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Craig B. Shumaker
(M.S. Thesis)

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INITIAL STAGE SINTERING OF COPPER AND NICKEL

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INITIAL STAGE SINTERING OF COPPER AND NICKEL

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ABSTRACT

The first sintering experiments using a high temperature hot stage scanning electron microscope have been completed. In addition to hot stage development, methods of data recording were perfected using a closed circuit television monitor.

Particle rearrangement and localized sintering postulated by Exner et al.⁹ are confirmed for real compacts and are shown to decrease with increased green density. During isothermal sintering of compacts of copper and nickel microspheres, enhanced densification was observed relative to the predictions of previous investigators.
I. INTRODUCTION

The most economical, and sometimes only way of forming ceramic objects, is by sintering. Although it is principally a process used for oxides, metals are sometimes sintered. Metals, however, have been used extensively in studying the initial stages of sintering due to their relatively low melting points and their ease of spheroidization.

Most early theoretical work concerned only neck growth kinetics. In 1949, Kuczynski$^1$ measured the neck growth of copper microspheres sintered to a flat copper plate in an attempt to obtain the self diffusion coefficient of copper.

Kingery and Berg$^2$ in 1955, first derived an expression for the linear shrinkage between two spheres. It is believed that only volume diffusion and grain boundary diffusion contribute to linear shrinkage between two spheres and therefore can be extended to apply to compacts. The general shrinkage kinetic equation used for both sphere to sphere and compact shrinkage is:

$$\frac{\Delta L}{L_0} = \left[ \frac{k \gamma D}{k T a^p} \right]^m \text{time}^m$$

where $\gamma$ = surface tension, $\Omega$ = atomic volume, $D$ = diffusion coefficient (volume or grain boundary), $a$ = particle radius, and $K$ = geometric constant (depending on the investigator). The exponent "$m$" and "$p$" vary depending on whether the diffusion mechanism is grain boundary or volume. Investigators have derived a range of time exponents as listed in Table I.
Table I. Values of constants for the shrinkage equation:

\[
\frac{\Delta L}{L_0} = \left[ \frac{K \rho D}{kT \alpha_p} \right]^m \text{time}^m
\]

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>K</th>
<th>p</th>
<th>m</th>
<th>Investigator(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk diffusion</td>
<td>5.34</td>
<td>3</td>
<td>0.49</td>
<td>Johnson⁴</td>
</tr>
<tr>
<td>20/\sqrt{2}</td>
<td>3</td>
<td>0.40</td>
<td>Kingery and Berg¹²</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>0.50</td>
<td>Coble⁴</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>3</td>
<td>0.46</td>
<td>Johnson and Cutler⁵</td>
<td></td>
</tr>
<tr>
<td>Grain Boundary Diffusion</td>
<td>2.14b</td>
<td>4</td>
<td>0.33</td>
<td>Johnson⁴</td>
</tr>
<tr>
<td>3b</td>
<td>4</td>
<td>0.33</td>
<td>Coble⁴</td>
<td></td>
</tr>
<tr>
<td>2.3b</td>
<td>4</td>
<td>0.31</td>
<td>Johnson and Cutler⁵</td>
<td></td>
</tr>
</tbody>
</table>

*b = thickness of the region of enhanced diffusion at the grain boundary.

Experimentally, many investigators⁵,⁶,⁷ found that compacts must be "pre-sintered" in order to observe uniform linear shrinkage. To account for (or avoid) this initial non-regularity, time-length corrections appeared in the literature.⁵,⁷,⁸

The recent work of Exner, Petzow, and Wellner⁹ shows that particles in compacts undergo rearrangements caused by compact density gradients. Volumes of compacts which are more regular in packing geometry shrink faster by sintering than irregularly packed, open regions of the compact. According to Exner et al.⁹ the less dense regions enlarge as a result of the high rate of sintering in adjacent areas. They⁹ postulated that chains of spheres tend to straighten themselves during sintering because
of asymmetrical neck curvatures. These German investigators extended their concept a step further to show that localized shrinkage can occur without being detected (Fig. 1). In Fig. 1, if two regions are bridged by a straight chain of spheres, the measured shrinkage will be accurate. If the connecting chain is not straight, it is possible that the two regions can shrink and not be detected because of chain straightening of the bridge.

