Final Report

DROP TUBE TECHNICAL TASKS

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Acknowledgements

I appreciate the efforts of many persons in the performance of this work. In particular, Dr. William F. Kaukler, who was extremely helpful in performing the metallurgical aspects of this project and for his leadership in performing the drops. Steve Straits and his colleagues at the Drop Tube did an exceptional job of getting drops whenever possible. Also to Dr. Ed Etheridge for his efforts as technical contract monitor.
I. Introduction

The Drop Tube Facility at Marshall Space Flight Center is a national asset used for studying a variety of solidification phenomena in a low gravity environment or as a containerless processing system. By virtue of the relatively short turn around times required to assess experimental parameters, it is possible to learn much about a particular experiment and possibly its behavior as an experiment aboard the space shuttle or space station, without leaving the ground. A unique facility of this type requires a large amount of resources available to perform the experiments, maintain the equipment and to provide useful information in order to design a good experiment.

The objective of this study was to develop criteria, using fundamental thermochemical dynamics, to assist a scientist using the Drop Tube Facility in designing a good experiment. The types of parameters involved in designing the experiments include the type of furnace, the type of atmosphere, and in general which materials are better behaved than others as determined by past experience in the facility. One of the major advantages of the facility lies in its ability to provide large undercoolings in the cooling curve during the drops. The ability to predict such undercoolings has not progressed due to the lack of information with most systems and lack of a suitable theory to predict such behavior. Consequently, we felt that a good beginning was to consider the effect of oxygen and other gases upon the amount of undercooling observed. The starting point of the thermochemistry was given by Ellingham\textsuperscript{1} and later transformed into what is known as the Richardson Chart (Figure 1).\textsuperscript{2,5} Having the local capability to calculate such quantities presented an early
objective. In addition data was to be obtained from experimental drops of elemental species, in order to observe the effect of surface oxidations upon the nucleation phenomena observed in each specimen.

II. Results

The thermochemical calculations for the free energies of formation have been programmed on two different computers available to drop tube personnel. The first version was programmed using the IBM personal computer and a later version was programmed on the Hewlett-Packard 9836 in the Drop Tube Facility on the 15th floor. This report contains the IBM version of the program, as well as several of the outputs, as Figure 3-6 and Appendix A. The thermodynamics used for the calculation is given in Figure 2. Data is taken from References 3 and 4. A major advantage of using local calculation capability over just extrapolating from Figure 1, is that as newer data becomes available in terms of materials and phase transitions, the drop tube user will be able to determine the thermochemistry more appropriately for his circumstance. Also it is envisioned that the gas effects will be extended to handle many more species in the future. Figures 3-6 show program flow, data presentation screens for NiO and NiO plot from IBM-PC.

The drops performed for this study are included in Tables I-III. In addition, information is given in terms of the mass, the observations performed and the resulting grain or dendrite measurements. As indicated later, we were not able to correlate the surface oxide formation with amount of undercooling, but we did establish that a new parameter needed to be considered for a better understanding of the resulting microstructures.
Gas solubility, not considered previously as important as oxide formation does show in our microstructure analysis that the morphology was affected more by varying ambient atmosphere than by surface oxidation effects. We still have not finished analyzing the specimens obtained during these drops, but Tables I-III summarize the data obtained thus far fairly completely.

A major undertaking of this effort has been the microstructural analysis performed by Dr. William Kaukler who has been extremely active in similar work with low gravity experimentation from drop tower and KC-135 studies. Dr. Kaukler has been assisted by Ms. Donna Warden, an undergraduate student at UAH in performing most of the grinding, polishing and photomicroscopy for the same studies. As seen in Table I, we have used specimens of copper, rhodium, platinum, and nickel. The only reason for using these elements were due to their availability and as far as we knew at the beginning of this work, they were not being worked by other research groups in cooperation with NASA.

III. Discussion of the Results

This discussion is presented to provide information about the type of information obtained from these sets of experiments. The breakdown can be classified according to the following areas:

Specimen Preparation for Metallography
Photomicrography of Specimens
Residual Gas Analysis
Analysis of Dissolved Gases
Summary of Etching Procedures
The complete interpretation and analysis will take some time to finalize. We hope that this preliminary information will be of use to other scientists who are interested in using the Drop Tube in studies of solidification phenomena.

IV. Drop Tube Specimen Preparation for Metallography

Over 60 drop tube specimens were mounted, sectioned by grinding, polished and analyzed metallographically. Tables 1-3 list the drop specimen parameters. Some specimens revealed microstructural details on their exterior surfaces. These specimens were examined by scanning electron and optical metallography prior to mounting and sectioning. Practically all the experimental results are derived from these metallographic studies. Microstructural correlations to the drop conditions are the prime observations. Photomicrograph of several interesting specimens are given in Figures 8-10.

Specimens were as small as 20 milligrams in weight for the electron beam experiments and 200-400 milligrams for the electromagnetic levitation experiments. Such small samples represented considerable difficulty in handling and in the proper performance of metallographic sectioning. All specimens were near perfect spheres and the considerable surface curvature made microscopic examination of exterior features nearly impossible. Surface features were of considerable interest to this study because normal shrinkage of the melt upon crystallization can reveal dendritic morphology, which may yield details of its thermal history. No correlation would or could be made between the site of apparent nucleation on sectioning and the surface morphology. Dendrite arm spacing, if found on the surface could be compared to the spacing, if seen, in the interior region of the specimen.
Most of the time consumed for this study was spent on the systematic development of the various metallographic techniques required to produce acceptable micrographs of the diverse specimen types. Many of the specimens were soft metals which were further softened by their high purity. Soft specimens scratch very easily, are deformed, are susceptible to surface deformation during mechanical polishing, provide little resistance to machining, retain grinding and polishing abrasives by embedding into the surface and cause other minor problems during metallographic analysis. In order to minimize these difficulties, the specimens were individually mounted and had embedded with them in the mount, a ring of glass around the specimen. This ring stabilizes the orientation of the specimen, greatly improves the characteristics of the polished specimen, and permits a less skilled metallographer to achieve superior results.

