\textsuperscript{57}.

Even at low concentrations, because sulfur atoms are of larger atomic size and more easily polarized in the presence of iron, sulfur is more surface-active. 0.002\% is a limit below which surface sulfide formation decreases steadily with less perturbing capability on surface tension. Nonetheless, the surface tension of liquid iron can diminish by 10\% in the presence of as little as 0.01\% oxygen or 0.005\% sulfur at 1550\degree C\textsuperscript{58}. Only an oxygen pressure of 6.2 \times 10^{-16} \text{ atm} is required to produce an equilibrium amount of 0.01\% in solution and causes a 10\% reduction in surface tension. The same phenomenon is observed in the case of copper\textsuperscript{59}. Gases like purified hydrogen, helium, or argon are not considered surface-active. A table of area per adsorbed atom at the surface of liquid metals has been prepared by Shimoji.

Harper\textsuperscript{60} has recommended a method to make good use of surface-active contaminants. A surface tension gradient mechanism produced by composition variation can offer reinforcement of the effect of viscosity and dampening of motion. This is the Plateau-Marangoni-Gibbs effect. It can hamper translational movement, govern oscillation, and control breakup.
1.3 Experimental

1.3.1 Lab set-up for free-falling samples

1.3.1.1 Apparatus

Drops were levitated in a stainless steel chamber of approximately twelve-inch inside diameter and sixteen-inch depth. Various Pyrex windows allowed functions like optical pyrometry and photography to be performed from outside the chamber while maintaining low vacuum or positive atmosphere pressure of selected gas(es). (Figure 1-1)

![Diagram of free-falling sample setup]

Figure 1-1. Top and side view of free-falling-sample setup

Before each run, the chamber was evacuated to a vacuum of 30 micron of mercury, then backfilled with helium or helium/argon mixture. A 30 kwatt, 400 kHz, Lepel RF Frequency generator, model T-30-3-KC-SW was used to provide power. High voltage power was modified by a 4:1 transformer for
maximum coupling with the samples in the levitation coils. Selected mixtures of gases were introduced through flange thru-put tubing depending on extent of cooling desired. Two sets of mirrors were located to reflect orthogonal views of samples during its free-fall.

1.3.1.2 Data Acquisition

Nikon N-2000 model single-reflex-lens camera fitted with Micro-105 f/2.8 microlens and TC-14A teleconverter lens was used for photography. Kodakcolor Gold 1600 film was used. ASA was set at 1600, with shutter speed set at 1000th of a second. Different f-stops were used. High f-stop numbers were most often used to obtain the advantage of better depth of field. After power was cut, pictures of the samples were taken when they dropped a distance of two inches down from their original levitating positions in the coils. Film was developed at local camera shops. Prints were enlarged and processed in the darkroom in the Department of Material Science with magnification from 5x to 7x.

1.3.1.3 Data Analysis

Prints were scanned into digital form utilizing ThunderScan scanner working on an Apple Imagewriter II in resolution of 300 dots per inch. Sample images were magnified 300% in the process. Calibration and analysis of images were done on an Apple Macintosh II computer using "Image" software. Calibration was done by photography after replacing the sample with a micrometer ruler, assuming no other optical correction necessary. (Figure 1-2)
Copper Sample Digitized Photograph with Computer Generated Gridlines Superimposed

Copper Sample Profile after Edge Extraction with Computer Software

Scanned sample image equipartitioned for volume calculation

Total Volume = \sum \text{all slices}
Volume of each slice = \left( \frac{(d_n + d_{n+1})}{4} \right) \text{Sqr} \times \Delta h \times \pi

Figure 1-2a. Volume calculation from sample profiles

Porfile of levitating sample as seen in Camera with Calibration Grid

Top View of levitating sample as seen in Camera & Radiance Quadrant Detector

Figure 1-2b. Volume calculation from sample profiles in alternative experimental setup
1.3.2 Lab set-up for levitated samples

The levitated-sample lab set-up was in most part similar to free-falling sample set-up except the photography plane was relocated upward for photography of the levitating sample in the coils. (Figure 1-3)

![Diagram of levitated-sample setup]

Figure 1-3. Schematic of levitated-sample setup

1.3.3 Alternative levitated-sample lab set-up

Provisions were made for the top/base-lateral views setup used by Ward and Saito. (Figure 1-4)
Figure 1-4. Alternate Levitated-Sample Setup
1.3.4 Stabilization devices under consideration

Vibration, rotation and oscillation of an unpredictable nature presented the biggest problems in the photography processes. Three experimental devices have been designed for control of these undesired features.

1.3.4.1 Stabilization ring/Current Concentrator

Begley et al\textsuperscript{61} have suggested that by replacing the upper levitation coils with a water-cooled ring plate rotatable along an axis perpendicular to the central axis of the coils, the stability of the sample can be improved because the ring plate can be tilted to compensate any lack of symmetry in the field. Ward et al\textsuperscript{62} proved the functionality of such device.

1.3.4.2 Gas jet control

![Gas jet control diagram](image)

Figure 1-5. Gas-jet-induced stabilization

The gas inlet tubing which points downward directly on the sample during levitation for control of cooling and dispersion of evaporated material from the sample, can rotate in an axis parallel to that of the central coil axis. In the process of experimentation, it has been observed that at times, by moving this tubing off the center of the sample, directing the stream of incoming gas only onto one side of the sample, the rate of rotation of the levitated sample drop could be abated. A gas jet nozzle design has been developed to be introduced from one of the window ports of the chamber with two degrees of freedom by
having a bellow-and-spring support. (Figure 1-5) Please see Figure 1-6 for experimental data.

Figure 1-6a. Gas jet control effect

Figure 1-6b. Gas jet stabilization effect

1.3.4.3 Coil design/Current Concentrator

All coils, unless intentionally misformed, will levitate solid metals to a certain extent. But depending on the sample’s size and other physical characteristics, only specific coils can levitate certain samples indefinitely after melting occurs. Comenetz et al\textsuperscript{63,64,65} presented extensive studies on coil designs. A major disadvantage of coils is the lack of symmetry in the electromagnetic field generated. Current concentrators can eliminate this problem and at the same time offer better coupling. A current concentrator is
made of a thin copper plate with copper tubing soldered on it in a specific pattern. (Figure 1-7)

Figure 1-7. Schematic of one version of current concentrator

The shortest path for the current to travel in the plate will take it adjacent to and closely around the centrally positioned sample, providing maximum energy transfer between the coil and sample and a symmetric field around the sample. Because of these advantages, current concentrators are likely to supersede coils as the future energy transfer medium for levitation apparatus.

1.4 Results

1.4.1 Re77, In 718, SS17-4PH, Re108 (Free-falling sample set-up)

For each metal or alloy, no more than one picture was acquired of each sample in each calorimetric drop since only one camera was used with no continuous mode of photography implemented. More than one image could be obtained in each frame if a strobe-light contrivance were available. Historically, ten to fifteen drops were needed for calorimetry and enthalpy measurements. Thus for each type of sample, no more than fifteen pictures were acquired. In practice, ten to twenty percent of pictures were no good
because of either inconsistency in timing in the part of timer which activated electronically the shooting mechanism after a preset delay of time (normally twenty-five millisecond,) or the oscillation or rotation of the drop caused irregular delays in the dropping of the sample after power cut-off. Another ten percent of pictures were discarded because of complications in the calorimetric dropping processes, i.e., sample spinned off the central axis of the coils and thus out of the field of view of the camera. The other seven to nine pictures, with lack of symmetry in the sample free-falling shapes, offered only the fact that drops were of a non-spherical shapes in the process of free falling, contrary to the presumptions of Dr. Bayazitoglu of the Material Science Department. Inconel 718 drops had the best near-symmetric shapes among the four metals and alloys examined. This could be because its samples were relatively smaller than the others with less surface for interactions with non-metallic impurities. Due to the lack of symmetry observed in these runs, a decision was made to adapt a new approach while concentrating on one type of sample.

1.4.2 Cu (Levitated sample set-up)

In Figure 1-8, sequential photographs of a copper sample are shown with the camera f number listed below. The samples were eventually dropped into the calorimeter. These photographs were taken at a relatively constant temperature of 1550 K. The weight of the sample was calculated to be 0.51859 g. The volumes of #2 and #11 shots were analyzed, twice each, and the density values calculated. Using Ward's formula, Density (g/cm³) = 9.370 - 9.442 x 10⁻⁴ x T (°K) ± 0.026 (Eq. 1), at 1550°K, the density of copper should be 7.906 (±0.026). The values are compared in the next table on page 21.
0.51859g
1550°K

Figure 1-8. The time-lapsed orthogonal profiles of a copper sample leviated at 1550°C
<table>
<thead>
<tr>
<th>Frame number</th>
<th>Density, g/cm³</th>
<th>% change from previous value</th>
<th>% difference from Ward's values</th>
</tr>
</thead>
<tbody>
<tr>
<td>#2,Whole</td>
<td>7.58</td>
<td></td>
<td>- 4.2%</td>
</tr>
<tr>
<td>#2,Whole</td>
<td>7.62</td>
<td>2.5%</td>
<td>- 3.6%</td>
</tr>
<tr>
<td>#11,Whole</td>
<td>7.17</td>
<td>3.6%</td>
<td>- 9.3%</td>
</tr>
<tr>
<td>#11,Whole</td>
<td>7.15</td>
<td>3.9%</td>
<td>- 9.6%</td>
</tr>
</tbody>
</table>

1.5 Discussion

1.5.1 Dynamics of drops

The samples studied in the initial set-up were under the influence of gravity and surface tension while having a translational movement downward. Acrivos and Harper had observed that translation of a globule would cause nonuniform viscous interaction on the surface with appearance of nonequivalent dynamic pressure gradient. At one point, surface tension could no longer sustain sphericity of the globule. As sphericity diminished, the flow field was distorted further until no more stabilization of translational movement existed. The motion then became no longer linear but rather helical or zig-zaging. At times drops did “spin off” in our experiments. Even though our drops were never falling long enough to achieve high speed in space, this could still be an interesting note.

