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**Ground Based Research in
Microgravity Materials Processing**

by

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The core activities performed during this time period have been concerned tracking the TEMPEST experiments on the shuttle with drops of Zr, Ni, and Nb alloys. In particular a lot of Zr drops are being made to better define the recalescence characteristics of that system so that accurate comparisons of the Drop Tube results with Tempest can be made.

A new inner liner, with minimal reflectivity characteristics, has been inserted into the Drop Tube in order to improve the recalescence measurements of the falling drops. The first installation to make the geometric measurements to ensure a proper fit has been made. The stovepipe sections are currently in the shop at MSFC being painted with low reflectivity black paint.

Work has also continued on setting up the MEL apparatus obtained from Oak Ridge in the down stairs laboratory at the Drop Tube Facilities. Some ground-based experiments on the same metals as are being processed on TEMPEST are planned for the MEL. The flight schedules for the KC-135 experiments are still to be determined in the near future.

Tom Rathz has spent a considerable amount of time in working on methods to produce pellets of new elemental systems for use at the Drop Tube. A number of immesible systems may be available for processing at the Tube or in TEMPEST if some of these methods are able to provide specimens which can be melted and levitated electromagnetically. His report on these activities is included in this report.

Attempted Processing of Ag-Ni Pellets
in a Containerless Environment

Pressing of Powders into Pellets

I. Introduction

Pressing Ag and Ni powders into small (5 mm dia x 5 mm height) pellets is the first step in producing samples for the proposed Drop Tube research. The procedures used are described in this report.

II. Experimental Details

Metal powders used in this research were purchased from Goodfellow Corporation. The Ni powder consisted of 2 micron mean diameter particles of 99.9% purity; the Ag powder consisted of 0.75 micron mean diameter particles of 99.97% purity. Size distributions are not available from Goodfellow because the non-spherical particle shape precludes determination of the shape of the distribution.

The powders were weighed and placed in a stainless steel mixer vessel and rotated at a predetermined rate for 20 minutes to produce a "uniformly" mixed powder. The rotation rate had been established using much larger quantities of powder. The rate was reduced to a much slower value for the last 5-10 minutes of sample preparation.

The powders were weighed according to the following scheme. Given a desired pressed pellet volume, V, containing an assumed fraction of voids, f, the actual total volume of the pellet can be found from:

$$V_T = V(1-f) \cdot \tag{1}$$

Knowing the volume fraction, f_v, desired of each constituent in the alloy permits the calculation of the volume of each constituent

$$\begin{aligned} V_1 &= V_T f_v \\ V_2 &= V_T (1-f_v) \end{aligned} \tag{2}$$

and thus the mass of each constituent knowing the densities, ρ:

$$\begin{aligned} M_1 &= V_1 \rho_1 \\ M_2 &= V_2 \rho_2 \end{aligned} \tag{3}$$

The actual fraction of voids existing in the pressed pellet is given by:

$$\text{(...)} = 1 - \frac{\rho_m}{\rho_l} \tag{4}$$

where the theoretical zero-void density is given as[1] :

$$\rho_l = \frac{\rho_1 \rho_2}{\rho_1 f_{w1} + \rho_2 f_{w2}} \tag{4}$$

where f_w is the weight fraction of the constituent in the alloy, and ρ_m is the measured density (from an Archimede's weighing) or a geometric density (weighing the sample and measuring its symmetrical dimensions). The desired sample dimensions were height = diameter = 0.5 cm and a volume of 0.0848 cc.

A pressing mold was made by the UAH machine shop based on previous designs used by Dr. J. Smith (no drawings are available). The measured piston diameter was 0.476 cm. The mixed powder was slowly poured into the mold and occasionally hand-tamped with the piston to make room for the remaining powder. Powder spillage was not considered a problem because the mixed powder was assumed to be homogeneous. An error analysis performed on the uncertainty in atomic composition (a/o) of the constituents in the pellet due to any possible spillage or sticking of a component in the measuring pan is given in the Appendix.

To compress the powders, a Carver, Model L press was used having a force resolution of 500 pounds. The press was held at 4000 pounds for 2-1/2 hours and was adjusted every 5 minutes for pressure variations.

III. Results and Discussion

The powders were pressed into pellets without any cracking. The loss of pressure during the pressing process was attributed mostly to leaky seals on the Carver press and only partially to further compaction of the powders. Even though no hydraulic fluid was found leaking from the seals, a different Carver press required only minimal re-adjustment of the pressure during the compaction process.

Assuming 30 v/o voids in the final pressed pellet, the actual volume of the powder was 0.0848 cc x 0.7 = 0.0594 cc. This choice of 30 v/o voids is somewhat arbitrary until actually measured and will depend on the final choice of pressing pressure; however, it helps in the calculation of the amount of material needed. For a Ni-Ag(20a/o) pellet (i.e.,

[1] Randall M. German, Liquid Phase Sintering (Plenum Press, N.Y., 1985).

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28.03 v/o Ag), the volume of nickel and silver needed is 0.7797x0.0594 cc = 0.0427 cc and 0.2803x0.0594 cc = 0.0166 cc, respectively. The mass of nickel and silver needed is 0.420 g and 0.175 g, and the corresponding weight percentages are 70.6 w/o and 29.4 w/o, respectively.