Each different metal that was studied required its own procedure for preparation. Mounting, grinding, and in general most polishing tasks were done the same way, but skill was required in order to develop and repeat the proper application of these steps. A variety of specimen etching techniques had to be attempted despite the ready availability of previously tested formulas and methods collected in reference texts. The specimens selected for this study were prepared from the most pure elements available. This leads to the most complicated feature of the metallographic studies. When a metal is very pure, morphological features formed during crystallization will not leave clear traces of their passing; whereas common alloys always leave a clear trace of their passing. These features can become indetectable to any method. Nearly always does grain recrystallization occur unimpeded by the pinning effects on grain boun-
daries of solute atoms. Prior structure usually could not be revealed, although dendrite arm spacing measurements on occasion could be made. The heat of recalescence and the slow cooling rates after crystallization together with the high purity enhance the rate of grain growth. At the very least, grain structures could be revealed by some etching techniques. Again the high purity and nobility of some of the elements studied required concentrated effort to find acceptable etchants. If chemical etchants were not successful, some success was obtained with electrolytic etching methods. A facility for electro-etching of metal specimens was established as a result of this requirement (See Figure 11). The high nobility of some of the metals required aggressive techniques for etching. Therefore, the only microstructures revealed were the grain boundaries. Summarized in this report are also the best etchants and additional cautions for such elements studied.

All the specimens had to be mounted in plastic "cold mount" prior to grinding. The best material was found to be a product from SPI, a polymethyl methacrylic material. Specimen mounts were standard metallurgical types, approximately 30 mm. in diameter.

Grinding was performed wet with tap water as the lubricant. Wet/dry grinding papers with corundum grit were used with the standard sequence of 120, 180, 230, 420, and 600 grit for all specimens.

Mechanical polishing was performed at first with alumina polishing suspensions in water having particle sizes of 5, 1, 0.3 micrometers. Coarse and then fine polishing was always performed with billiard cloth for the fine polish and "Super Finale" cloth for coarse. For the latter half
of the study, a more expensive and troublesome diamond polish was performed. Surface finish was superior and polishes were done more quickly, but scratches were always found and highly revealed by the etching process. Both coarse and fine diamond polishing was performed with 1 and 0.25 micrometer diamond particles used in a suspension of diamond polishing oil. The best cloth was found to be "Rayvel" from Beuhler for both grit sizes.

Copper was prepared by the first mechanical polishing followed by a chemical polish prior to the chemical etch. The chemical polish removed the scratches of the mechanical polish and produced a superior surface. The formula is included together with the etchants.

V. Photomicrography of Specimens

Metallographic examination of the drop tube specimens combined exterior observation by optical and electron microscopy with micrography of the polished and etched sections. The features which were examined for included dendrite size and spacing, surface oxidation, grain size, porosity, and sites of nucleation if found. The dimensions of these features are such that only low magnifications are required. Given the dimensional range, more stereological measurements per micrograph can be made for the lower magnifications, thus providing improved statistics.

A Zeiss Ultraphot Research Microscope and Unitron U-II Metallograph were used for optical metallography. A Jeol UM-3 Scanning Electron Microscope was also used for surface examination. Nearly all the metallography centered around the micrography of polished and etched sections of the drop tube specimens. When photographs were taken with the Zeiss microscope, either Polaroid type 58 film (color) or type 57 film
(black and white) was used, and with the Unitron, Polaroid type 108 or 107 film was used. Kohler, bright field illumination was used in most cases. Occasionally, when polished but unetched specimens were studied, Nomarski interference contrast illumination was used to reveal the subtle variations in surface texture. Surface examination and optical photomicrography were done using dark field illumination on the Zeiss microscope. This type of lighting enhances the contrast for the very rough structures, sometimes seen due to solidification shrinkage in interdendritic cavities.

All the special lighting techniques are available on the Zeiss microscope. Three objective lenses yield three different magnifications; 40X, 65X, and 260X. Only Kohler illumination was available with the Unitron U-11 and all micrograph were taken with the 10X objective, resulting in a 136.5X magnification in the photomicrograph.

Except when Nomarski illumination was used (which creates a pseudo-color image), the specimens showed no color. As a result black and white micrographs were taken of these specimens. The exception is the copper specimens which, when etched, revealed various shades of orange and brown. Some color micrographs were taken of these.

VI. Residual Gas Analysis

Knowledge of the quality of the atmosphere in the drop tube environment is critical for studies of this nature. The partial pressures of the significant gaseous species; oxygen, hydrogen, water, carbon monoxide, helium and carbon dioxide collectively can control the chemical potential for reaction at the elevated temperatures used with these types of materials. Either oxidation or reduction of the metal could be per-
formed during its fall through the ambient atmosphere within the tube by suitable gas selection. Even a high vacuum (less than 10^-6 atmospheres) can contain enough oxygen or water vapor to cause some reactive metals to oxidize significantly. Quantification of the amount of these gases can most easily be performed with a residual gas analyzer or mass spectrometer. In our study, a UTI 100C quadrupole was borrowed from another group and used in the earlier phases of the study, but it was an older system and had many problems in providing data when required. Consequently the Drop Tube Facility purchased a Dycor Electronics M/100M series quadrupole mass spectrometer for dedicated use at the facility. This unit was installed at the top of the tube, in the bell jar region above the isolation valve. This unit has a mass range of 1 to 100 amu and utilizes an electron multiplier, thus allowing us to make sensitive partial pressure measures of gases and vapors. Other features of this particular model includes programmed computer control, large CRT display, and printer output of display information. Various display formats are available, including analog, bar representation, tabular, etc.; enabling the data to be displayed a number of different ways.