Remenyik’s high-speed cinematography of bubbles with oscillations of such a dynamic nature that the bubbles “spit off” small “bublets” from the surface, or even self destruct, can also be observed in our experimentation though the cause might be of different nature. According to Adornato and Brown, a levitated liquid drop would start with a large aspect ratio which diminished while the drop lost its mass until it reached approximately its Rayleigh limit,
evaporating and maintaining its surface charge all this time. The drop would eventually break up as the aspect ratio started to increase once the Rayleigh limit was reached. So apparently, many factors affected such disintegration.

If there were good coupling between the coils and the samples, one way to avoid unmannerly or even disheartening behaviors of the drops, was to crank up power in several stages with enough time intervals for the whole sample to reach thermal equilibrium. Scriven could have explained such practice in noting:

"motion within a drop or around a bubble brings inertial and viscous forces into play, and these by their action on the interface recruit surface tension as well. Small amplitude oscillations leave the inertial effects nearly linear and so normal-mode analysis has been standard in theory and experiment. Early motion of a deformed drop may be virtually irrotational, but viscosity generates vorticity near the interface and diffuses it eventually throughout the drop."*

Another experimental observation by Wong and Tang* can be utilized to improve the stability. They noted that a drop of inviscid liquid, once supplied with surface charge, its oscillation could be controlled by use of coulombic forces.

Ward observed that the rotational speed of the drop around the magnetic axis of the coils increased as temperature increased and that with a decrease of input power, elongation of the profile vertically occurred with the position of the sample drop falling lower in the levitation coils. These were observed in our experimentations also.
Thermal expansion coefficient allows for calculation of volume change upon fusion of a liquid metal. Comparison of the densities of metals as liquids and solids at melting point temperature can also provide such information:

\[ \Delta V_m = (D_s/D_l) - 1 \quad \text{Eq. 1-7} \]

where \( D_l \) and \( D_s \) are the density of the liquid and solid metal at the melting point, respectively. Another method involves consideration of the magnetic behavior of metals. Klemm (quoted by Kubaschewski\textsuperscript{72}), suggested that the entropy of fusion (\( \Delta S_m \)), is directly proportional to the fractional volume change on fusion (\( \Delta V_m \)) and that "the proportionality constant is the reciprocal of 65 cal per degree for what he term "true metals" (Li, Na, K, Rb, Cs, Cu, Ag, Au, Mg, Ca, Al, Co, Ni, Ti, Pb)".

1.5.2 Impurity Problems

The fact that it is a liquid at ambient temperature is the main reason why the surface tension of mercury is accurately known. Surface tension values for other liquid state drops and bubbles all tend to diverge rather than converge, especially at high temperatures. One reason could be the ubiquitous presence of surface-reactive elements like oxygen. In the case of liquid metal drops, the predicament only worsens since at high temperature, \textit{everything reacts with everything}\textsuperscript{73}. Traps for specific gases must be constructed for minimization of contamination caused by oxygen, nitrogen and water. The addition of a diffusion pump should help to alleviate the contamination problem, too.
1.5.3 Copper sample results

The realization of an inadequate vacuum environment and necessary modifications of the chamber for high precision calorimetry allowed only these few experimentally acceptable density values of liquid copper at one particular temperature to be considered for discussion. With density being mass per unit volume, a decrease in the density value can be either attributed to a decrease in mass, or an increase in volume, or the two happening simultaneously, or a significant decrease in mass occurring concomitantly with an insignificant decrease in volume. A proposed explanation for the reduction from Ward’s value could be construed from two factors: the first being weight loss due to evaporation, the second being volume expansion caused by disruption of surface tension induced by contaminating chamber residual gas(es) due to inadequately pre-pumping. The first factor could be supported by observing the 4 to 5 % decrease in the density value between frame #2 and #11, that certainly enough mass could have been lost during the initial stage of heating when higher temperature was achieved and the later lower temperature reached and maintained only through helium gas jet cooling. If this was the case, the initial sample could have weighed some 8 gm, losing some 0.5 gm, or ~ 6% of its mass in the first stage and another 6 % in the much longer though constant temperature stage. The validity of the second factor could be justified by the noticeable reduction in surface tension caused by oxygen gas in liquid metals observed by many. With the chamber being radiatively heated, degassing of the chamber could happen, releasing resiliently residual oxygen molecules. This oxidation phenomenon has also been observed in the latest UO₂/Gd₂O₃ project when even repetition of pumping the chamber down to 10⁻⁵ torr region with assistance of diffusion
pump and then back-filling with 99.999% pure helium did not prevent the formation of a molybdenum oxide layer on the cell when it was heated and kept at 1400 °C. A third possible factor could be inaccurate sample temperature measurement caused by incorrect sample surface emissivity: the presence of significant amounts of contaminating gases with resulting compound formation on the surface would not only disrupt the surface tension but also affect the surface emissivity at the same time. To get agreement with Ward et al., we would need a temperature correction of ~ 280K, (i.e., an emissivity change from 0.1 to 0.015).

1.6 Further Work Needed

The technique and equipment for obtaining density information of liquid metals have been established. With the addition of a diffusion pump and various gas trapping schemes and modules, one showed be able to minimize gas impurity contamination problem in future work. Surface tension information can also be extracted with appropriate procedures.
1.7 Notes

1. If the overall degree of linear enlargement is $X$ then

$$\text{volume} = (\sum a^2 \cdot d)[ \pi / (4 \times 1000 \times X^3)] \ (\text{cm}^3)$$

with $a$, horizontal width of side profile and $d$, height of each horizontal slice of the side profile, being measured in millimeters, to the closest tenth of a millimeter. The density then is

$$D = (w \times 4 \times 1000 \times X^3) / (\sum a^2 \times d) \ \pi \ (\text{g/cm}^3), \ w \text{ being weight of the sample}$$
Chapter Two

High Temperature Enthalpy Studies of Gd$_2$O$_3$ doped UO$_2$, $U_{(1-y)}Gd_yO_2$

2.1 Introduction

2.1.1 General

Thermodynamic properties of Gadolinia (Gd$_2$O$_3$) doped UO$_2$, $U_{(1-y)}Gd_yO_2$, at high temperature, i.e., 700 - 3200 K are of interest to the nuclear fuel industry. In light water reactors (LWR's), improvements in various areas have been noted after doping UO$_2$ fuel units with Gadolinia. Enhancement in reactor performance and protraction of fuel-burn-up time have been observed.

In fast breeder reactor (FBR) accident scenarios, e.g. hypothetical whole core disruptive accident (HCDA) and post accident heat removal (PAHR), these properties are also of essence for reasonable scenario development and analysis.

A controversy concerning the specific heat values of UO$_2$-Gd$_2$O$_3$ at various doping-percentages at high temperatures exists$^{74}$. By obtaining incremental enthalpy data for these materials at selected temperatures, specific heat values can be calculated for determination of the existence of excess specific heat values after doping.

This chapter will present the results obtained for the incremental enthalpy values of $U_{(1-y)}Gd_yO_2$ samples of various doping percentages at temperatures between 1700 and 2100K.
2.1.2 Theoretical

The various types of $U_{(1-y)}Gd_yO_2$ samples were prepared under hydrogen atmospheres with nearly stoichiometric oxygen to metal ratios from solid-solutions of gadolinia and $UO_2^{75,76}$. Exponentially increasing excess heat capacity of $U_{0.927}Gd_{0.073}O_{1.998}$ in the temperature range between 1100 and 1370K was initially reported by Inaba $et$ $al^{77}$, using direct heating pulse calorimetry. The excess heat capacity was later observed by the same group to increase as the gadolinium percentage of the solid-solution was augmented in their subsequent studies.