In the past, experimental procedures for studying isothermal sintering have used dilatometers to measure shrinkage of compacts, electron images to measure neck growth and the length change of lines of spheres, and the hot stage optical microscope to measure neck growth and two sphere shrinkage. The recent developments in scanning electron microscopy by Fulrath has allowed continuous observation of the sintering phenomena at temperatures up to 1600°C with magnifications from 50 to 5000X.

This thesis presents initial work on the first stage sintering of copper and nickel microsphere compacts using data obtained from the SEM (scanning electron microscope). Experimental measurements of isothermal shrinkage obtained in this study, to be described below, do not agree with the time dependence predicted by existing sintering theories. It is postulated that sphere to sphere shrinkage theories cannot be applied to real compacts without considering the influence of the initial green density of the compact.
Fig. 1.* Straight chain connection and irregular chain connection.

*From Exner et al.⁹
II. HIGH TEMPERATURE SEM

The use of the hot stage on the SEM in sintering studies offers two important advantages compared to other methods of studying the sintering process. First, one can continuously observe a specimen's surface geometry from room temperature in the case of electrical conductors to the sintering temperature and then observe further changes during the isothermal run. Non-conductors, which develop an electrical charge due to the electron beam usually show sufficient surface conductivity that they can be easily observed at a few hundred degrees centigrade without applying conductive coatings. Secondly, the ease in changing magnification allows the observation of a specimen surface at both high and low magnification at approximately the same time. This feature is especially important for comparing neck growth rates with linear shrinkage rates.

A further advantage of hot stage SEM investigations is related to the possibility of introducing statistical analysis to shrinkage data of powder compacts by measuring dimensional changes between particles or across many particles on the surface of view.

There are problems in hot stage SEM investigations. First, the vacuum environment limits the temperature of investigation of a given material to that where vaporization losses or transport are not significant. Further, there are problems in determining the surface temperature of a porous sample in vacuum. An entry hole for the primary electron beam and exit for the secondary electrons allows radiation losses from the sample surface. Limited conduction through the porous compact can limit the surface temperature to values significantly below the temperature of the sample cup and produce significant thermal gradients. This heat loss

*Appears as a section from previous paper by R. M. Fulrath and author.¹⁰
Fig. 2. Scanning electron microscope hot stage.
can be minimized by keeping the viewing port diameter small. However, a small diameter viewing port limits the low magnification range. A compromise between radiation losses and low magnification limit must be made. Figure 2 shows the hot stage used in this study. The sample is in the platinum cup shown in the center of the stage. The temperature is monitored by spot welded platinum and platinum-rhodium wires to the rim of the cup. Also shown is the top platinum radiation shield with the viewing port.

Probably one of the most difficult problems encountered in working at high temperatures has been in data recording. In normal operation of the SEM and CRT image is recorded at very slow scanning speeds on Polaroid film using a positive-negative type with a one minute exposure. This allows the maximum number of scan lines per frame. Also the primary beam current is in the $10^{-10}$ to $10^{-11}$ ampere range for maximum resolution.

At high temperatures where thermal expansion of the hot stage components and sample changes are occurring rapidly, shorter exposure times are necessary. By using higher primary electron beam currents, one can use a TV scanning mode. Photographs of the TV screen or video taping can be used to permanently record the image. Loss in resolution is encountered due to the low number of scan lines compared to the slow scan CRT images.
III. EXPERIMENTAL

A. Specimen Preparation

The copper microspheres used in this study were obtained from Federal Mogul Corporation and Alcan Aluminum Corporation. Federal Mogul Corporation supplied the nickel and tungsten spheres. Sphere size fractionation was done with an Allen-Bradley Sonic Sifter Model L3 using standard sieves. Spectrographic and oxygen analysis of spheres used are listed in Table II.