VII. Performing Residual Gas Analysis on the Drop Tube

The Dycor quadrupole mass spectrometer has been installed into the bell jar region using a scheme which allows the bell jar region to be monitored at both low and high pressure regimes. Two different valves for controlling the sampling parameters of the tube are used in this scheme. A variable leak valve, which allows sampling at very high pressures, is available for pressures above 10^-4 atmospheres and for pressures below that value a manually operated gate valve is available. Using these two valves
the quadrupole is capable of operating over a very large dynamic range. Under the conditions of our measurements, we used the same turbomolecular pump that pumps on the belljar region to pump out the quadrupole region. A major disadvantage of this approach is that the maximum sensitivity of the instrument is not achieved because the sensing environment is not at a lower pressure than the environment being sensed. We have since then installed a Cryogenic pumping system in order to attain pressure values for the quadrupole region to be much less than for the belljar region. In particular it is important to clean up the water vapor if we are to measure it correctly.

For our measurements, we used a value of 125 for the setting on the variable leak valve and systematically stayed with that leak rate. No actual measurement of the leak rate was made since we did not have the cryogenic pump installed and such a measurement would have been difficult. Working with ratios of known gaseous components is sufficient in most cases. In operation, the use of the variable leak valve allowed a controlled leak from the belljar region into the quadrupole region to occur. The continuous stream of gas passed through the ionizer region of the mass spectrometer chamber being pumped upon by the turbomolecular pump. In this way we were able to obtain scans of the belljar atmosphere under prescribed conditions. An example of such a scan is given in Figure 11. A noticeable feature of the scans obtained with this system is that the peak heights are influenced by two parameters not built into the software controlling the display information. One parameter is the efficiency of ionization (and associated cracking pattern) and the other is mass discrimination effects of both the variable leak valve and the mass spectrometer...
itself. This type of variable leak valve uses the volume between two cylindrical surfaces to determine the leak rate and provides a difference in leak rate by varying the overlap region of the two cylinders. Unfortunately this technique does give some mass discrimination and small molecules such as helium and hydrogen do leak at a proportionately higher rate than larger molecules. This can be calibrated and to some extent compensated for, as can other types of mass discrimination once their causes are identified.

VIII. Dissolved Gases

As indicated earlier the major objective of this project was to determine the effect surface oxides would have upon heterogeneous nucleation in undercooled pure metal droplets. This study has indicated that the proper approach is to also account for the effect of gas solubilities, in addition to the chemical reactivity of the various gases present in the atmosphere of the drop tube. Redox reactions and the oxides that result are not the only gas related effects upon the microstructure. Free energies of formation of these oxides and their sensitivity to temperature and pressure were discussed earlier in this report. During the examination of the specimen sections fine dispersions of porosity were found within many of the specimens. The morphology of these pores indicate that they formed as a result of the nucleation of dissolved gas throughout the melt upon cooling. Many specimens show the formation of these pores occurred in the liquid that was last to solidify in the interdendritic regions. The porosity often outlined the interdendritic regions and thus verifies that they resulted from the segregation or partitioning effect of the advancing solidification front.
The cleanliness of these pores prevents a direct assessment of the gas species which caused their formation, hence we felt that a survey of the data for gas solubility was the next best approach order to select the best candidate. One must also recognize that the formation of oxide does not indicate lack of solubility of the oxygen in the melt since solubility measurements do not always preclude a reactive mechanism at work. For porosity to form most readily the solubility of the gas in the solid should be significantly lower than in the melt. In addition, adequate partial pressure of the gas would be required to cause the solution of the gas. In the experiments presented here, the small droplet sizes with their high surface to volume ratios and the high temperatures within the furnace region would ensure rapid solution.

Three elemental gases can be considered that could cause the porosity observed. They are hydrogen, oxygen and nitrogen. Both oxygen and hydrogen also may go into solution from dissociated water vapor that is always in the drop tube atmosphere. The noble gases helium and argon do not dissolve in any metal to a measurable degree. Sievert's Law applies with hydrogen at least

\[ S_a = k\sqrt{P_a} \]

solubility being proportional to the partial pressure of the gas.

A summary of data discussed in reference gives us the following information.

Nitrogen is insoluble in the following metals up to 1400 C. for the following three metals:

Copper
Nickel
Palladium.
Hydrogen is soluble in the following metals:

- **Copper** - 0.03 atomic percent at melting point for liquid
  - 0.009 atomic percent at melting point for solid
- **Nickel** - 0.1 atomic percent at 1453 °C solid
  - 0.2 atomic percent at 1453 °C liquid
- **Platinum** - low solubility
  - 0.0164 atomic percent at 1342 °C. Tm = 1769 °C
- **Palladium** - 0.7 atomic percent at 1552 °C, solid
  - 0.4 atomic percent for liquid
  - High solubility, but decreases as T goes up
- **Rhodium** - little solubility, very low

**Oxygen:**

- **Palladium** - PdO decomposes at 750 °C
  - Solubility is 0.63 atomic percent at 1200 °C.
- **Platinum** - no data found
- **Rhodium** - dissolves a considerable amount at high temperatures. Rh2O3 decomposes at 1100 °C in 1 atmosphere of oxygen
- **Copper** - Copper and oxygen form a eutectic with low solid solubility of oxygen in copper where there was less than 0.036 atomic percent at 1000 °C. The eutectic temperature is 1065 °C and the eutectic (with cuprous oxide) composition is 1.5 atomic percent. There is unlimited solubility of oxygen in copper or nickel some 20 °C above the eutectic temperatures.
- **Nickel** - Nickel and oxygen form a eutectic with increasing solubility with decreasing temperature where we have 0.044 atomic percent oxygen in the solid at 1200 °C. The eutectic temperature is 1438 °C, and the eutectic point is 0.87 atomic percent oxygen.