Controversy as to the origin of excess heat capacity in pure $UO_2$ predated that concerning $U_{(1-y)}Gd_yO_2$. In the case of pure $UO_2$, various investigators have reported an anomalous increase in heat capacity at temperatures above 1500K$^{78,79,80}$, attributing the cause to the formation of Frenkel pairs of oxygen with the formation energy approximated to be 5 eV$^{81}$. Several other investigators$^{82,83,84}$, however, found this value unacceptably large and suggested that the cause could be due to electronic excitation processes with the formation of electron-hole pairs, $2U^{4+} \rightarrow U^{5+}(h) + U^{3+}(e)$, where the electron-hole pair activation energy was calculated to be around 2 eV. After the reevaluation of the dilational heat capacity data$^{85}$ of $UO_2$, taking into consideration the isothermal compressibility and thermal expansion, Browning $et$ $al^{86}$ reversed their opinions and concluded that in $UO_2$, no excess enthalpy is present due to either model at temperatures below 2500K and suggested that excess enthalpy could be present at higher temperatures due to the Bredig transition$^{87}$. 
Inaba et al argued that it is acceptable to attribute the excess enthalpy phenomenon observed in either pure UO$_2$ or U$_{(1-\gamma)}$Gd$_\gamma$O$_2$ to the same mechanism. Thus the dilational term which predominates in the concluding calculation of Browning et al in the case of pure UO$_2$ is not necessarily as significant as in the case of U$_{(1-\gamma)}$Gd$_\gamma$O$_2$ in which case anharmonic heat capacity$^{88}$, thermal expansion and the isothermal compressibility could also be particularly relevant. They speculated that the formation of Frenkel pairs of oxygen is the decisive factor in activating the phenomenon of the excess heat capacity with minor contribution from the formation of electron-hole pairs and that the observed excess heat could be the onset of the Bredig transition as seen in SrCl$_2$$^{89}$, even though Ralph and Hyland$^{90}$ did not observe the presence of the Bredig transition in pure UO$_2$ at temperatures until 2610K.

2.2 Experimental

2.2.1 Apparatus

2.2.1.1 RF Power Supply Source & Heating Coil

A Lepel model T-30-3-KC-SW, 30 kwatt 400 kHz RF generator supplied the power for heating. The voltage was reduced through a 4:1 step-down transformer before it reached the copper coil wound for induction heating of small samples. 1/8” O.D. copper tubing was used for construction of the coil. The inner diameter of the coil was slightly larger than 1”. The cylindrical coils consisted of ten to twelve turns, with approximately 3/16” spacings between turns.
2.2.1.2 Vacuum Chamber

The vacuum chamber consisted of a stainless steel main chamber with various ports on the wall available for implementation of diverse instrumentation, i.e., optical pyrometry, vacuum gauge feed-thrus and in this project, a cell support and dropping mechanism comprising a set of stainless steel rods and ceramic tubes. (Figure 2-1.) The ports that were designated for optical usage were fitted with 0.5" thick Pyrex windows. The calorimeter block with its isothermal jacket was located in the middle and lower region of the chamber. (Figure 2-2.)

![Diagram of Vacuum Chamber Top View](image)

**Figure 2-1. Vacuum Chamber Top View**
2.2.1.3 Calorimeter Block & Isothermal Jacket

The block and the cup were made of aluminum and copper respectively. The entire surfaces of the cup and the tantalum foil that lined the inner surface of the cup were coated with fine graphite powder to provide an optimal heat transfer environment. The lining was to prevent reaction between the hot sample and the cup and no reaction was observed. Two cylindrical tunnels were drilled from bottom on both sides alongside the central axis of the block for accommodation of the quartz thermometer sensor and a heater cartridge.
In this project, the heater cartridge contemplated for electrical calibration was not used.

The jacket itself was made of stainless steel with built-in layers, from outside to inside, respectively: a constant temperature water circulation layer, an originally evacuated vacuum but later helium-filled layer and a Mylar and fiberglass insulation layer. (Figure 2-3)
The original design goal was to construct an optimally insulated calorimeter in which thermal leakage would be minimized. It was later realized that thermal leakage from the calorimeter to the surrounding, i.e., the laboratory atmosphere, still presented a significant correction problem in this design. This problem was particularly astute in this project when samples of significant mass and high temperatures, hence containing tremendous thermal energy, were dropped into the block that was maintained at ambient room temperature. Improved insulation, particularly with the chamber concomitantly evacuated to high vacuum of $10^{-6}$ torr, did help to reduce thermal leakage to sub-millidegree Celsius per second range before and some sufficient time after the drop when the calorimeter block module without and with the fallen sample was in a state of thermal equilibrium. This adversely affected the effort to quantify the thermal leakage energy because the quartz thermometer utilized for temperature measurement was only able to provide valid readings in the millidegree Celsius per second range. Initial experimental runs usually lasted at least eight hours each because of this: more time was necessary for establishment of valid temperature readings for acceptable temperature gradient/thermal leakage correction calculation. In more recent runs, the previously evacuated layer in the jacket was filled with helium to two atmospheres to facilitate and expedite the thermal leakage correction effort.

2.2.1.4 Isothermal Bath Units

The constant temperature water jacket was first connected to a White Rogers refrigeration/temperature control unit that could chill the water down to the ice point and was capable of maintaining temperature to ± 2 °C of set point.
This temperature variation was deemed unacceptable and the jacket was then connected to a Haake Model FE constant temperature circulator unit that was able to maintain temperature to ± 0.1 °C of a pre-selected temperature value if there was no prolonged, i.e., no more than 5 minutes at 1800 °C, radiative heating of the jacket by the sample cell. This inability to remove excess heat was attributed to the small volume of circulating distilled water, approximately four gallons, of the circulator unit and also the ambient temperature of the water source that provided the “chilling” water for the unit. More heat was being supplied radiatively by the sample through the jacket to the unit than being transferred away by the “chilling” water. In the next modification of the calorimetry instrumentation, this problem will be rectified by procurement of a commensurately large container, i.e., a large waste disposal unit, with an adequate amount of water to act as a satisfactory heat sink.

2.2.1.5 Calorimeter Block Temperature Acquisition

A Dymec quartz crystal thermometer Model 2901A was used for calorimeter block temperature measurement. This unit was capable of temperature measurement between -40 to 230 °C. It performed its function by utilizing a small quartz disc as a piezoelectric resonator. The resonant frequency of the crystal sensor varied in relation to the thermal condition of its surrounding. It had an absolute linear accuracy of better than ± 0.15 °C from -40 to 230 °C and better than ± 0.02 °C from 0 to 100 °C, both referred to straight lines through the respective temperature ranges. For short term stability, maximum variation from reading-to-reading at constant probe temperature was less than ± 0.0002 °C for absolute measurements with no reading-to-
reading variation for differential measurements. The long term stability was zero drift less than ± 0.01 °C at constant probe temperature for 30 days.

The sampling time interval could be adjusted at the front panel by turning the knob labelled "Display Interval" from approximately 0.20 to 5 seconds. A reading time of 1 sec was required for resolution of 0.001 °C. The quartz crystal probe was located about one inch below and aside from the bottom of the calorimetry reception cup.

A DATACap, Inc. INSTRU-mate Model 202 data coupler was connected to the Quartz thermometer controller in order to receive the parallel BCD (Binary Coded Data) thermometer data and transmit the data serially to a EIA RS-232-C device, which in this project was the Apple Macintosh IIci computer that was in charge of data acquisition. A customized cable was constructed for this connection between the serial ports of the data coupler and the computer. The Dymec thermometer contained a GPIB port that could be linked up directly to the Mac IIci if a GPIB board was installed. There would be no significant advantage in this alternate setup.

2.2.1.6 Optical Pyrometers

Two two-color IR optical pyrometers were used in this project for sample cell temperature measurements. In the first half of this project, an Ircon Modline Model R-35C10-4-1-1 two-color pyrometer that was capable of measurement between 1500 to 3500 °C was used. After calibration, it supplied a voltage that corresponded to the temperature reading in degree Celsius, i.e., 1655 mV = 1655 °C, to the data acquisition board in the Mac IIci.
In the later half of the project, a Mikron M77EM controller with M77LS sensor was used. This unit was capable of measurements between 900 to 2300 °C. It also supplied a voltage that corresponded to the temperature in degree Celsius. It had a “Slope” adjustment feature on the sensor that would correct the signal sent to the controller for compensation of emissivity differences in the surfaces of various types of samples. The sensor was factory calibrated for either a blackbody surface with temperature ranges starting around 1100 °C or a surface with tungsten characteristics above 1100 °C. Surfaces of greybodies, materials like carbon, graphite, silicon carbide, oxidized steel, oxidized stainless steel, oxidized nickel, oxidized iron and oxidized cobalt, behaved similarly to blackbodies, thus required no adjustment of “Slope” under “Blackbody” setting. Tungsten characteristic emittance were observed in the following materials when the surfaces were not oxidized: molten grey iron, stainless steel, steel, iron, tungsten, cobalt, molybdenum, tantalum, nickel, rhodium, and platinum. For measurements of these surfaces under “Tungsten” setting, “Slope” adjustments would be required. For this project, “Slope” was set to 1.045 after concomitant measurement comparison with a micro-dot dissappearing filament pyrometer assuming the emissivity value of the molybdenum cell to be 0.3.

2.2.1.7 Computer Data Acquisition System

2.2.1.7.1 General

A stock Apple Macintosh IIci configured with 8 megabytes of Random Access Memory (RAM), 80 megabytes of hard disk storage memory was the computing platform, running under Apple Macintosh System Software version 6.0.7. A National Instrument NB-MIO-16XL (multiple-input-output)
board, capable of process control and data acquisition, was installed in the Nubus slot 4 of the Mac IIci. National Instrument LabView II version 2.0.6 software was the programming environment selected for controlling the data acquisition hardware board. The computer receives the calorimeter block temperature data from the quartz thermometer through one of its two RS-232/422 serial ports and the sample temperature data from the two-color IR optical pyrometer through the NB-MIO-16XL board.