In an effort to minimize the oxide layer on the copper spheres, the copper was washed in 10% HCl, rinsed in methanol, and vacuum dried. In one sintering run, Cu-E, the spheres were heated at 530°C for 9 hr in one atmosphere of hydrogen in an attempt to remove dissolved oxygen. The oxygen content for Cu-E was reduced from 0.59 w/o to 0.44 w/o. The nickel spheres were not pretreated.

To estimate initial green densities, two different methods were used. The first used a 100 gram weight attached to a teflon plunger which was hand tapped to compact the spheres in the 3/16 in. diameter platinum specimen cup. A dial indicator on the plunger was used to estimate the green density. Because spheres could flow between the plunger and cup wall, this method was subject to considerable error. The second method was more accurate: Two weight percent Carbowax (polyethylene glycol) was added to the spheres as a binder by dissolving the wax in toluene and evaporating the toluene. A 3/16 in. die was used to press to the desired green density. The Carbowax was evaporated at 300°C under vacuum for 1 hr. The height of the die pressed compacts was about 0.060 in., whereas the plunger compacted specimens were usually one-third
Table II. Spectrographic and oxygen analysis of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Impurity Analysis w/o</th>
<th>Oxygen Analysis w/o</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Federal</td>
<td>Si 0.2</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>Mogul</td>
<td>Mn 0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Co 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu 0.015</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe 0.015</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(All others below 0.01)</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Federal</td>
<td>Fe 0.005</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>Mogul</td>
<td>Ni 0.005</td>
<td></td>
</tr>
<tr>
<td>Copper***</td>
<td>Alcan</td>
<td>Pb 0.025</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(All others below 0.005)</td>
<td></td>
</tr>
</tbody>
</table>


**Experiments Cu-A and Cu-B.

***Experiments Cu-C, Cu-D, and Cu-E.
as high (0.020 in.). The method of measuring green densities is listed in Table III with a (C) for plunger compaction and a (D) for die pressing.

B. Experimental Conditions and Data Recording

Vacuum in the hot stage chamber ranged from 2.0 to $6.0 \times 10^{-6}$ torr for each of the eleven experiments. Heating rates of the compacts to the isothermal sintering temperatures were between 25 and 35°C/min. Temperatures of each experiment are listed in Table III along with the particle sizes used.

Magnifications from 50X to 150X were used along with three methods of data recording. Thirty-five mm photographs of the TV monitor were taken on five runs. In run Ni-B photographs were taken from the CRT with 120 film at a CRT scan speed of 5 sec at a magnification of 400X. From both the 35 mm and 120 film 8-1/2 in. x 11 in. prints were made for shrinkage measurements. In the remaining experiments, Polaroid P/N 55 photographs of the TV monitor were taken with a Graflex camera. Shrinkage measurements were made directly from 1-1/2 ft. x 2 ft. projections of the Polaroid negative. A typical Polaroid photograph appears in Fig. 3.

For the isothermal sintering experiments, a series of photographs were taken as dictated by a log time scale with the first photograph taken when the specimen reached the desired isothermal sintering temperature. To measure shrinkage from the prints, pinholes were made at topographically predominant areas of the surface (i.e., the dark area between three spheres).

The pinhole locations were chosen close to the perimeter of the photograph in order to measure across as many spheres as possible. One
Table III. Experimental conditions for eight isothermal and three thermal expansion experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>Run No.</th>
<th>Size ( \mu m )</th>
<th>Temp.(^o)C (frac. of absolute melting temp.)</th>
<th>Green Density % 0th</th>
<th>No. of measurements per photo</th>
<th>TV monitor magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Ni-A</td>
<td>-30+20</td>
<td>1200 (0.85)</td>
<td>43% (C)</td>
<td>16</td>
<td>150X</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-B</td>
<td>-30+20</td>
<td>1195 (0.85)</td>
<td>42% (C)</td>
<td>28</td>
<td>150X</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-C</td>
<td>-30+20</td>
<td>1110 (0.80)</td>
<td>40% (D)</td>
<td>16</td>
<td>50X</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-A</td>
<td>-44+37</td>
<td>950 (0.90)</td>
<td>43% (C)</td>
<td>16</td>
<td>100X</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-B</td>
<td>-30+20</td>
<td>810 (0.80)</td>
<td>43% (D)</td>
<td>16</td>
<td>50X</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-C</td>
<td>-44+37</td>
<td>950 (0.90)</td>
<td>42% (C)</td>
<td>16</td>
<td>100X</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-D</td>
<td>-30+20</td>
<td>810 (0.80)</td>
<td>40% (D)</td>
<td>16</td>
<td>50X</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-E</td>
<td>-44+37</td>
<td>950 (0.90)</td>
<td>28% (C)</td>
<td>16</td>
<td>150X</td>
</tr>
<tr>
<td>Tungsten</td>
<td>W-1</td>
<td>-30+20</td>
<td>800 to 1200</td>
<td>42% (D)</td>
<td>6</td>
<td>50X</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-1</td>
<td>-30+20</td>
<td>same</td>
<td>42% (D)</td>
<td>3</td>
<td>50X</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni-2</td>
<td>-30+20</td>
<td>same</td>
<td>50% (D)</td>
<td>5</td>
<td>50X</td>
</tr>
</tbody>
</table>