In summary then nitrogen cannot cause the observed porosity in all cases because of the variety of ambient atmospheres used. Also since the helium-hydrogen mixture contained no more than 5% hydrogen, and the overall pressure used was normally around 200 - 300 Torr, then the partial pressure of the hydrogen would be only around 0.1 to 0.2 Torr. A high solubility of
0.7 atomic percent of hydrogen in Palladium at 1 atmosphere would then give only 0.0001 atomic percent. Alternately, the solubility of hydrogen in copper liquid would only be 0.000005 atomic percent for the low partial pressure of hydrogen in the tube. So it is unlikely that raw hydrogen was solubilized by the melt. The low partial pressure of hydrogen was confirmed as well by the mass spectrometer measurements.

Since porosity was observed predominantly in the nickel samples processed in air and helium-hydrogen mixture and in the palladium samples process in air, it is a fair conclusion that the dissolved gas was oxygen, either from the atmosphere or from the oxide.

IX. Summary of Etching Procedures

1. Chemical Polish for Copper:

   After mechanical polish at 5 micron alumina or diamond grit, submerge specimen in solution for several seconds at a time until surface scratches have been removed. Use at room temperature or warmer.

   Nitric Acid 30 ml
   Hydrochloric Acid 10 ml
   Phosphoric Acid 10 ml
   Glacial Acetic Acid 50 ml

   Taken from reference .

2. Chemical Etchant for Copper:

   Immediately after chemical polishing with procedure given above, followed by rinsing; a brief few seconds in this etchant
will reveal grain and dendrite structures. The etchant is a dilute (10%) solution of a commercially available etchant for printed circuit boards, which primarily contains ferric chloride solution.

3. Chemical Etchant for Nickel

Use freshly prepared for 5 to 30 seconds, thereby revealing grain boundaries in high nickel alloys. Use after mechanical polishing.

Nitric Acid 50%
Glacial Acetic Acid 50%

Taken from reference .

4. Chemical Etchant for Palladium

This etchant is a dilute solution of a commercially available chromic acid/sulfuric acid solution used as a glassware cleaning acid. A 5 to 10% dilution of the glass cleaner solution was found to work for palladium, where no other techniques worked. The treatment needed 30 to 60 seconds in order to work at room temperature or warmer.

5. Electro-etchant for Platinum, Rhodium, and Iridium

The following solution was found to be the best to reveal grain boundary structure in the above elements. A graphite cathode was used with 6 volts AC to the sample and electrode. The solution was used at room temperature and constantly stirred to
remove the adherent bubbles formed during the reaction. Often as many as 2 minutes of treatment was required for rhodium and as little as 20 seconds for platinum. Etching was performed after the mechanical polishing and etching.

Taken from reference 6.

6. Specimen Cleaning - General procedure

In all cases the general procedure was to rinse the specimen with water, then with alcohol and dried with clean pressurized air between each treatment. Often considerable drying and rinsing was required to prevent acid trapped in pores in the specimen from attacking the surface when it subsequently exits from the specimen.
BIBLIOGRAPHY


### TABLE I

**Summary of Drop Tube Specimens**

**Legend:**
- **pee:** picture, electro-etched
- **pe:** picture, chemically etched
- **pr:** picture, real surface (light microscopy)
- **sem:** scanning electron microscope
- **C:** cooling curve