2.2.1.7.2 NB-MIO-16XL Board

The NB-MIO-16X series boards were capable of performing tasks like analog, digital and timing input/output (I/O). Their features included a 16-bit analog-to-digital converter (ADC) with up to 16 analog inputs, two 12-bit digital-to-analog converters (DACs) with voltage outputs, eight lines of TTL (transistor-transistor logic)-compatible digital I/O, and three 16-bit counter/timer channels for timing I/O. The 16XL model differed from the 16XH in its software-programmable gain settings of 1,10,100 and 500 for low-level analog input signals in comparison to software-programmable gain settings of 1,2,4,8 for high-level analog input signals of the 16XH model. In this project, only analog channels 1 and 9 were used for the configuration of an unipolar, differential mode, measuring actual input voltage between 0 to 5V, with software-programmable gain set to 1.

The data line between the pyrometers and the computer was particularly susceptible to electrical noise disturbance, especially after the activation of the RF generator power during sample heating. The reason was that the pyrometer was not a ground-referenced signal source. The solution to this problem was the insertion of two 100 kΩ resistors between each individual
channel and the ground channel per instruction diagram for differential connections for floating signal sources on page 2-21 of the NB-MIO-16X User Manual.

2.2.1.7.3 LabView & Program of Data Acquisition (PODA)

Computers evaluate problems digitally in binary state while human beings disseminate information and ideas most efficiently through iconographic illustrations and diagrams. Early programming languages were a compromised medium for communication between digital-minded computers and analog-inclined users. Their vocabulary tended to be cryptic and obscure and thus consigned the task of programming to highly specialized translators who were known as a sub-species of *Homo Sapiens*, the "computer programmers". Even for users whose interactions with computers were of a non-programming nature, they were still required to familiarize themselves with a "simplified" subset of a programming language. The advent of the Apple Macintosh personal computers with its graphical user interface (GUI) dissolved to a significant extent this artificial barrier between end-users and the computers. For example, one only needed to drag the icon that symbolizes the specific file in which one was interested to the trashcan icon in order to delete that particular file, instead of typing curt and abbreviated text commands that must be free of syntax error.

Created in this graphical revolution, the LabView programming environment required no advanced or even any degree in computer science for coding programs. Coding programs in this environment was not unlike drawing up a structural diagram for setting up a modern kitchen. One icon, or in LabView terminology, a virtual instrument (VI), could represent a
microwave oven while another could represent a refrigerator, etc. One structural diagram designed for making scrambled eggs could consist of refrigerator, trashcan, stirrer, oven and sink with lines connected these units in either temporally sequential or functionally relational order. With the NB-MIO-16XL multifunction board and appropriate solid-state relays for interfacing with the various units mentioned in the scrambled eggs task setup, one program could be coded to automate the fine art of making scrambled eggs. On the computer screen there would be icons representing the various types of control gauges, like buttons and digital LCD readout panel similar to those control interface features on the real units, perform the same tasks.

In this project, the file name for the program of data acquisition is PODA(2-Color). The front panel of PODA is shown in figure 2-4. It includes two continuously-graphing displays of both the thermodynamic temperature of the sample in K and the calorimeter block temperature in °C. The “Slope” display indicates the change in calorimeter block temperature in °C per second. The “Sample Read Interval” knob/input panel allows control of the pyrometer data reading intervals. The “Write File Interval” input panel controls the temporal delays before the computer writes once the following set of data to a previously created and named file: the laboratory (computer) clock time, the calorimeter block temperature, the Slope value and the thermodynamic temperature of the sample surface. The “CB” (Calorimeter block) and “Pyr” (optical Pyrometer) buttons enable/disable acquisition of the respective data. The default status is “On” for both. The “Pyr” button is normally pushed off after the free-fall drop of samples.
Figure 2-4. The front panel of PODA (Previous Page)

Figure 2-5. One state of the block diagram of PODA. Looking sideways, the left block is the pyrometer VI. The upper right block is the calorimeter block VI. The lower right block is the data file writing VI.
Figures 2-5 to 2-8 show all cases of the various subVI's utilized in the block diagram. Figure 2-9 is a hierarchical structure diagram of all subVI's of PODA. A subVI is basically a VI that is used by another VI internally. The block diagram demonstrates the aforementioned "structural diagram" graphical overlay.
Configure the A/D converter to Differential inputs, -10V to +10V.

Figure 2-8. The other case of the pyrometer subVI and the other cases of subVI's within it.
Figure 2-9. The hierarchical structure of the various sub VI's used in PODA
2.2.2 Experimental Procedure

2.2.2.1 Sample Preparation

The samples were from the General Electric Nuclear operation in San Jose, California, provided by Dr. C. Patterson. They were encapsulated under vacuum in molybdenum cells and sealed by electron beam welding using a design by Dr. M. S. Chandrasekharaih. (Figure 2-10) This would prevent change in oxidation state of the oxide materials in the sample through interaction with atmosphere. The encapsulated molybdenum cells were then stored in a desiccator for minimization of gas adsorption on the surfaces of the cells. The surface of each cell was degreased by rinsing with methanol before being transferred to the vacuum chamber for heating.

![Diagram](Image)

**Figure 2-10. Encapsulated Sample Cell Schematic**

2.2.2.2 Vacuum Chamber Preparation

The capsules were inductively heated with a Lepel 30 kwatt 400 kHz generator with the samples being simultaneously heated conductively inside. (Figure 2-1 and 2-10) Before heating was initiated, the chamber was evacuated with both a forepump and a diffusion pump that eventually established a vacuum in the $6 \times 10^{-6}$ torr region. This vacuum was maintained for at least an hour if the chamber had been previously maintained in high vacuum, otherwise, the vacuum would be maintained for at least one and a half hours to minimize
the presence of residual oxygen molecules absorbed on the chamber wall. In the early experimental runs, the chamber was sustained in this high vacuum during heating. This condition was modified after realization that irregular thermal energy transfer between the fallen cell and the calorimeter block reception cup due to the variable dropped cell position within the cup caused significant error in the thermal leakage correction calculation. In the new procedure, helium of 99.999% purity was introduced into the chamber until a pressure of 460 torr was established in the chamber before induction heating started.

2.2.2.3 Heating Coil

The heating coil was wound from 1/8” copper tubing, in a single direction with ten turns. Minute amounts of oxygen and other reactive impurities caused formation of a soot-like black fine powder on the inner surface of the coil during heating. Hence, between experiments the inner surface of the coil needed to be brushed to remove this black non-electrically-conductive substance the accumulation of which on the surface of copper decreased its thermal conductivity and thus its energy transfer efficiency.

2.2.2.4 Sample Support/Dropping

The sample cell was inserted into the heating coil, hanging within and supported by the tungsten wire loop (Figure 2-4) and the 1/8” diameter stainless steel rod around which the loop was temporarily attached. A 1/4” ceramic tube encased the 1/8” stainless steel rod except at both ends where protruding out of the ceramic tube was one inch or more of the steel rod at the two sides of the chamber wall. Vacuum integrity would be maintained by
using Cajun and swagelock feedthru fittings and connectors. The stainless-steel-rod/ceramic-tube module was mobile linearly along an axis that passed through the center of the coil and chamber to facilitate alignment of the sample cell in the coil. To drop the cell, the 1/8" stainless steel rod would be withdrawn to the extent that none of it still protruded out of the ceramic tube so that the wire loop would no longer be supported, allowing the sample to fall.

2.2.2.5 Procedure for a Typical Run

The inner surface of the work coil was cleansed sufficiently of any residual surface pollutance. The sample was then installed into the heating coil. The alignment of the sample with the center of the coil and the center of the calorimeter block reception cup was established. The chamber was evacuated to high vacuum with the vacuum maintained a sufficient time, ranging from 60 to 90 minutes, depending on the previous condition of the chamber if it was exposed to atmospheric contamination or not.

The constant temperature bath circulator was already turned on for regulation and maintenance of the constancy of the calorimeter block jacket temperature. Quartz thermometer controller needed to be turned on if it was not left on, at least three hours beforehand for warm-up purposes.

The water pumps feeding the cooling water into the RF generator were turned on. The RF generator main power switch and the heating filament were activated. It would be approximately five minutes before the "Ready" light came on. The two-color IR pyrometer and the computer were turned on with PODA opened, ready for operation.
Helium of 99.999% purity was introduced into the chamber after establishment of sufficient evacuation until a pressure of 460 torr was reached. The calorimeter block radiation gate valve was closed to prevent sample radiation from heating the block. PODA was initiated with a filename, normally consisting of the date, type of sample and experiment order number for the day which were assigned to the data file pertaining to this particular run. RF generator power control was activated and set to a value between 0 and 15 for desired sample temperature ranging between 300 to 2400 °C. The sample cell was heated at a constant temperature for approximately 12 minutes to allow for establishment of thermal equilibrium between the encapsulated sample pellets and the molybdenum cell. The cell position would then be examined and most possibly adjusted for re-alignment because thermal expansion of the stainless steel rod tended to disturb the pre-heating alignment. The radiation gate valve was then opened with the stainless steel rod immediately withdrawn to allow for the free fall of the sample into the reception cup of the calorimeter block. Immediately after the touchdown of the cell, the radiation gate valve and the insulation flap on top of the calorimeter block were closed. The former was for institution of an isolated system enclosed by the constant temperature jacket. The latter was for minimization of thermal leakage from the cell before the establishment of complete thermal equilibrium between the it and the block. The RF generator power was cut off.