Table 1 list the information on the samples made to date. The percent voids was calculated from the final pellet dimensions and mass assuming a theoretical density of 9.97 g/cc as given by (4). The percent voids continued to decrease for increasing force until the piston failed at 6000 pounds. Thereafter, 4000 pounds was taken as the working force for this mold. For a piston with a diameter of 0.476 cm and a cross sectional area of 0.0276 sq. in., a force of 4000 pounds produces a pressure of about 145,000 ±18,000 psi. Typical pellet sizes are 0.481 cm diameter with height variations of 0.4 ±0.1 cm produced by mass variations of ±30 mg.

IV. Summary and Future Work

The samples can be made in a pelletized form in a simple but time-consuming process. The uniformity of the mixed constituent powders is an assumption that needs to be verified. If the uniformity is true, then powder losses due to spillage does not affect the sample except to shorten its height.

In future work, multiple samples will be made in one pressing by making a longer mold to hold many compactions in series. This mold would also have the volume to receive all the powder at one time without being hand-compressed to make room for the remainder.

Future pressings will use a gauge with 50 pound increments for better reproducibility. The application of the 6000 pounds on sample AN8 which bent the piston may have also caused misalignment in the remaining mold as well: the piston is beginning to stick after a pressing. If a new mold is required, the problems of spillage and of one sample per press will be eliminated by building a longer mold to accommodate several samples at one time.

Reducing and Sintering Ag-Ni Pellets

I. Introduction

After pressing the Ag-Ni powders into small pellets, a reduction of the oxygen in the sample and a liquid-phase sintering was performed. This report describes the procedures and some preliminary results of these two processes.

II. Experimental Details

The as-received powders from Goodfellow Company are in a very surface oxidized state. Also, the pressed powders will be contaminated with zinc-stearate which is used as a lubricant for the mold walls. After having pressed the Ag-Ni powders into 5 mm diameter x 5 mm height pellets, the next step in the sample preparation process is reducing the oxygen and the zinc-stearate from the samples.

The reducing furnace was a Lindberg "tube" furnace in which a stainless steel tube having 3/4" ID and 12" length was inserted. Pure hydrogen was flowed through the tube at a rate of about 1 cc per 3 seconds. Perforated stainless steel discs were used to keep the samples separated during the reducing process. The time-temperature profile consisted of 1 hour at 115C, 2 hours at 200C, and 2 hours at 300C. The samples were then cooled to room temperature over a 3 hour period.

After reducing, the samples were liquid-phased sintered. This process was accomplished using the furnace ("R2D2") located in Dr. Jim Smith's lab. The furnace has a 7 cm long isothermal zone with a diameter of 1.5". The 5 mm diameter x 5 mm length samples were placed in round-ended, 1/4" diameter, 1/2" long alumina crucibles. An assembly of these were stacked together and carefully pushed into the furnace alumina tube. The height of the stack of the six sintered samples (AN4-AN9) was 22 cm.

The furnace used a 1 cc per second flow of He-5%H gas. The time-temperature profile for this sintering process is shown in Figure 1. The amount of mass lost from this process was to have been measured; however, the samples were intermingled when retrieved from the furnace resulting in the loss of their identity.

III. Results and Discussion

Only samples AN3-AN9 were reduced. No measurable weight loss, shape change, or discoloration occurred from the reducing process. A non-reduced (AN2) and a reduced sample (AN3) were sent to MSFC Chemistry Branch for oxygen analysis. An EDAX analysis indicated a presence of measurable quantities of oxygen; thus, after waiting two months, the destructive chemical analysis was not done out of fear of ruining the O_2 sensor. It is not known at this time if the H_2 reduction process had any effect on the oxygen in the samples. Another variable in the reduction process is the degree of compaction of the powders which causes a variation in the penetration of the H_2 gas into the pellet. Related to the compaction variable is the resulting change in the void fraction and bubble formation which is very detrimental in high temperature, levitated melts. These variables will be studied during the future course of this investigation.

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Referring to Figure 2, a eutectic temperature exist at about 960C. A sintering temperature of about 980C was sought so that liquid-phase sintering could be performed. The liquid phase will cause the pellet to deform or sag under gravity. This would be detrimental to the eventual sample-size levitation requirements if the shape of the sample were not maintained. A "machinable" 96%-alumina (type 960) from Cotronics Corporation was purchased with the intent of making crucibles with dimensions close to those of the pellets. However, it was found that the alumina required high-carbon steel, high-cost machine tools for machining and the alumina probably uses Ag-reactive silica as its remaining 4% composition. Thus, 1/4" ID, 99.8% purity, round-bottom alumina tubes from Coors Ceramic were used.

The temperature difference between the furnace coil and the sample at the top of the stack is attributed to the difference in the location of the thermocouples for each. Assuming the coil thermocouple (TC) is located in the 7 cm long region of the isothermal zone, the top sample TC was about 14 cm above the isothermal zone. This is why the samples inside the zone were soaked for an hour at temperatures close to 1100C while those at the top of the stack were close to 850C. It would be then be expected that some of the pellets were not liquid-phase sintered while others not only were liquid-phase sintered, but probably lost much more mass than those at 850C.

Retrieving the samples from the furnace upon completion of the sintering process resulted in the mixing of the samples. Table 2 provides a comparison of the masses of the samples both before and after sintering. This did not provide a means of sample identification because the amount of mass lost during sintering was different for each sample. Similarly, the sintering process caused a distortion of the shape of the sample rendering a dimensional measurement for identification of little use. As seen in Table 2, these changes in the samples after sintering were very large. These mass losses plus the generally accepted fact that most immiscible materials snow large positive deviations from Raoult's law in their activity coefficients suggest that even this sintering technique will not suffice to overcome the tremendous evaporation losses in the melt.