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<td>He+H atmos, pe</td>
</tr>
<tr>
<td>NT474</td>
<td>Cu</td>
<td></td>
<td></td>
<td>High purity, He+H atmos, pe</td>
</tr>
<tr>
<td>NT559</td>
<td>Ni</td>
<td>374.03</td>
<td></td>
<td>Vacuum, pe, C</td>
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<td>Ni</td>
<td>285.24</td>
<td></td>
<td>Vacuum, sem, pe, C</td>
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<tr>
<td>NT577</td>
<td>Cu</td>
<td>240.14</td>
<td>238.78</td>
<td>He+H atmos, incomplete melt, not mounted</td>
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<tr>
<td>NT578</td>
<td>Cu</td>
<td>232.25</td>
<td>230.8</td>
<td>He+H atmos, fell from coil, not mounted</td>
</tr>
<tr>
<td>NT581</td>
<td>Cu</td>
<td>244.30</td>
<td>240.31</td>
<td>He+H atmos, not mounted</td>
</tr>
<tr>
<td>NT582</td>
<td>Cu</td>
<td>189.10</td>
<td>185.98</td>
<td>He+H atmos</td>
</tr>
<tr>
<td>NT583</td>
<td>Cu</td>
<td>184.89</td>
<td>183.07</td>
<td>He+H atmos, not mounted</td>
</tr>
<tr>
<td>NT584</td>
<td>Cu</td>
<td>268.30</td>
<td></td>
<td>He+H atmos, not high purity, not mounted</td>
</tr>
<tr>
<td>NT585</td>
<td>Cu</td>
<td></td>
<td>231.77</td>
<td>He+H atmos, half splat, data as NT584</td>
</tr>
<tr>
<td>NT586</td>
<td>Cu</td>
<td></td>
<td>233.77</td>
<td>He+H atmos, elongated half splat, test</td>
</tr>
<tr>
<td>NT587</td>
<td>Cu</td>
<td>177.89</td>
<td>176.14</td>
<td>He+H atmos, incomplete melt, not mounted</td>
</tr>
<tr>
<td>NT589</td>
<td>Ni</td>
<td>371.30</td>
<td>371.00</td>
<td>He+H atmos</td>
</tr>
<tr>
<td>NT590</td>
<td>Ni</td>
<td>380.74</td>
<td>380.74</td>
<td>He+H atmos</td>
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<tr>
<td>ID#</td>
<td>Material</td>
<td>Initial Weight</td>
<td>Final Weight</td>
<td>Comments</td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
<td>---------------</td>
<td>--------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>NT591</td>
<td>Pd</td>
<td>269.02</td>
<td>258.51</td>
<td>He+H atmos, pe</td>
</tr>
<tr>
<td>NT592</td>
<td>Pd</td>
<td>196.76</td>
<td>189.19</td>
<td>He+H atmos, pe</td>
</tr>
<tr>
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<td>163.73</td>
<td>162.54</td>
<td>He+H atmos, not levitated, not mounted</td>
</tr>
<tr>
<td>NT624</td>
<td>Pt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NT625</td>
<td>Rh</td>
<td></td>
<td></td>
<td>E-beam, no data, C</td>
</tr>
<tr>
<td>NT627</td>
<td>Pt</td>
<td></td>
<td></td>
<td>E-beam, incomplete melt, not mounted, C</td>
</tr>
<tr>
<td>NT630</td>
<td>Pt</td>
<td></td>
<td></td>
<td>E-beam, vacuum, pee, C</td>
</tr>
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<td>Pt</td>
<td>65.4</td>
<td></td>
<td>E-beam, no data</td>
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<td>Pt</td>
<td>50.23</td>
<td></td>
<td>E-beam, wire sample, C</td>
</tr>
<tr>
<td>NT661</td>
<td>Pt</td>
<td>24.28</td>
<td></td>
<td>E-beam, no data, not mounted</td>
</tr>
<tr>
<td>NT662</td>
<td>Rh</td>
<td>20.61</td>
<td></td>
<td>E-beam, irregular shape, may have wire in it,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>NT663</td>
<td>Pt</td>
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<td></td>
<td>E-beam, wire imbedded in it, C</td>
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<tr>
<td>NT664</td>
<td>Rh</td>
<td>23.2</td>
<td></td>
<td>E-beam, wire imbedded in it, C</td>
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<tr>
<td>NT665</td>
<td>Rh</td>
<td>30.7</td>
<td></td>
<td>E-beam, may have wire imbedded in it</td>
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<tr>
<td>NT670</td>
<td>Ir</td>
<td>76.81</td>
<td></td>
<td>E-beam, wire imbedded in it</td>
</tr>
<tr>
<td>NT671</td>
<td>Ir</td>
<td>33.92</td>
<td></td>
<td>E-beam, may have wire imbedded in it</td>
</tr>
</tbody>
</table>
TABLE II.

Summary of Drop Tube Specimen Grain Size

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Element</th>
<th>Atmosphere</th>
<th>Grain Size (cm)</th>
<th>Standard Dev. (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT221</td>
<td>Rh</td>
<td>E-beam</td>
<td>.0171</td>
<td>.0076</td>
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<tr>
<td>NT269</td>
<td>Pd</td>
<td>E-beam</td>
<td>.0131</td>
<td>.0035</td>
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<tr>
<td>NT344</td>
<td>Cu</td>
<td>He+H</td>
<td>.0969</td>
<td>.0031</td>
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<td>NT351</td>
<td>Cu</td>
<td>He+H</td>
<td>.0252</td>
<td>.0175</td>
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<tr>
<td>NT448</td>
<td>Ni</td>
<td>He+H</td>
<td>.0252</td>
<td>.0103</td>
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<td>NT449</td>
<td>Ni</td>
<td>He+H</td>
<td>.0297</td>
<td>.0102</td>
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<td>He+H</td>
<td>.0184</td>
<td>.0093</td>
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<td>NT453</td>
<td>Ni</td>
<td>Air</td>
<td>.0163</td>
<td>.0048</td>
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<td>NT454</td>
<td>Ni</td>
<td>Air</td>
<td>.0304</td>
<td>.0105</td>
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<td>NT460</td>
<td>Pd</td>
<td>Air</td>
<td>.0056</td>
<td>.0022</td>
</tr>
<tr>
<td>NT461</td>
<td>Pd</td>
<td>Air</td>
<td>.0056</td>
<td>.0022</td>
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<td>NT462</td>
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<td>Air</td>
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<td>.0019</td>
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<td>Pd</td>
<td>He+H</td>
<td>.0221</td>
<td>.0078</td>
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<td>NT474</td>
<td>Cu</td>
<td>He+H</td>
<td>.0236</td>
<td>.0084</td>
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<td>NT560</td>
<td>Ni</td>
<td>Vacuum</td>
<td>.0143</td>
<td>.0071</td>
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<td>NT582</td>
<td>Cu</td>
<td>He+H</td>
<td>.0249</td>
<td>.0118</td>
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<tr>
<td>NT585</td>
<td>Cu</td>
<td>He+H</td>
<td>.0074</td>
<td>.0037</td>
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<td>NT586</td>
<td>Cu</td>
<td>He+H</td>
<td>.0246</td>
<td>.0136</td>
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<td>Ni</td>
<td>He+H</td>
<td>.0192</td>
<td>.0088</td>
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<td>Ni</td>
<td>He+H</td>
<td>.0223</td>
<td>.0119</td>
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<tr>
<td>NT591</td>
<td>Pd</td>
<td>He+H</td>
<td>.0151</td>
<td>.0057</td>
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<tr>
<td>NT592</td>
<td>Pd</td>
<td>He+H</td>
<td>.0111</td>
<td>.0061</td>
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<tr>
<td>NT625</td>
<td>Rh</td>
<td>E-beam</td>
<td>.0044</td>
<td>.0024</td>
</tr>
<tr>
<td>NT630</td>
<td>Pt</td>
<td>E-beam</td>
<td>.0085</td>
<td>.0021</td>
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</tbody>
</table>
### TABLE III.