The pyrometer subVI of PODA could be turned off at this stage. The shutdown procedure for the RF was initiated by turning off the filament. Five minutes or more would elapse before the main switch and the water pumps were turned off. For the next two to three hours, depending on sample types
and heating temperature, the computer would monitor the calorimeter block temperature and record it at specified time intervals. At the end of this period, the POMA program was ended. It was important that there was no accidental computer power failure during this period or the data file structure would be damaged and the data rendered unrecognizable and inefficacious. The chamber would be pressurized to ambient conditions and the sample cell could be retrieved along the same path it fell down by utilization of a special device consisting of a 1/4" diameter aluminum rod with a copper wire hook at one end for the purpose of engaging the wire loop at the top of the fallen sample if the wire loop has stayed relatively upright. Otherwise, breakage of the wire loop would result, requiring retrieval by lowering and exposing the whole calorimeter block module.

2.2.3 Data Dissemination

The data file was saved by POMA/LabView in a tab-delimited text-only format. Files of this format usually needed to be accessed by other programs through the usage of "Import..." command. The files consisted of records of data acquired. Each record included four items: laboratory time, calorimeter block temperature, difference in the calorimeter block temperature in the past second and the thermodynamic surface temperature of the sample. A "Tab" character was inserted between any two items. A "Carriage Return" character was inserted at the end of the last item, indicating termination of the record. Time intervals between records were user-specified in POMA before experiments, and were 10-seconds in the latest data.

The data of a file were imported into a new document of DeltaGraph, a commercially available graphing software, and the four types of items/values
became four columns that could be manipulated independently. A plot of the calorimeter block temperature versus laboratory time could be plotted. The time when thermal equilibrium was established between the calorimeter block and the fallen sample cell could be thus estimated. (Figure 2-11)

The calorimeter block temperature column was then copied into a new document of Microsoft Excel, another commercially available spreadsheet software. Another column in Excel was formulated to register the difference in any two consecutive calorimeter block temperature values. This second column of difference was copied back to DeltaGraph to be plotted against laboratory time with a curve-fit equation obtained that described the calorimeter block thermal leakage behavior during the purely-drifting period after establishment of thermal equilibrium between the calorimeter block and sample. (Figure 2-12) This equation was used to formulate a new Excel column that calculated and presented the thermal leakage quantity in the user-specified time intervals, i.e., 10 seconds. Another column was then formulated to add these thermal leakage corrections to the original calorimeter block temperature values, presenting a new set of calorimeter block temperature values.

This column of data was then copied into the DeltaGraph document for plotting. (Figure 2-13) The difference between the temperature before drop and the final plateau temperature would be the temperature gained by the calorimeter block if no thermal leakage occurred.
Figure 2-11. Plot of calorimeter temperature versus laboratory time

Figure 2-12. Plot of temperature change of calorimeter block in 10 second intervals versus calorimeter block temperature
2.2.4 Data Analysis

2.2.4.1 Calorimetry Data

The temperature of the calorimeter block was recorded at user-defined time intervals, i.e., 10 seconds, during each run. (Figure 2-11) The change in the block temperature at these intervals was calculated and plotted against block temperature. (Figure 2-12) Assuming the heat loss/transfer between the block and the constant temperature jacket obeys Newton's Law of heat transfer,

\[ \frac{d\theta}{dt} = k(\theta_j - \theta) \]

(k = heat exchange constant, \( \theta \) = cal block temperature, \( \theta_j \) = jacket temperature) i.e., the rate of heat transfer was equal to the product of a heat transfer constant and the difference in temperature between the calorimeter
block and the constant temperature jacket; after curve-fitting data during the drifting period, a linear equation was obtained. This was used for a heat loss correction of the experimental data. Figure 2-11 became Figure 2-13 after the necessary heat loss correction. The change in the calorimeter temperature was then the difference between the initial starting temperature and the averaged final plateau temperature.

2.2.4.2 Sample Temperature

The sample temperature was the averaged value of the thermodynamic temperatures over the 12-minute constant temperature sample heating duration. Correction for the emissivity was made using the value $\varepsilon_{650\text{nm}} \sim 0.3$ for the molybdenum cell.

2.2.4.3 Enthalpy Calculation

In order to calculate the molar enthalpy for the desired type of sample at high temperature relative to its value at 25°C, the following data were needed: A, initial calorimeter block temperature, B, corrected final calorimeter block temperature, C, sample temperature, D & E, moles (from mass) of the molybdenum (cell) before and after the run, F, moles (from mass) of the sample, G, calorimeter block constant, H & I, molar specific heat values of molybdenum at the final calorimeter block temperature and at sample heating temperature respectively. Other corrections that could improve the accuracy of the results were J, sample heat loss through radiation during the fall and K & L, molar specific heat values of the sample at 25 °C and at the final calorimeter block temperature respectively. The molar enthalpy would then be: $(((B - A) \times G) + J - ((E \times I) - (E \times H))) / (F \times C) + (K - L)$. In this phase
of this project, J was calculated to contribute less than 0.5% correction and was thus not considered in all results. Since K = L, this had no effect on the results. The significance of radiation heat losses was minimized by reducing the distance between the heating coil and the calorimeter block to only six inches below the former. An Excel file named “Database” was formatted so that after the input of A through I, enthalpy value would be calculated while at the same time serving also as a database for all results.

2.2.5 Calibration

The calorimeter constant, i.e., the amount of energy required to raise the block 1°C, was obtained by performing drops with empty molybdenum cells since the enthalpy increments for pure molybdenum are well established\(^9\). The value was calculated to be 1.62 ± 0.01 KJ/°C. Runs were performed with pure UO\(_2\) sample for comparison with literature values\(^9\) at high temperature (Figure 2-14) in order to establish the experimental validity of this approach. An electric calibration module should be installed in the future to provide high absolute accuracy.
Figure 2-14. Latest runs of Pure UO₂ sample in comparison with literature values (Hyland and Ohse)

2.2.6 Results for UO₂ - X % Gd₂O₃ Samples

For sample temperature ranging between 1700 and 2100K, the results indicate no excess enthalpy for U₁₋ₓGdₓO₂ than would have been obtained if the two components were separated, heated and measured, i.e., there is simple additivity depending on the amounts of UO₂ and Gd₂O₃, respectively. The results for 3, 7, 10 weight-% U₁₋ₓGdₓO₂ (0 ≤ y ≤ 14.203) are shown in Figures 2-15, 2-16 and 2-17 respectively. In each plot, also shown are the values calculated from a linear combination of enthalpy values for pure UO₂ and Gd₂O₃. It is noted that a linear fit to the experimental points falls quite close to the calculated Gd₂O₃/UO₂ lines in each case. The deviation is thought to be within experimental error, ± 1%. The numerical values for these data points are listed in Table 1. The sample Gd₂O₃ weight-percentage-to-mole-percentage conversion chart is listed in Table 2.
Figure 2-15. Enthalpy values for 3%-Gd₂O₃ doped UO₂

Figure 2-16. Enthalpy values for 7%-Gd₂O₃ doped UO₂
Figure 2-17. Enthalpy values for 10%-Gd$_2$O$_3$ doped UO$_2$
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Table 1 Numerical values of the graphed data in Figure 2-15.2-16 and 2-17
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\[
\text{Weight \% Gd}_2\text{O}_3 \text{in } \text{U}_{1-y}\text{Gd}_y\text{O}_2 = \frac{\text{Atomic \% Gd}_2\text{O}_3 \times 1}{2} \times \frac{\text{M. W. Gd}_2\text{O}_3}{\text{M. W. U}_{1-y}\text{Gd}_y\text{O}_2}
\]

Table 2. Composition Evaluation Conversion Table of \( \text{U}_{1-y}\text{Gd}_y\text{O}_2 \) (0.00 \( \leq \) \( y \) \( \leq \) 0.142)

2.3 Further Work Needed

Several modifications of the instrumentation are being implemented to improve precision and accuracy. The current aluminum calorimeter block have been replaced with a heavier copper calorimeter block with the aim of lowering the temperature rise of the calorimeter block to below 10°C. The removal of the inner insulation layers of the constant temperature bath jacket
will enhance the constant temperature environment. Gas traps for oxygen and water will be installed to minimize impurity problems. A radiation-shield plate inside the chamber between the heating coil and the calorimetry module together with enlargement of the constant temperature bath fluid reservoir will also improve the constancy of the module environment.

Enthalpy data for 6, 8 and 12 %-Gd$_2$O$_3$ doped UO$_2$ are being obtained to supplement the enthalpy data for the 3, 7 and 10 %-Gd$_2$O$_3$ doped UO$_2$. 
Chapter Three
High Temperature Enthalpy Study of a Ni-based Superalloy

3.1 Introduction

"At high temperatures, everything reacts with everything."\textsuperscript{93} This observation elucidates one of the main obstacles of scientific researches at high temperatures when special or oftentimes possibly self-defeating precautionary measures need to be taken for thermodynamic and physical property measurements. A containerless environment is highly desirable for research of this nature because it eliminates the almost certain reactions between the liquid metals and the container, a major contamination headache.