IV. Summary and Future Work

Following the reduction process, samples will be analyzed for oxygen content at various times, temperatures, and piston pressures to find the conditions to minimize the oxygen level in the samples. Once optimized, the appropriate pre-Drop Tube sample conditioning must be found which will avoid sample de-gassing or bubble formation when melted in the levitation coil. Sintering must be considered as a part of this conditioning.

To perform future sintering using the 7 cm isothermal zone of R2D2, another sample packing arrangement must be found that also allows easy identification of each sample. However, with a new press being built to allow multiple samples to be made at one squeezing, another furnace might have to be found with a larger isothermal zone to accommodate the ever-increasing number of samples. Also, the density of the sintered samples will be recorded in future samples as an indicator of the void density and the troubles, if any, these cause in the levitation process.

Drop Tube Processing Ag-Ni Pellets

I. Introduction

This report concerns the attempts to levitate and melt Ag-Ni pellets in the Drop Tube. The experimental details and results will be presented.

II. Experimental Details

After the Ag-Ni powders were pressed into pellets, the first sample (AN1) made was immediately tested for its levitability. A laboratory 15 kW Lepel RF generator was used with a 1/4" ID, 7-turn coil to levitate AN1 while in an air environment. Some pluming occurred but was attributed to the rapid burning of the sample in atmospheric conditions.

Before processing the pressed powders in the Drop Tube using the 10 KW Lepel generator, calibration/test specimens were used. A schematic of the Drop Tube processing chamber is shown in Figure 3. While under a vacuum, several elements (Ni, Zr, Ti, Nb, Ta) were sequentially processed. An Ircon R-series two-color pyrometer was used to measure temperature in the processing chamber.

Once the drop/sample is released into the Tube, amplified silicon photodiodes detect the iridescence of the drop and send its output voltage to a high-speed A/D device. If any undercooling occurs in the droplet as it falls, the photodiodes will detect a rapid ($^-200\mu s$) increase in the iridescence due to the latent heat being released by the phase change. It is still uncertain at this time whether the heat released by the phase change of the reaction $L_1 \rightarrow L_1 + L_2$ will be large enough to be detected as compared to the large change produced by a $S \rightarrow L$ transformation.

The pellet samples were going to be vacuum processed in the Drop Tube. However an arcing problem required that the Tube be backfilled to 720 Torr of 99.999% Ar before processing.

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III. Results and Discussion

A plot of typical Ircon pyrometer data is shown in Figure 4 of a Ti sample. The noise on the pyrometer data of Figure 4 is possibly due to two sources: static (i.e., body force) instability of the drop about a center of the magnetic potential well produced by asymmetries in the levitation coil (0-45 sec.) and dynamic (i.e., surface) perturbations (45-62 sec) produced by ripple/modulations on the electromagnetic field generated by the Lepel power supply. The Ircon pyrometer itself has a 0.3% repeatability (6C at 2000C) and 1% relative accuracy (20C at 2000C). The apparent melting temperatures of the calibration samples are listed in Table 3. There appears to be a fairly constant shift of about 173 C above the actual melting temperature. This also indicates that the difference in emissivities between these metals does not greatly affect the measurements taken by this pyrometer.

The first pellet made was successfully levitated in air. This sample was the least dense of the pellets (AN1). Because of the ease of oxidation of Ag, the samples should not be heated in air. Even though smoke plumed from the air levitated powdered sample (AN1), it appeared to be less than that which occurred with arc-melted bulk materials. Because this is the first time Ag-Ni pellets have been attempted to be levitated and melted, the pellets unknown resistivity and interparticle connectivity compared to, say, a pure copper slug may require that several pellets be used to get the proper Lepel power-supply output frequency and power settings.

Samples "AN4"[2] and "AN6"[1] were attempted to be processed in the Drop Tube under a vacuum, but as the sample began to liquefy, a corona appeared around the sample which quickly resulted in arcing and shutting down of the Lepel. The sample then fell to the bottom of the Tube. The samples were then re-processed under the high purity Ar atmosphere with no arcing problems. However, a plume of vapors began to form as soon as the "cylindrically" shaped sample began to "spheroidize". As seen in the pyrometer plot (Figure 5) for "AN4", the plume was so thick that the temperature could no longer be measured. After about 8 seconds of heating, the samples were released into the Tube.

"AN4" hit the side of the Tube due to a static instability upon release. "AN6" fell to the bottom of the Tube without incident. Upon retrieval the sample was found to have some of the previous drop's dust particles stuck in its surface. No recalescence was expected or

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[2] The parenthesis used for these samples' numbers are to reflect the mixup of the samples when removed from the sintering furnace. The sample numbers from this point forward are a best guess as to what they were before sintering.

seen by the photodiodes since it was doubtful that the single-liquid phase temperature was attained and with this amount of pluming the iridescence of the drop was probably blocked. The decision was made that further laboratory studies were necessary to shed some light on a possible process whereby the pluming could be minimized.

IV. Summary and Future Work

The Drop Tube process would have been successful if not for the vaporization of the sample. Other samples will be pre-processed in the lab in an attempt to reduce the vaporization problem before processing in the Tube and to assure that some data will be obtained if anything should happen to "AN6" during analysis. With the UAH Auger system not working at present, SEM analysis will be strongly considered.