**Summary of Dendrite size Measurements**

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Element</th>
<th>Dendrite Size (cm)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NT417</td>
<td>Pd</td>
<td>0.0066</td>
<td>0.0023</td>
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<td>NT420</td>
<td>Pd</td>
<td>0.0086</td>
<td>0.0021</td>
</tr>
<tr>
<td>NT427-8</td>
<td>Ni</td>
<td>0.0030</td>
<td>0.0008</td>
</tr>
<tr>
<td>NT460</td>
<td>Pd</td>
<td>0.0056</td>
<td>0.0022</td>
</tr>
<tr>
<td>NT461</td>
<td>Pd</td>
<td>0.0056</td>
<td>0.0022</td>
</tr>
<tr>
<td>NT462</td>
<td>Cu</td>
<td>0.0059</td>
<td>0.0019</td>
</tr>
<tr>
<td>NT474</td>
<td>Cu</td>
<td>0.0111</td>
<td>0.0042</td>
</tr>
<tr>
<td>NT582</td>
<td>Cu</td>
<td>0.0070</td>
<td>0.0014</td>
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<tr>
<td>NT624</td>
<td>Pt</td>
<td>0.0011</td>
<td>0.0004</td>
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<tr>
<td>NT625</td>
<td>Rh</td>
<td>0.0024</td>
<td>0.0006</td>
</tr>
</tbody>
</table>
Figure 1. Richardson (or Ellingham) Diagram
Figure 2. Thermochemical calculations for Richardson charts

High Temperature $T$

$\text{metal(H,S,) + } \text{O}_2(N,S) \rightarrow \text{metal oxide(H,S)}$

$\Delta H$ $\frac{\Delta S}{\Delta H}$ $\frac{\Delta S}{\Delta S}$

$298K$

$\text{metal + } \text{O}_2 \rightarrow \text{metal oxide}$

$H(T) = \Delta H^{0}_{298} + \Delta H$

where $\Delta H = \int_{298}^{T} cp \ dT + \sum_{i=1}^{n} H_i$

$S(T) = \Delta S^{0}_{298} + \Delta S$

where $\Delta S = \int_{298}^{T} cp/T \ dt + \sum_{i=1}^{n} H_i/T$

$\Delta H(T) = H(\text{metal oxide}) - H(\text{metal}) - H(\text{O}_2)$

$\Delta S(T) = S(\text{metal oxide}) - S(\text{metal}) - S(\text{O}_2)$

$\Delta G(T) = \Delta H - T \Delta S = RT \log P_{O_2}$
Figure 3. Menu driven program flow nodes for easy user interface
**Reaction**  
\[ 2 \text{Ni} + \text{O}_2 \rightarrow 2 \text{NiO} \]

**Temperature Range** 1 is 25 to 252 Degrees C

**Enthalpy**  
\[ 0 \quad 0 \quad -57500 \]

**Entropy**  
\[ 7.14 \quad 49 \quad 9.100001 \]

**Heat Capacity Coefficients**  
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8</td>
<td>-0.43</td>
<td>-1.935</td>
<td>0</td>
</tr>
<tr>
<td>7.02</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-4.99</td>
<td>37.58</td>
<td>3.89</td>
<td>0</td>
</tr>
</tbody>
</table>

At 252 degrees C, phase transition values are

**Enthalpy**  
\[ 140 \quad 0 \quad 0 \]

**Entropy**  
\[ 0.222 \quad 0 \quad 0 \]

Figure 4. Thermochemical constants for first temperature range
REACTION 2 NI + 02 ---> 2 NIO

TEMPERATURE RANGE 2 IS 253 TO 292 DEGREES C

ENTHALPY 0 0 -57500

ENTROPY 7.14 49 9.100001

HEAT CAPACITY COEFFICIENTS
A 7.1 7.02 13.88
B 1 0 0
C -2.23 0 0
D 0 0 0

AT 292 DEGREES C PHASE TRANSITION VALUES ARE

ENTHALPY 4200 0 0
ENTROPY 2.436 0 0

ENTER <CR> TO GET NEXT DATA OR <X> & <CR> TO GO TO MENU? 

Figure 5. Thermochemical constants for second temperature range
REACTION 2 Ni + O2 → 2 NiO

TEMPERATURE RANGE 3 IS 293 TO 1984 DEGREES C

ENTHALPY 0 0 -57500

ENTROPY 7.14 49 9.100001

HEAT CAPACITY COEFFICIENTS
A 9.3 7.02 11.18
B 0 0 2.02
C 0 0 0
D 0 0 0

AT 1984 DEGREES C PHASE TRANSITION VALUES ARE

ENTHALPY 0 0 0

ENTROPY 0 0 0

Figure 6. Thermochemical constants for third temperature range
Figure 7. Ellingham chart for N₂O from IBM
PC screen dump with overlaid 10₂ scale
Figure 8. Photomicrographs of two Palladium drops. Data is given in Table 1.
Figure 9. Photomicrograph of two different Nickel drop specimens. Data is given in Table I.
Figure 10

Photomicrographs of two unique specimens, copper and nickel. Data is summarized in Table I.
Figure 11. Electro-etching apparatus constructed for this work.
Figure 12. Mass spectrum using Dycor system and subtraction of background feature.
FREE ENERGY PROGRAM
written in Microsoft BASICA
for the IBM Personal Computer

Comments: This program has been written with a menu driven user
interface for ease of use. Each task such as enter data, read data
from the disk, calculate free energies to a specified temperature, or
to plot data is determined through a primary menu.