Electromagnetic levitation was first patented by Muck\textsuperscript{94} in 1923. Wroughton\textsuperscript{95} et al developed and introduced the technology for attainment of high temperatures in a containerless environment with conducting materials. Beginning in the late 1960's, this technique was continually refined and utilized by Bonnell, other students and co-workers of Margrave at Rice University for measurement of thermophysical properties of various refractory metals at high temperature.\textsuperscript{96-107}

The thermodynamic characteristics of nickel-based superalloys are of particular interest to the manufacturers of turbine-blades. Enthalpy increments of a proprietary superalloy above its melting point have been measured in a containerless environment.
3.2 Experimental

3.2.1 Apparatus

3.2.1.1 RF Power Supply Source & Heating Coil

The power supply source was the same as in previous chapter.

A levitation coil was required in this project. 1/8" O. D. copper tubing was used for construction of the coil. Various coils were tested and utilized but all were single coils with top and bottom turns counterwound in reverse directions. Initially, coils were constructed of two turns at the top, three turns at the bottom with the I. D. of bottom coils slightly larger than 3/8" to allow sample loading through the bottom. It was found that the bottom turns were not able to provide enough lifting force because the sample disc shrunk into a sphere of smaller radius upon melting, away from the coil and which diminished the lifting force immediately\textsuperscript{108}. In recent experiments, coils constructed of two turns at top, four turns at bottom with the I. D. of bottom coils slightly smaller than 3/8" were used successfully for levitation.

3.2.1.2 Vacuum Chamber

The same stainless steel chamber as used previously was utilized with some modifications, specifically the additions of a helium input control module and a pre-levitation sample support rod (Figure 3-1, 3-2).
Figure 3-1 (above), 3-2 (below) Top and lateral views of chamber
The helium inlet module consisted of a vacuum-tight gas valve with a gas line outside of the chamber and an inverted "L"-shaped Pyrex glass tubing the arm of which could traverse most of 360° with one region of the traversing path coincided with the center of the levitation coil. With the tubing positioned right above the pre- or levitated sample, helium gas could be allowed into the chamber, flowing down immediately on top of and around the sample for achievement of temperature control by conductive gas cooling.

The pre-levitation sample support rod was an 1/4" O. D. "L"-shaped solid copper rod with a vertical copper fitting soldered onto the end of the lower line of the "L" into the center of which a short section, i.e., 1", of 1/4" O. D. Pyrex glass tube could be inserted. This Pyrex glass tube was wrapped with Teflon tape to ensure a snug fit in its insertion into the copper tube fitting. The arm of this rod could also traverse most of 360°, limited by the chamber wall. One region of the traversing path coincided with the center of the levitation coil.

3.2.1.3 Calorimeter Block & Isothermal Jacket

The block module was basically identical to that utilized in the previous chapter. The only differences were that the cup was also made of aluminum and no graphite-painting was implemented because heat transfer rate was not foreseen as a potential problem with the small levitated samples.

3.2.1.4 Isothermal Bath Unit

Identical as in the previous chapter.
3.2.1.5 Calorimeter Block Temperature Acquisition

Identical as in the previous chapter.

3.2.1.6 Optical Pyrometer

The same Mikron M77EM controller with M77LS sensor module of the previous chapter was used. The emissivity behavior of the sample was assumed to be identical to that of tungsten. The “Slope” was set to 1 under “Tungsten” in the module. This assumption probably meant that the absolute temperature accuracy was ± 30 - 40 °C.

3.2.1.7 Computer Data Acquisition System

Identical as in the previous chapter.

3.2.2 Experimental Procedure

3.2.2.1 Sample Preparation

Sample discs of 0.125" and 0.250" thickness were cut from the sample rod of 3/8" diameter provided by Dr. Vinod Kalianpur of the General Electric Company, Schenectady, New York. The smaller sample discs were used for the liquid drop measurements. Holes of 10 millimeter were drilled through the center of the larger sample discs with a 10-mill-diameter tungsten wire looped through it for suspension by the same stainless steel/ceramic tube sample support/dropping module used in the previous studies. The solid samples were not levitated in order to prevent melting. The surface of each sample disc was degreased by rinsing with methanol before being transferred to the levitation chamber.
The disc shape of the samples was used since the sample was in the form of a 3/8" rod and it was found to present substantial difficulty when machined. The ideal shape for samples to be levitated was a sphere or other approximately isogemetric shapes like a cube or a dodecahedron, that could metamorphose into a sphere of the same mass but smaller volume without significant change in all distances between points on the surface of the object to its center in the transition. In this manner, all points on the surface of the sample would be sustained by a relatively constant lifting force and the levitation of the sample would not be disturbed. In the case of the disc-shape sample, the narrow cross-section region of the sample could never extend as close to the coil as the wide cross-section region did before melting to compensate for the exponentially lost lifting force suffered by the wide section region of the sample which would rapidly shrink inward. The result of this was that even though a work coil was good for levitating a solid sample disc, its inner diameter would be too large for levitation of the same sample in spherical shape after occurrence of liquidation. This demanded the utilization of a smaller inner-diameter bottom coil in the project when measurements on the liquid state were desired.

3.2.2.2 Vacuum Chamber Preparation

The chamber underwent a similar preparation procedure as that in the previous chapter for minimization of impurity gas pollution.

3.2.2.3 Heating/Levitation Coil

The work coil regularly showed the formation of a soot like black fine powder on the inner surface, a problem already observed before previously. Hence it
was necessary to remove this undesired layer between runs with a brush. A side effect of this cleaning procedure was an often necessity of readjusting the position of the coils which could be distorted from their original desired spatial location, i.e. the gap between the upper and lower turns between which the sample would levitate could be decreased if the upper turns were brushed down, or the horizontal levels of the coils could be tilted if the brushing was not parallel along the central axis of the coil. If the sample levitation gap was too small, the sample could either overheat to cause excessive evaporation of the sample if it could be levitated or it might simply melt down along the pre-levitation sample support rod because of localized overheating on the surface before its levitation.

3.2.2.4 Sample Loading/Dropping

3.2.2.4.1 Solid Samples

For solid samples, levitation was not necessary. The dropping mechanism of the previous chapter was utilized. The inner diameter of the work coil was slightly larger than the outer diameter of the sample disk to allow the disk to move through with no difficulty. Placement of the tungsten wire loop of the sample disc onto the stainless steel rod of the support/drop module comprised the loading of the sample. Withdrawal of the stainless steel rod would allow the sample to free-fall into the calorimeter module.

3.2.2.4.2 Liquid Samples

Standard procedure was to position the top end of the Pyrex tube of the sample pre-levitation module within the coil gap followed by the placement of the sample disk through the coil gap on top of the Pyrex tube end.
3.2.2.5 Procedure of a Typical Run

The inner surface of the work coil was cleansed sufficiently of any residual surface pollutants. The sample would then be loaded and aligned for accurate free-fall down into the reception cup in the calorimeter block. The chamber was then evacuated until a vacuum in the region of $10^{-6}$ torr was reached. Evacuation for maintenance of this vacuum would be sustained for forty-five to ninety minutes depending on the previous condition of the chamber if it was exposed to atmospheric contamination or not.

The constant temperature bath circulator was already turned on for regulation and maintenance of the constancy of the calorimeter block jacket temperature. The quartz thermometer controller needed to be turned on at least three hours beforehand for warm-up purpose.

The water pumps feeding the cooling water into the RF generator were turned on. The RF generator main power switch and the heating filament were activated. It would be approximately five minutes before the "Ready" light came on. The two-color IR pyrometer and the computer were turned on with PODA opened, ready for operation.

For solid samples, helium of 99.999\% purity was introduced into the chamber after establishment of sufficient evacuation until a pressure of 460 torr was reached. For liquid samples, the chamber was filled with helium of 99.999\% purity until a positive pressure was established in the chamber to prevent entrance of contaminating gas molecules.

The calorimeter block radiation gate valve was then closed to prevent sample radiation from heating the block. PODA was initiated with a filename which
normally consisted of the date, type of sample and experiment order number for the day, assigned to the data file pertaining to this particular run.

For solid samples, RF generator power control was activated and set to a value between 0 and 12 for desired sample temperatures ranging between 300 to 1200 °C. The sample position could be realigned if necessary for dropping purpose. The sample was maintained at a particular temperature for three to five minutes before dropping.

For liquid samples, RF generator power control was activated and set first to a value between 0 and 10 until partial levitation could be observed. Helium flow from the inlet tube was increased to decrease sample temperature. Power was then increased with necessary increase of helium flow until the sample levitated. Power was increased if a higher temperature was desired. The constancy of sample temperature was maintained for a period of three to five minutes before dropping.

In the sample-dropping stage, the radiation gate valve was opened with either the stainless steel rod immediately withdrawn to allow for the free fall of the solid sample into the reception cup of the calorimeter block or by termination of the power supplied to the liquid sample levitation work coil by pushing the “off” button on the power control box. Immediately after the touchdown of the sample, the radiation gate valve and the insulation flap on top of the calorimeter block were closed. The former was for institution of an isolated system enclosed by the constant temperature jacket. The latter was for minimization of thermal leakage from the cell before the establishment of complete thermal equilibrium between it and the block. In the case of solid samples, the RF generator work coil power was deactivated.
The pyrometer subVI of Poda could be turned off at this stage. The shutdown procedure for the RF was initiated by turning off the filament. Five minutes or more would elapse before the main switch and the water pumps were turned off. For the next hour or two, depending on sample types and heating temperature, the computer would monitor the calorimeter block temperature and record it at prespecified time intervals. At the end of this period, the Poda program was quit. It was imperative that there was no computer power failure during this period or the data file structure would be damaged and the data rendered unrecognizable and inefficacious. The chamber could be pressurized to ambient condition if necessary. For the solid samples, the sample disk could be retrieved along the same path it fell down by utilization of a specialized device consisted of a 1/4" diameter aluminum rod with a copper wire hook at one end for the purpose of engaging the wire loop at the top of the fallen sample. For liquid samples, it was necessary to lower the whole calorimeter block module for extraction of the reception cup. The cup was weighed, reinstalled back in the module and the module was then reattached to the chamber.