Work on developing the laboratory levitation system has finished and experiments with this device will be given in another report. If the lab system develops problems, the Drop Tube will be considered as an alternate in this process development scheme. This alternate plan is not desirable because the Drop Tube in its present condition must be entirely backfilled (200 ft^3) and evacuated to change out samples, etc. In the meantime, the part being ordered to build a new press so more samples can be made has tripled in cost and has taken two months longer than expected to obtain - considerably more time and money than it may be worth if this powder method doesn't work to eliminate the vapor problem.

Laboratory Levitation Experiments of Ag-Ni

I. Introduction

This report concerns the Ag-Ni levitation and melting experiments performed in the laboratory located next to the MSFC Drop Tube Facility.

II. Experimental Details

After 6 months construction, the levitation chamber in the Drop Tube lab is complete enough to begin experimentation. A schematic of the system is shown in Figure 6. The 5-nines pure Ar and He gases provide control of the heating/cooling of the sample independent from that produced from the levitation requirements. The temperature of the sample was monitored with an R-series Ircon two-color pyrometer having a sampling rate of 100 readings per second. The data was acquired with a National Instruments 16-channel A/D board and their LabView™ software. The prism and optical glue were chosen to have a flat absorption band over the wavelength range of the pyrometer detectors.

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Before proceeding with experiments on the pressed pellets, the same pure elements that were used on the Drop Tube were attempted. This provided pyrometer calibration as well as debugging of the entire system and operational procedures. The RF generator used to levitate and heat the samples was a 15 kW Lepel power supply.

III. Results and Discussion

Several minor problems still exist in the system that will require modification before it is fully operational. To avoid these problems and to get some results, the gas flowing over the hot samples was "dumped" into the laboratory which was then evacuated until "aired out". The elemental samples could not be melted when He gas was used as a non-flowing atmosphere. The samples could not be cooled below their melting temperature when Ar was flowing. Therefore, a mixture of the two gases was installed to control the sample temperature. However, a component in the Lepel burned and put it out of working order before a test of this gas mixture could be made.

Some data on elemental samples was obtained before the Lepel breakdown. Figure 7a shows a plot of temperature versus time for a Ti sample. A small recalescence is seen in Figure 7b at 89.7 seconds of 20-40 degrees of undercooling. This plot gives some indication of the problems of using the Ircon pyrometer to record recalescence: the noise in the Ircon pyrometer from the electronics and from the sample surface oscillations may mask the recalescence event at its maximum sampling rate of only 100 readings per second.

None of the pressed powders had the chance of being processed in the laboratory system before the Lepel stopped working.

IV. Summary and Future Work

The laboratory levitation system works but can still use some minor improvements regarding sample insertion, pyrometer alignment, and chamber pump-down. The data acquisition is "canned" software provided by National Instruments; any modifications to this software, such as voltage-to-temperature conversion and plot-printing, is still beyond the scope of the author.

A silicon photodiode will be required to observe recalescence so that the problems with the Ircon pyrometry can be avoided. The optics and narrow bandpass filter are still required.

The Drop Tube Lepel will have to be used to finish the lab experiments if the new 2.5 kW Lepel are not installed in time or does not have the necessary heating/levitating power. This means some Tube modifications to accommodate a gas flow down a quartz tube surrounded

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by the levitation coil. If this works, the resulting temperature control could be a big improvement that has been much needed for the Drop Tube. It is hoped that a pre-processing scheme can be found that would help in the alloying/vapor problem and dispose of bubbles that may expand or explode in the solution from the remaining voids.

Appendix

One question that arose in dealing with powders is how much error in the a/o is caused by a loss of a certain amount of mass of one powder due to the weighing procedures. An error analysis was performed and resulted in the error formula:

$$\Delta(a/o)_x = K \left[\frac{(a/o)_x}{(w/o)_x} \right]^2 \Delta(w/o)_x$$

where $K = (at.wt.)_x / (at.wt.)_y$, $\Delta(w/o)_x = \Delta M \sqrt{M_y^2 + M_x^2} / (M_x + M_y)^2$, and $\Delta M = \Delta M_x = \Delta M_y$ is the error of the scales being used to weigh the masses, M. $(w/o)_x$ is the weight percent that corresponds to the $(a/o)_x$. Using a 500 mg class P absolute calibration standard for the scales, the error in the weight of any individual powder was ±0.2 mg which produces a calculated relative error of about 0.02 a/o. In actuality, an error of ±1 mg was typical due to the sticking of the powder in the measuring cup, resulting in a relative error of about 0.1 a/o.

Table 1. Sample Information

sample number	atomic % Ag	height (cm)	mass (gm)	press force (lbs)	geometric density (g/cc)	% voids
AN1	20	0.337	0.42	2000	6.85	31.2
AN2	18.7	0.430	0.5592	2000	7.16	28.1
AN3	18.3	0.435	0.5421	2000	6.85	31.3
AN4	18.6	0.458	0.5783	2000	7.21	27.7
AN5	17.8	0.215	0.2816	2000-3000	7.21	27.7
AN6	18.3	0.426	0.5751	3000	7.43	25.5
AN7	18.5	0.395	0.5569	4000	7.76	22.2
AN8	18.8	0.366	0.5649	4000**	8.49	14.8

*Sample pressed at 6000 lbs for 10 seconds before piston failed.