9 REM SET-UP AND PRIMARY MENU
10 DIM C$(3),M(3),H(3),S(3),A(3,9,4),HP(3,5),SP(3,5)
20 DIM TP(20)
30 KEY OFF
40 CLS
50 PRINT:PRINT
60 PRINT "FREE ENERGY CALCULATIONS MENU"
70 PRINT:PRINT
80 PRINT:PRINT
90 PRINT:PRINT
100 INPUT "ENTER CHOICE"; C
110 GOTO 100
120 STOP

REM THE DATA ENTRY SUBROUTINE WITH DATA ENTERED FROM TABLES IN 299
REM THE REFERENCE TABLES OF BARIN, ET AL.
300 CLS
310 INPUT "enter metallic reactant "; C$(1)
320 INPUT "enter gaseous reactant "; C$(2)
330 INPUT "enter reaction product "; C$(3)
340 FOR I = 1 TO 3
350 CLS
360 PRINT "enter data for "; C$(I)
370 INPUT "enter number of phases"; N(I)
380 FOR J = 1 TO N(I)
390 INPUT "enter upper temperature "; T2(I,J)
400 PRINT
410 PRINT "enter heat capacity coefficients A,B,C,D for "; C$(I)
420 PRINT "enter A coefficient"; A
430 PRINT "enter B coefficient"; B
440 PRINT "enter C coefficient"; C
480 INPUT "enter D coefficient"; D
490 A(I,J,1) = A; A(I,J,2) = B; A(I,J,3) = C; A(I,J,4) = D
495 PRINT
500 INPUT "enter 'N' if no phase change occurs at upper
temperature"; N$
510 IF N$ = "N" THEN 540
520 INPUT "enter enthalpy change at phase change temperature "; HP(I,J)
530 INPUT "enter entropy change at phase transition "; SP(I,J)
540 NEXT J
550 NEXT I
560 RETURN
600 CLS
610 F$ = "DATA"; INPUT "ENTER NAME OF DATA FILE "; F$
620 INPUT "ENTER DISK DRIVE A OR B"; D$
630 FILE$ = D$ + ":" + F$ + ".DAT"
640 OPEN FILE$ FOR APPEND AS #1
650 FOR I = 1 TO 3
660 FOR J = 1 TO N(I)
670 WRITE #1, I, C$(I), M(I), N(I), H(I), S(I)
680 FOR J = 1 TO N(I)
690 WRITE #1, I, T2(I,J), A(I,J,1), A(I,J,2), A(I,J,3), A(I,J,4)
700 WRITE #1, HP(I,J), SP(I,J)
710 NEXT J
720 NEXT I
730 CLOSE 1
740 RETURN
699 REM RETRIEVE DATA FROM DISK
700 CLS
710 F$ = "DATA"; PRINT "ENTER NAME OF DATA FILE "; INPUT F$
720 FILE$ = F$ + ".DAT"
730 INPUT "ENTER NAME OF REACTION PRODUCT "; R$
740 OPEN FILE$ FOR INPUT AS #1
750 IF EOF(1) THEN 1060
760 FOR I = 1 TO 3
770 INPUT #1, I, C$(I), M(I), N(I), H(I), S(I)
780 FOR J = 1 TO N(I)
790 INPUT #1, I, T2(I,J), A(I,J,1), A(I,J,2), A(I,J,3), A(I,J,4)
800 INPUT #1, HP(I,J), SP(I,J)
810 NEXT J
820 NEXT I
830 IF C$(3) = R$ THEN 960
840 CLOSE 1
850 QOSUR 3000
860 RETURN
899 REM THIS ROUTINE PRINTS THE THERMODYNAMIC VALUES
900 FOR J = 1 TO PMAX
905 CLS
910 PRINT "REACTION", M(1); C$(1); " + " C$(2); " = " M(3); C$(3)
915 PRINT "ENTHALPY", H(1), H(2), H(3)
925 PRINT "ENTROPY", S(1), S(2), S(3)
1145 PRINT :PRINT
1150 PRINT "TEMPERATURE RANGE ";J:; " IS ";TP(J); " TO ";TP(J+1); "
1155 PRINT :PRINT
1160 PRINT "HEAT CAPACITY COEFFICIENTS"
1170 PRINT "A", AX(1,J,1),AX·2,J,1),AX(3,J,1)
1180 PRINT "B", AX(1,J,2),AX·2,J,2),AX(3,J,2)
1190 PRINT "C", AX(1,J,3),AX·2,J,3),AX(3,J,3)
1200 PRINT "D", AX(1,J,4),AX·2,J,4),AX(3,J,4)
1205 PRINT
1220 PRINT "ENTHALPY",HX(1,J),HX(2,J),HX(3,J)
1230 PRINT "ENTROPY", SX(1,J),SX(2,J),SX(3,J)
1240 LOCATE 24,5
1250 INPUT "ENTER • CR\ TO GET NEXT DATA OR <X> & <CR> TO GO TO MENU":A$
1260 IF A$ = CHR$(88) THEN RETURN
1270 NEXT J
1280 RETURN

1299 REM THIS SUBROUTINE CALCULATE THE DELTA G VALUES
1301 CLS
1310 LPRINT "REACTION",M(1);C*(1);" + "C*(2) → "M(3);C*(3)
1320 LPRINT: LPRINT "TEMP","DELTA H","DELTA S","DELTA G"
1340 T1A = T1(1) + 273
1360 INPUT "ENTER MAXIMUM TEMPERATURE FOR THIS CALCULATION"; TMAX
1370 FOR T2A = T1A TO TMAX + 273 STEP 50
1380 GOSLIB 2000
1390 LPRINT T2A,HREACT,SREACT,6T2
1400 NEXT T2A
1410 NEXT T2A
1460 PRINT "MOLAR ENTHALPIES ARE ";HTOTAL(1),HTOTAL(2),HTOTAL(3)
1490 PRINT "MOLAR ENTROPIES ARE "; STOTAL(1),STOTAL(2),STOTAL(3)
1550 PRINT "THE FREE ENERGY AT ";TMAX; " DEGREES C IS ";GT2; "CAL/"M(3); "MOLE
1560 PRINT
1580 INPUT "ENTER • CR\ TO RETURN TO MENU OR <PrtSc> TO PRINTER": X$
1590 RETURN