*(C) for plunger compaction and (D) for die pressed.
Fig. 3. Typical Polaroid P/N 55 photograph of 8 in. television monitor.
pinhole in each corner and one on each edge of the photograph made up
the eight holes from which the 16 measurements were made. No measure-
ments between adjacent pinholes were made. Measuring accuracy was better
than 0.5%. Because variation in enlargement of the negatives and film
shrinkage could render the shrinkage calculations misleading, markers
were taped to the TV screen in order to normalize the length measurements.
The normalizing "X's" can be seen in Fig. 3.

C. Computer Calculations and Plots

For the isothermal sintering experiments, a computer program was
written to normalize the measurements and calculate the average \( \Delta L/L_0 \)
and standard deviation for each time. See Appendix A for printout of
the program and calculations for experiment Ni-C. Cal Comp plotter graphs
were prepared which show percent \(-\Delta L/L_0\) versus time (min) on log scales.
The plots include error bars (\(\pm\)) for each point and the slope as deter-
mined by a linear least squares analysis.

A series of conditions were set by which the program would generate
plots. If all the \( \Delta L/L_0 \)'s were negative the program would plot such data
using time \(= 0\) minutes as the base time and use all data in the linear
least squares slope calculation. After the initial plot the data was
again inspected to determine at which time the first continual shrinkage
commenced. If shrinkage did not begin at time \(= 0\), the slope was recal-
culated based only on the continual shrinkage points and replotted. A
third plot would be computer drawn in which all \( \Delta L/L_0 \) calculations were
based on the first point of continual shrinkage as the new base time and
new \( L_0 \).
If sample expansion occurred at the start of the isothermal run, the program plotted the first graph with base time = 0, but used the first negative value of $\Delta L/L_0$ for slope calculation. Again, if the first negative $\Delta L/L_0$ point was not the first point of continual shrinkage, the slope was recalculated and plotted on a second graph. The final graph again replotted the data selecting the first shrinkage point as the slope base and $L_0$.

On the isothermal sintering plot figures, the symbol © indicates an expansion, † indicates a shrinkage less than 0.1%, whereas greater than 10% shrinkage is denoted by ††.
IV. RESULTS AND DISCUSSION

A. Isothermal Sintering Experiments

Despite the fast heating rates of the compacts from room temperature to the isothermal sintering temperature, considerable neck growth could be seen from high magnification photographs. Figure 4 shows neck growth on runs Ni-A, Cu-A, and Cu-C at time = 0 minutes. By the time the specimen cup had reached temperature, the neck radius to particle radius ratio had already increased to nearly 0.3, the assumed limit of linearity of many neck growth theories.\textsuperscript{1,3}

Because of the apparent difficulty of isothermally measuring neck growth and inconsistent quality of high magnification photographs further isothermal neck growth studies were not attempted.

The slopes (shrinkage rates) of the log $\Delta L/L_0$ versus log time plots are listed in Table IV along with base times of each plot as generated by the computer program. Figures 5 through 12 are the plots of the eight isothermal sintering experiments.