Table 2

Sample Number		SAMPLE PROPERTIES							
		Pre-Sintering		Post-Sintering*					
		Weight (gm)	Height (mm)	Weight (gm)	Height (mm)	Mass Loss (mg)			
AN1		0.42	3.37						
AN2		0.5592	4.3						
AN3		0.5421	4.35						
AN4		0.5783	4.58	0.5478	5.29-5.33				
AN5		0.2816	2.15	0.2791	3.49	2.5			
AN6		0.5751	4.26	0.5596	5.72				
AN7		0.5569	3.95	0.5569	5.3				
AN8		0.5649	3.66	0.5521	5.36				
AN9		0.5549	3.63	0.5528	4.88-5.02				

* Because of the sample mixup, these values do NOT necessarily belong to this particular sample, except for AN5.

Table 3

5/16/94									
		Pure Element Pyrometer Data from Drop Tube							
		Ircon Tapp		Uncertainty		Del T Error			
	Element	(C)		(C)		(C)			
	Ni	1625		+/- 10		172			
	Ti	1850		10		180			
	Zr	2020		15		168			

Sintering of Ag-Ni Pellets
AN4-AN9

Figure 1

Figure 2. Ag-Ni Phase Diagram

VERTICAL MOTION
GEAR BOX

ROTATION
GEAR BOX

PYROMETER
VIEW

CROSS SECTION OF
EM LEVITATOR COIL

RF POWER

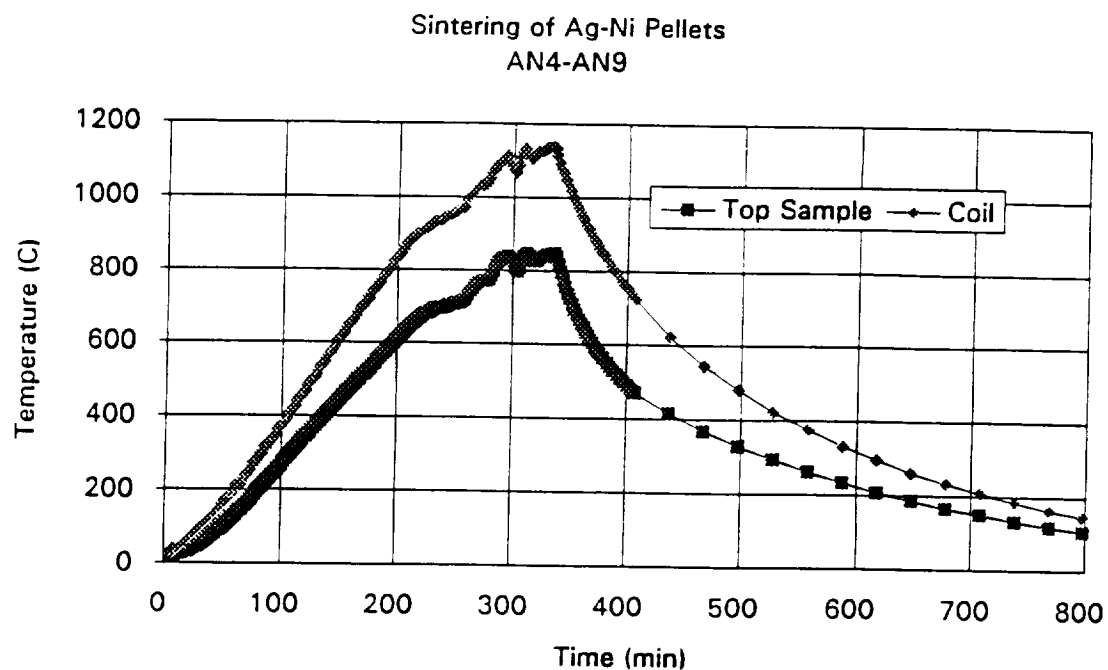PERIMETER MOUNTED PEDASTAL
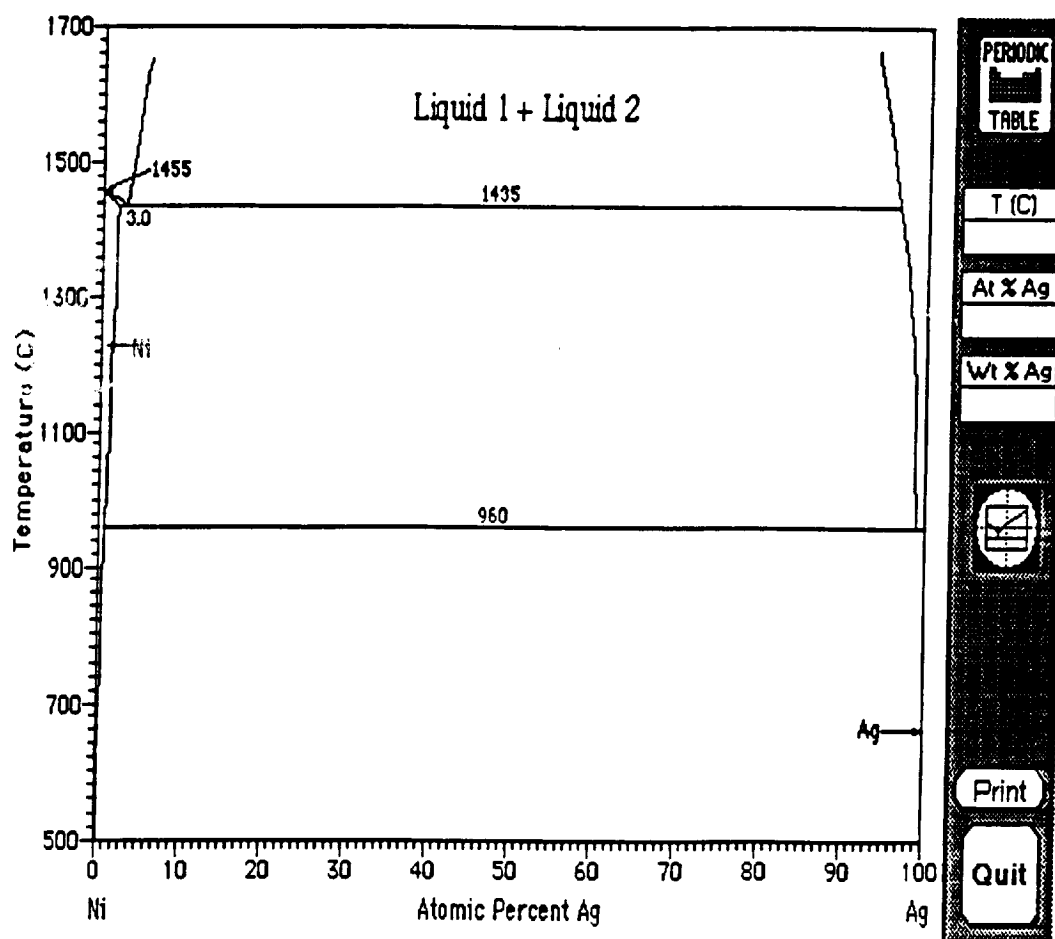(TYPICAL 7 PLACES)
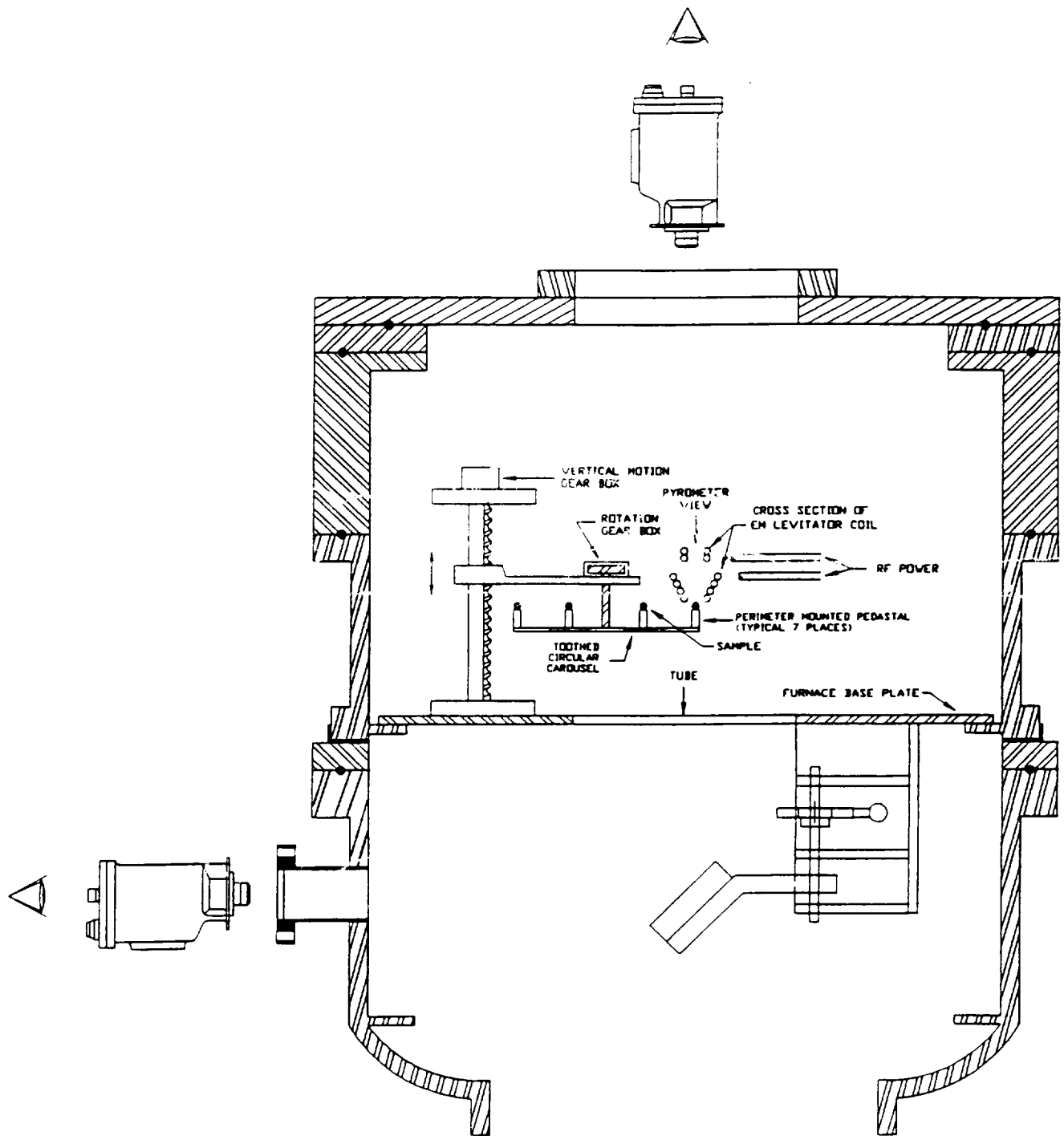
SAMPLE