1999 REM THIS SUBROUTINE PERFORMS THE SUMMATION OVER THE COEFFICIENTS
2000 FOR I = 1 TO 3
2010 HS(I) = H(I); SS(I) = S(I)
2020 T1A = TP(J) + 273
2040 HS(T) = HS(I) + HX(I,J-1); SS(I) = SS(I) + SX(I,J-1)
2050 HCAPA(I) = AX(I,J,1) * (T2A-T1A)
2060 HCAFBB(I) = AX(I,J,2) *.5 * 10^-3 * (T2A*T2A-T1A*T1A)
2070 HCAPC(I) = AX(I,J,3) * 10^-5 * (1/T1A - 1/T2A)
2080 HCAPD(I) = AX(I,J,4) *.333 * 10^-6 * (T2A*T2A*T2A - T1A*T1A*T1A)
2090 HTOTAL(I) = HS(T) + HCAPA(I) + HCAFBB(I) + HCAPC(I) + HCAPD(I)
2100 ENTRA(I) = AX(I,J,1) * LOG(T2A/T1A)
2110 ENTRB(I) = AX(I,J,2) * 10^-3 * (T2A-T1A)
2120 ENTRC(I) = AX(I,J,3) * 10^-5 * (2*(T1A^-2 - T2A^-2))
2130 ENTRD(I) = AX(I,J,4) *.5 * 10^-6 * (T2A*T2A-T1A*T1A)
2140 STOTAL(I) = SS(I) + ENTRA(I) + ENTRB(I) + ENTRC(I) + ENTRD(I)
2150 NEXT I
REM THIS SUBROUTINE PERFORMS THE GRAPHICAL TASKS FOR A SINGLE
REM REACTION
CLS
INPUT "ENTER MAXIMUM TEMPERATURE FOR THIS CALCULATION"; TMAX
GOSUB 4000
TSC = 180/3000
FESC = 600/300000'
T1A = TP(1) + 273
HGRD = M(3)*H(3) - M(1)*H(1) - H(2)
SGRD = M(3)*S(3) - M(1)*S(1) - S(2)
GRFE = HGRD - T1A*SGRD
STEPM = 190-T1A*TSC
SFE = J0-GRFE*FESC
PSET (SFE, STEPM)
FOR J = 1 TO PMAX
FOR T2A = TP(J) + 273 TO TP(J+1) + 273 STEP 50
IF T2A < TMAX THEN 2680
GOSUB 2000
TCOR = 390-T2A*TSC
FECOR = 10-GT2*FESC
LINE -(FECOR,TCOR)
NEXT T2A
NEXT J
LOCATE 21
INPUT X$
RETURN

SUBROUTINE TO SORT THERMODYNAMIC ENTRIES ACCORDING TO TEMPERATURE
TP(1) = 25: K = 2
FOR I = 1 TO 3
FOR J = 1 TO N(I)
TF(K) = T2(I,J)
K = K + 1
NEXT J
NEXT I
PMAX = K - 1
D = 0
FOR I = 1 TO PMAX-1
FOR K = I + 1 TO PMAX
IF TF(I) < TF(K) THEN 3150
IF TF(I) = TF(K) THEN TF(K) = 99999: GOTO 3150
SWAP TF(I), TF(K)
NEXT K
NEXT I
FOR I = 1 TO PMAX
IF TF(I) = 99999 THEN D = D + 1
NEXT I
PMAX = PMAX - D
FOR I = 1 TO 3
REM SUBROUTINE TO GRAPH SEVERAL REACTIONS ON ONE GRAPH
CLS
FP$ = "DATA":PRINT "ENTER NAME OF DATA FILE "::INPUT FP$
FILE$ = D$+".DAT"
FOR CMP = 1 TO 10
PRINT "ENTER REACTION PRODUCT OR 0 FOR NONE";CMP;:INPUT RF$(CMP)
IF RP$(CMP) = "0" THEN 3580
NEXT CMP
NUM = CMP + 1
INPUT "ENTER MAXIMUM TEMPERATURE FOR THESE CALCULATIONS"; TMAX
GOSUB 4010
TSC = 180/3000
FESC = 600/300000
FOR CMP = 1 TO NUM
R$~ RP$(CMP)
S$ = 10-BRFE*FESC
F'SET (SFC, STEMP)
FOR TCA = TIA + 50 TO TMAX + 273 STEP 50
NEXT TCA
NEXT CMP
LOCATE 25, 3
RETURN
REM SUBROUTINE FOR GENERATING GRAPHIC FORM ON IBM PC SCREEN
T$=" -50 -100 (Leal) -150 -200 -250
CLS
SCREEN 2
LINE (10, 5)--(620, 190), ,B
FOR Y = 1 TO 6
LINE (5, 190-Y*30)-(12, 190-Y*30)
4060 LINE(615,190-Y*30)-(620,190-Y*30)
4070 YV = Y*500
4080 LOCATE 25-Y*3.9,73:PRINT USING "####";YV

4090 NEXT Y
4100 T$=" kcal  -50    -100    -150    -200    -250    -300 "
4110 FOR X = 1 TO 6
4120 LINE (10+X*100,195)-(10+X*100,185)
4130 NEXT X
4140 LOCATE 25,1:PRINT T$;
4150 RETURN