3.2.3 Data Dissemination

This was identical as in the previous chapter with all variable parameters remaining the same. The following real experimental charts illustrated the steps of thermal leakage correction pertaining to this chapter. Please note the temperature rise of the calorimeter block was only between one and two degrees. The temperature rise of the calorimeter was obtained by the following procedure. First the calorimeter block cooling rate was obtained from a section (Figure 3-4) of the cooling curve after the sample has
equilibrated with the calorimeter block. The temperature behavior of the calorimeter block is shown in Figure 3-3. Figure 3-5 shows the rate of cooling \((d\theta/dt)\) plotted versus calorimeter block temperature. This second curve is fitted with a polynomial equation which is subsequently used to correct for thermal leakage present in the original data.

![Calorimeter Block Temperature vs Time](image)

Figure 3-3. The complete plot of the calorimeter block temperature versus time before thermal leakage correction

Figure 3-6 shows the temperature behavior that would be obtained if there was no heat loss due to thermal leakage. The temperature rise of the calorimeter is the difference between the measured starting and calculated final temperature.
Figure 3-4. A curve-fitted plot of the calorimeter block temperature versus time before thermal leakage correction after equilibration between the dropped sample and the calorimeter block.

Figure 3-5. Plot of the change in the calorimeter block temperature at 10-second intervals versus calorimeter block temperature.
Figure 3-6. Plot of the calorimeter block temperature versus time after thermal leakage correction

3.2.4 Data Analysis

3.2.4.1 Calorimetry Data

Identical as in the previous chapter.

3.2.4.2 Sample Temperature

Sample temperature was the averaged value of the thermodynamic temperature data in the 3 to 5-minute constant temperature sample heating duration. Correction of brightness temperatures was made by assuming the emissivity of the liquid sample sample was ~ 0.10. This leads to ± 15 °C uncertainty in the absolute temperature.
3.2.4.3 Enthalpy Calculation

In order to calculate the enthalpy per gram value of the sample at high temperature relative to its value at 25°C, the following data were needed: A, initial calorimeter block temperature; B, corrected final calorimeter block temperature; C, sample temperature; D, mass of the sample; E, calorimeter block constant. Other corrections that could improve the results were F, G, sample heat loss through radiation and convection during the fall and H & I, enthalpy per gram values of the sample at 25 °C and at the final calorimeter block temperature respectively. The enthalpy value would be: \(((B - A) \times E) + F + G) / (D \times C) + (I - H)\). In this phase of this chapter, F and G were not considered significant in all results while H and I were not available but should be approximately the same, canceling each other. An Excel file called "DatabaseCu&Superalloy" was formatted so that after the input of A through E, specific values would be calculated while at the same time serving also as a database for all results.

3.2.5 Calibration

Copper samples were levitated easily and prepared for calibration purpose. The effort was abandoned because of low emissivity value of copper. The two-color pyrometer was unable to register any significant amount of emissive light from solid copper for valid temperature measurements.

The calorimeter constant, i.e., the amount of energy required to raise the block for 1°C, was assumed to be the same as that of the previous chapter, 1.62 ± 0.01 KJ/gram. An electric calibration module will be installed in the future.
3.2.6 Results

The sample was analyzed with an Energy Dispersive Spectrometer. The composition was found to be 60.77% Nickel, 14.59% Chromium, 9.89% Cobalt, 3.97% Titanium, 2.95% Aluminum, 1.40% Carbon, 0.2068% Vanadium, 0.05461% Hafnium with the remaining 7% possibly being either Tungsten, Molybdenum, and Tantalum with Tungsten the most likely.

The experimental results are shown plotted in Figure 3-7 and listed in Table 3-1. Both the liquid and solid data have been fitted to a straight line with slopes that give heat capacities of 1.26 and 1.08 joules/gram for the liquid and solid state. Total enthalpy values are represented by the following equation:

\[
H^L_T = (1.262 \times 10^{-3})T - 0.686
\]

\[
H^S_T = (1.079 \times 10^{-3})T - 0.728
\]

A partially melted sample with a measured temperature of 1399 K was also dropped and exhibited an enthalpy value intermediate to the liquid and solid as expected. The total heat of fusion can be obtained from the enthalpy difference between the liquid and solid lines near the liquidus-solidus temperature zone. At temperature of 1405 K, a value of 0.299 kilojoules/gram is obtained.
Figure 3-7. Experimental results

<table>
<thead>
<tr>
<th>T drop, K</th>
<th>KJ/gm</th>
</tr>
</thead>
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<tr>
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<tr>
<td>1196</td>
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<tr>
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<tr>
<td>1399</td>
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</tr>
<tr>
<td>Solidus-liquidus</td>
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<tr>
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</tr>
<tr>
<td>1710</td>
<td>1.490</td>
</tr>
</tbody>
</table>

Table 1. Numerical results for the Ni-Superalloy
3.3 Further Work Needed

This work demonstrates the experimental functionality of current laboratory instrumentation for enthalpy measurements on solids and levitated liquid metals. Future projects will include other superalloys, pure elements like gold and hafnium and conductive compounds like TiC, TaC, TiB₂, etc.
Chapter Four
Contact Angle Studies of Liquid Titanium with Selected Ceramic Materials

4.1 Introduction

There is great interest in the interactive behavior of liquid metals like titanium with various ceramic materials. For example, the surface tension of liquid titanium is a significant factor in this process. Photographs have been taken during the process of melting titanium samples on surfaces of selected ceramic materials for studies of the contact angles during the process.

4.2 Experimental

4.2.1 Apparatus

4.2.1.1 RF Power Supply Source & Heating Coil

The power supply source was the same as in previous chapters.

The heating coil was made from 1/8" O.D. copper tubing. It was wound in a single direction with three turns. The spacing between the bottom turn and the turn above it was intentionally enlarged, approximately 3/16" wide, to allow full view coverage of the top surface of the ceramic block with the titanium sample resting on the top. The I. D. of the coil was approximately 3/8".

4.2.1.2 Vacuum Chamber

The same stainless steel chamber described previously was utilized with some modifications, specifically the omission of the helium input control module
(Figures 4-1, 4-2). The pre-levitation sample support module of the previous chapter was retained.

Figure 4-1. Schematic of the instrumentation, top view

Figure 4-2. Schematic of the instrumentation, lateral view
4.2.1.3 Optical Pyrometer

The same Mikron M77EM controller with M77LS sensor module of the previous chapter was used. The emissivity behavior of the sample was assumed to be identical to that of pure tungsten metal. The "Slope" was set to 1 under "Tungsten" in the module.

4.2.1.4 Computer Data Acquisition System

4.2.1.4.1 Sample Temperature

Identical as in the previous chapters.

4.2.1.4.2 Image Digitizing Hardware

A DataCopy model 230M optical scanner with the manufacturer-provided scanning software of MacImage (version 2.20 by Xerox Imaging Systems, Inc.), connected to an Apple Macintosh IIcx computer of the Rice University Computer & Information Technology Institute was utilized for digitizing sample photographs.

4.2.1.4.3 Image Processing Software

The public domain image analysis software, "Image", version 1.13J, written by Wayne Rasband of the Research Services Branch of N. I. H. was utilized for angle measurements of digitized photographs.
4.2.1.5 Video System

A Sony Handycam Model F-55 8-mm camcorder was utilized for video recording of the interaction between titanium sample and the ceramic surfaces.

4.2.1.6 Photography System

A Nikon 2000 camera fitted with a TC-201 2X teleconverter and a Micro 105mm 1:2.8 lens was used for maximum magnification close-up photography of the interaction between the titanium samples and the ceramic pieces. Kodak Gold ASA 200 was the film used. Film was developed at local camera shops.

Prints were enlarged and processed in the darkroom in the Department of Material Science with magnification from 5x to 7x. Kodak Polycontrast II RC FM paper was used for prints. Kodak SII activator, Kodak Ektamatic S30 stabilizer, orbiter bath, fixer, pakosol solution were utilized for print processing.

4.2.2 Experimental Procedure

4.2.2.1 Sample Preparation

One 1/8”-diameter titanium rod was furnished by the Howmet Company. Approximately 3/8” long cylindrical samples were cut from this rod. One side of the samples was filed sufficiently flat to allow stable positioning of the samples on top of the flat surface of the ceramic sample blocks that were 1/4”-side square and 1/8” deep.
The ceramic block samples were cemented to one end of 2" long 1/4"-diameter ceramic tubes that were subsequently inserted into the copper tube fitting of the sample support module. Teflon tape wrapping around the 1/4" ceramic tube at the insertion point was used to ensure a stable vertical orientation of the tube. Figure 4-3.