TOOTHED
CIRCULAR
CAROUSEL

TUBE

FURNACE BASE PLATE

Fig 3 Schematic of the Drop Tube bell-jar in which the samples are processed
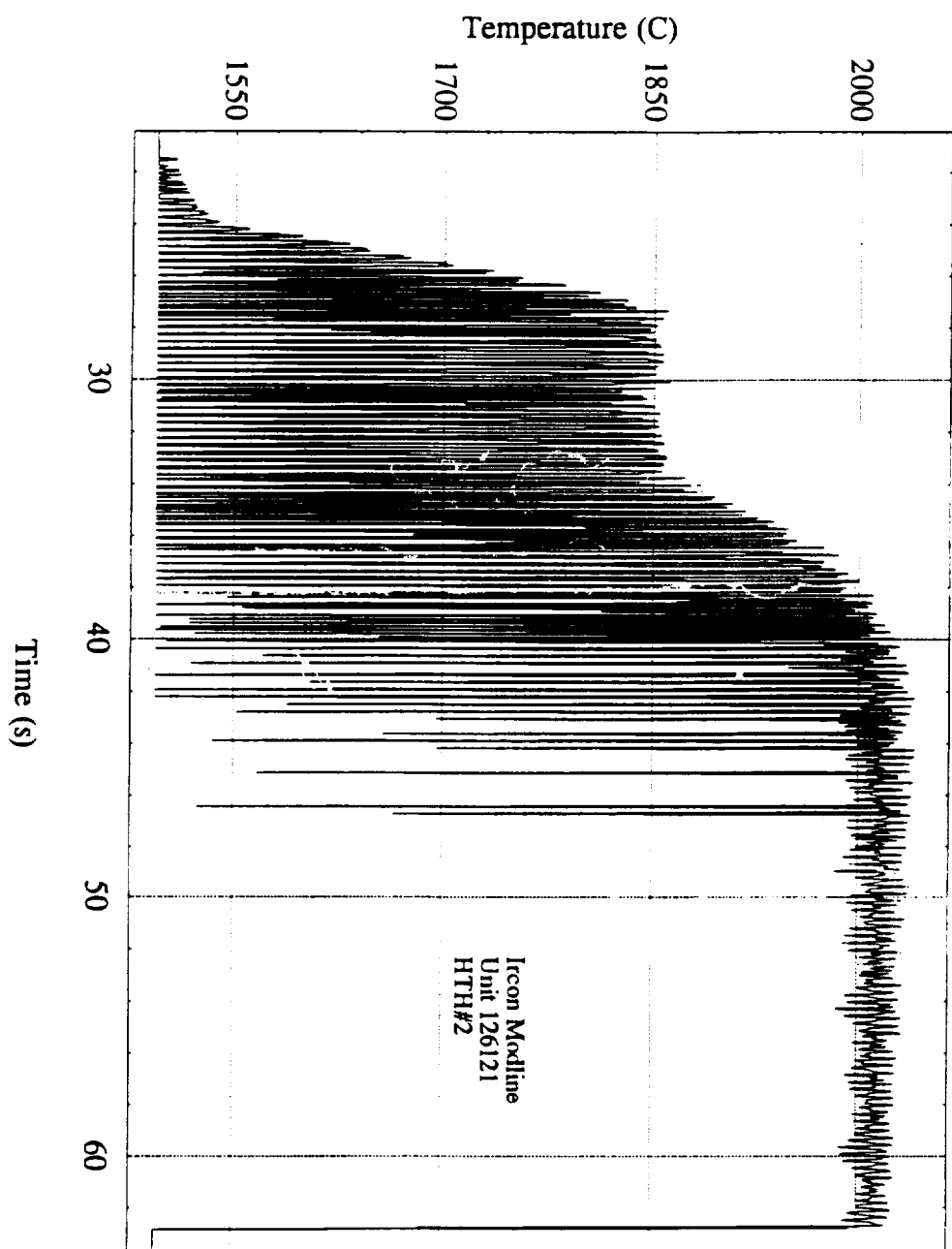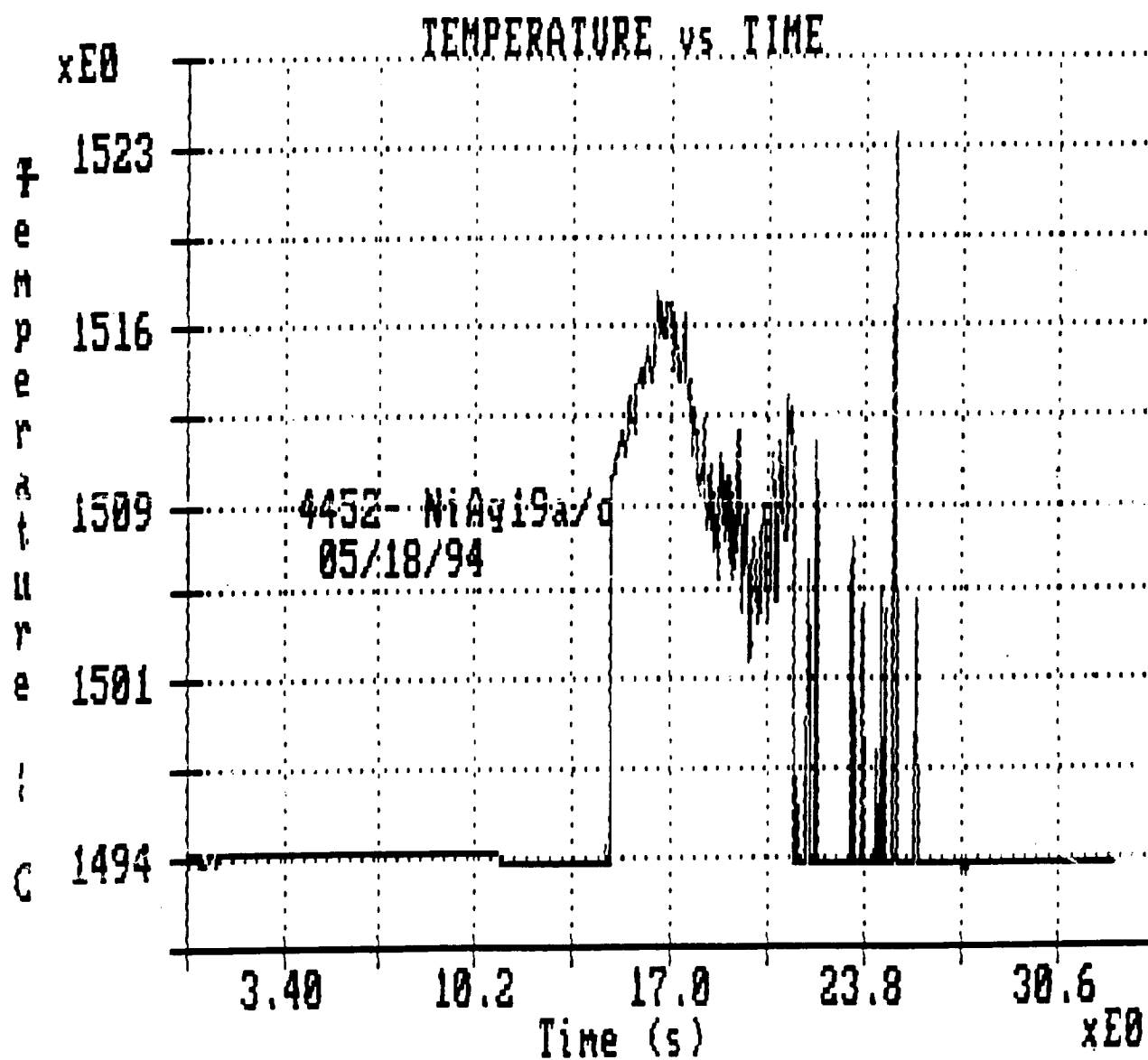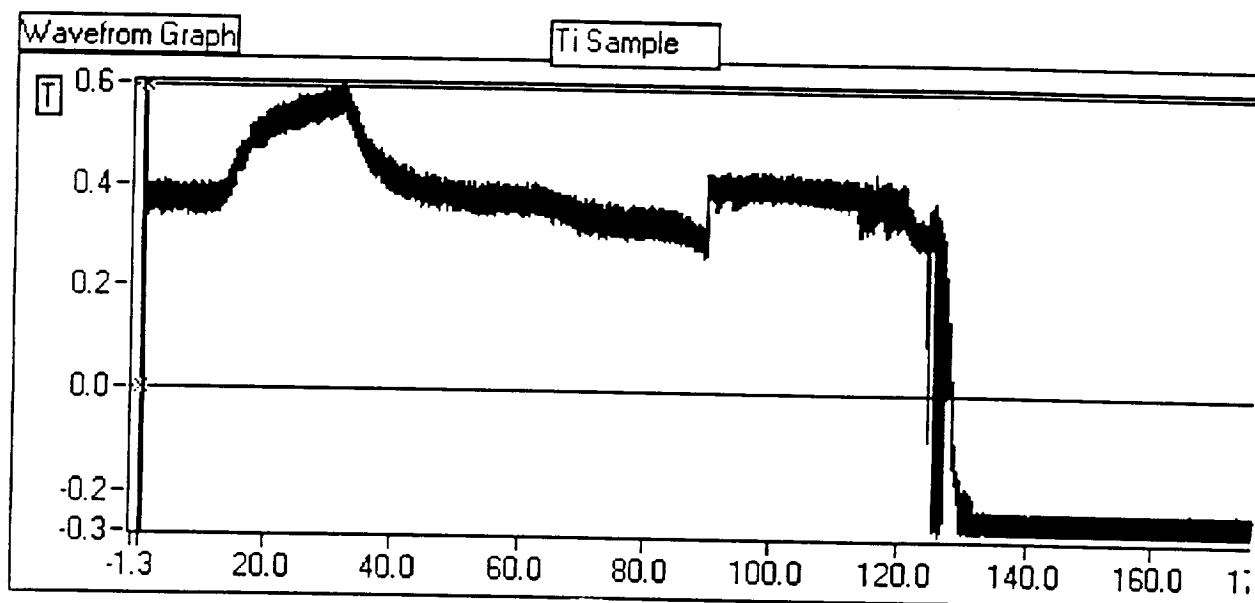before being released into the Tube section.

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Temperature (C)

2000

1850

1700

1550

30   40   50   60

Time (s)

Figure 4

4444- Ti 5mm dia

Ircon Modline
Unit 126121
HTH#2

Figure 5

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Wavefrom Graph **Ti Sample**

T

0.6 —
0.4 —
0.2 —
0.0 —
-0.2 —
-0.3 —

-1.3   20.0   40.0   60.0   80.0   100.0   120.0   140.0   160.0   1

Figure 7 a

Wavefrom Graph **Ti Sample**

T

0.4 —
0.4 —

0.3 —

0.3 —

89.0   89.2   89.4   89.6   89.8   90.0   90.2   90.4   90.6   90.8   9

Figure 7 b

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