![Diagram of sample support schematic](image)

Figure 4-3. Simplified sample support schematic

4.2.2.2 Vacuum Chamber Preparation

The chamber underwent a similar preparation procedure as that in the previous chapters for minimization of impurity gas pollution. The exception was that no back-filling of 99.999% pure helium was performed prior to sample heating.

4.2.2.3 Heating Coil

Regular brushing of the inner surface of the work coil was performed for minimization of surface impurity residues for maintenance of efficient power transfer.
4.2.2.4 Sample Loading

In each run a new titanium sample and a new ceramic sample block cemented on a tube were utilized. After attachment of the block-tube module to the support module through insertion of the former into the copper tube fitting of the later, the whole was positioned so that the block was able to be fully viewed in the visualization gap region of the work coil. The titanium sample was then located on top of the ceramic sample block with a tweezer with its longitudinal axis aligned for its cross-section view to be oriented for the 35mm film photography camera.

Minor adjustment was often required for vertical positioning of the titanium/ceramic-block because after evacuation of the chamber, the whole support module experienced a pressure differential that forced the module lower as a result of the fact that the whole module was supported by only an O-ring in the Cajon-fitting of the copper rod on the top chamber flange.

4.2.2.5 Photograph Processing

Development of Kodak Gold 200 films was accomplished in local photography laboratories. After acquisition of the negative films, they were projected with magnifying lens for exposure in darkroom on individual pre-cut 3” x 5” dimension print paper. Exposure times varied between 10 to 30 seconds. The exposed print was immediately placed into Kodak Ektamatic Processor, an automatic Activating/Stabilizing unit, with the appropriate solutions filled. Subsequently, it was submerged in the following solutions for various time spans: fixer for 10 minutes, orbital bath for 5 minutes, water for 15 minutes, and pakosol solution for at least 5 minutes. The pakosol
solution treatment was necessary to prevent the surface of the prints from adhering to the surface of the drying drum in the case of usage of the later for prompt dehydration of the prints.

4.2.2.6 Photograph Digital Scanning and Analyzing

The prints were placed in the flatbed scanner. The MacImage program was started to scan the print at a resolution of 300 dots per inch with 16 grey-level information. After appropriate cropping with MacImage of the area of interest, typically a rectangle including the shining sample and top portion of the ceramic block, the image was saved in a file of “TIFF” (Tagged InFomation File) format. The Image program was started to import the “TIFF” format files. After selecting the angle measurement tool from the tool palette, the two contact angles were measured. The numerical results could be saved into another file of “Text” format for word processing.

4.2.2.7 Procedure of a Typical Run

The inner surface of the work coil was cleansed of any residual surface pollutants. The samples and the support module would then be positioned and aligned for a proper photography session. The chamber was evacuated until a vacuum in region of 10^{-6} torr was reached. Evacuation for maintenance of this vacuum would be sustained for forty-five to ninety minutes depending on the previous condition of the chamber if it was exposed to atmospherical contamination or not.

The water pumps feeding the cooling water into the RF generator were turned on. The RF generator main power switch and then heating filament were activated. It would be approximately five minutes before the “Ready”
light came on. The two-color IR pyrometer and the computer were turned on for operation.

The 8mm camcorder was also powered on and maintained on a "Standby" status. The optical camera viewfinder was then examined for assurance of proper sample cross-section visualization and necessary adjustments were performed. The continuous frame-advancement feature was activated on the camera for 2.5 frames per second regulated photography sessions.

PODA was initiated with a filename, normally consisting of the date, type of ceramic sample and experiment order number for the day, assigned to the data file pertaining to this particular run. 8 mm camcorder status was altered to "Record".

RF generator power control was activated and increased from setting of 0 to 15 in less than a second, concomitantly with the initiation of the optical camera photography session. The sample temperature surged upward to the melting point after a one- to two-second delay. One to two seconds after melting, a gradual eruption from the molten sample surface and overflowing of the molten sample were observed. Power control of the work coil was deactivated at this time. Optical photography, video recording and PODA sessions were also terminated. The chamber would be pressurized to ambient condition. RF generator shutdown procedure would be initiated.

Normally a 32-frame film would record two experimental runs.
4.2.3 Data Dissemination

The pyrometer component of the acquired data underwent a similar procedure as in the previous chapters for dissemination because PODA still recorded the four types of data as in the previous chapter. The difference in this project was that only the pyrometer and laboratory time reference data were of interested and utilized, with the other data discarded (Figures 4-4, 4-5).

**Figure 4-4.** Histogram of titanium temperature (Ceramic type 1, run #5)

**Figure 4-5.** Histogram of titanium temperature. (Ceramic type 2, run 7)
4.2.4 Data Analysis

4.2.4.1 Sample Temperature

The titanium temperature was the averaged value of the thermodynamic temperature data in the 3 to 5-minute constant temperature sample heating duration. Emissivity corrections were made, assuming $\varepsilon_{650\text{nm}} \sim 0.65$

4.2.4.2 Image Processing

Sample-block photographs were at least five-time magnifications of the true dimensions of the objects of interest. Scanned in the resolution of 300 dots per inch (dpi), the image when exhibited on the Apple 14” high-resolution 72-dpi color monitor, was visually enlarged four times for complete display of all the information in the pixels of the image. Thus measurements of the angles could be performed with 1/1500 inch precision.

4.3 Results

In the video tape that was furnished to the sponsor of this study, two experimental runs were recorded. The video record was mainly for qualitative process control since the magnification was not sufficient to contribute to the quantitative analysis of the angles. The initial view showed the two color pyrometer (blue) on the left and the camera on the right. The background noise was due to pumps. The R. F. coils and sample came into view as the camera was zoomed to its maximum setting. The sample could be noticed between the lowest two coils, locating on the ceramic sample. Immediately before heating the sample, the video camera was switched to its highest shutter speed, one-four-thousandth of a second, causing the screen to
become dark. The sample rapidly heated to the point when it began to erupt and eject material. The second heating was carried out with a blue filter in place in order to prevent camera blooming. The second sample was also rapidly heated to the point where material was erupted. At this point the ignition of a discharge due to gases evolved from the substrate was observed. The entire coils glowed. A slow motion video of this second run followed. The heating and spreading of the sample over the ceramic substrate could be seen prior to sample eruption and discharge phenomena.

![Figure 4-6. Contact angle definition](image)

Results of three runs were analyzed for contact angle measurements. The measured values as a function of time are given in Table 1. The left sides of the samples gave consistently larger angles than the right sides. The angle measurement was defined as shown above in Figure 4-6.

![Figure 4-7. Sample-coil relative position sketch](image)

A possible explanation for the observed phenomenon was that the samples were consistently placed in the region of a coil-generated electromagnetic
force field that was not symmetric in distribution. A simple explanation assuming conductive characteristics of the work coil surface were identical everywhere, would be that the average distance between the sample and the surface of the work coil was shorter at the right than that at the left of the sample (Figure 4-7). The result would be that an unsymmetrical force field in which leftward motion was favorable for the molten sample.

The initial contact angles were high when titanium was in the solid state. The angles decreased with time as the titanium melted. The diminishing of the contact angle persisted as titanium liquified and according to the pyrometer data, remaining at a constant temperature. This continuation phenomenon could be attributed to thermal equilibration of the ceramic block with the molten titanium at the interface region. Four to five seconds after initiation of heating, particle eruption could be observed on the surface of molten titanium. Gas incorporation into the molten titanium from the decomposing substrate was suspected for this observation.

Two types of ceramic samples were provided for interaction with molten titanium. No discernable significant difference was observed in the interactions. Numerical values of the contact angles are provided below in Table 1. Selected photographic data of interaction between titanium and ceramic type 1 in experimentation run #5 are provided in the next page in Figure 4-8.
Figure 4-8's. Ceramic sample type 1, run#6
Frame 6 - 11, all have been digitally retouched for maximum contrast
In current stage of experimentation, surface tension information can not be quantitatively extracted from the contact angle measurements acquired, only comparisons of a qualitative nature can be accomplished.

A possible experimentation modification that could allow for quantitative measurements of surface is shown in Figure 4-9. The titanium samples will be levitated. The ceramic tube with the cemented ceramic sample block will not be supported from below by the sample support module. Instead, it could be attached to a balance from above. The readout on the balance will provide information for all forces acting on the ceramic tube-block, i.e., gravitational force by earth in normal condition. After the titanium sample is stably levitated in constant temperature, surface tension force will be measured when the ceramic tube-sample comes into contact with the molten titanium. Contact angle measurements can be used for calculation of contact area. Cursory surface tension information can thus be obtained. Interpretation of the interfacial tension between molten titanium and oxide-based ceramics will be strongly dependent on the the type of chemical reactions occurring.

![Figure 4-9. Surface tension measurement diagram](image-url)
<table>
<thead>
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<th>Time</th>
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<th>Ceramic Type 2, run 6</th>
<th>Ceramic Type 2, run 7</th>
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<td></td>
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<td>Right Angle</td>
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<td>70</td>
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</table>

Table 1. Numerical values of the results

4.4 Future Work Needed

Another modification of the experiment would be to heat titanium more slowly and observe the change of the contact angle (Ti/Ceramic) as the liquid titanium wets and/or reacts with the ceramic surface.

With the additional implementation of a force measurement device, i.e., a balance, and a stable levitation environment with high precision photography capability, surface tension/interaction behavior of molten metals with selected ceramic materials can be obtained.
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