Two trends appear from analyzing the isothermal plots. First, the runs in which the specimen was prepared with the plunger compactor have less error in both the average $-\Delta L/L_0$ values and the slope than do the specimens prepared by die pressing. (The exception is experiment Ni-B which was run at higher magnification and will be discussed in detail in the next section.) Also, the die prepared specimen plots show a time lag before sintering was observed. The difference in results observed between the specimens prepared by plunger compaction and die pressing can be explained on the basis of specimen cup wall constriction.
Fig. 4. High magnification photographs of samples Ni-A, Cu-A, and Cu-C at time = 0 minutes.
Table IV. Shrinkage rates from isothermal sintering experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Fig. No.</th>
<th>Slope (shrinkage rate)</th>
<th>Standard Deviation</th>
<th>( L_0 ) Base time (min)</th>
<th>Slope Base time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-A</td>
<td>5</td>
<td>0.609</td>
<td>0.029</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni-B</td>
<td>6a</td>
<td>0.663</td>
<td>0.075</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.818</td>
<td>0.074</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>0.742</td>
<td>0.059</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Ni-C</td>
<td>7a</td>
<td>0.606</td>
<td>0.046</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.641</td>
<td>0.058</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>0.577</td>
<td>0.037</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Cu-A</td>
<td>8</td>
<td>0.357</td>
<td>0.023</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu-B</td>
<td>9a</td>
<td>0.696</td>
<td>0.073</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.772</td>
<td>0.093</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>0.663</td>
<td>0.088</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Cu-C</td>
<td>10</td>
<td>0.647</td>
<td>0.050</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu-D</td>
<td>11a</td>
<td>0.995</td>
<td>0.226</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>1.40</td>
<td>0.189</td>
<td>0</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>0.625</td>
<td>0.0</td>
<td>81</td>
<td>81</td>
</tr>
<tr>
<td>Cu-E</td>
<td>12</td>
<td>0.606</td>
<td>0.045</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig. 5. Isothermal sintering graph of experiment Ni-A. 
$L_0$ base time = 0 min and slope base time = 0 min.
Fig. 6. Isothermal sintering graphs of experiment Ni-B.
Fig. 7. Isothermal sintering graphs of experiment Ni-C.
Fig. 8. Isothermal sintering graph of experiment Cu-A. 
$L_0$ base time = 0 min and the slope base time = 0 min.
Fig. 9. Isothermal sintering graphs of experiment Cu-B.
Fig. 10. Isothermal sintering graph of experiment Cu-C.
$L_0$ base time = 0 min and slope base time = 0 min.
Fig. 11. Isothermal sintering graphs of experiment Cu-D.
Fig. 12. Isothermal sintering graph of experiment Cu-E. 
$L_0$ base time = 0 min and slope base time = 0 min.
Because the metal spheres were poured directly into the specimen cup and then compacted with a teflon plug, the plunger compacted specimens had only one free surface. Whereas since the die pressed specimens were pressed and set in the cup, they had no restraining force exerted by the cup wall. Also, the plunger compacted specimens were only 0.020 in. thick, a third as thick as the die pressed compacts. Therefore, the free surfaces used for measurements on the die pressed specimens were unaffected by the cup relative to the plunger prepared compacts.

The other significant observation seen in the sintering plot figures is that shrinkage rates, regardless of time-length corrections, were well above (except Cu-A) the predicted and previously observed slopes of 0.31 to 0.50 listed in Table I. Because of the limited amount of data, any cause of the lower shrinkage rate for run Cu-A (i.e. particle size, sintering temperature, or impurity content) must be speculative.

As a test of the reliability of the statistical method, the data from run Cu-C was replotted using only the six measurements between the four corner pinholes of each photograph, the resultant slope was found to be only $0.441 \pm 0.057$ (Fig. 13). Therefore, careful selection of the data points used can give a range of time exponents, and hence the necessity of a thorough statistical analysis is emphasized.

Varying time exponents resulting from the selection of specific data measurements, the different results between the two methods of compact preparation, and time-length corrections strongly suggest sphere rearrangement (re: Exner et al.⁹).
Fig. 13. Replot of the data from experiment Cu-C using only six measurements.
B. Rearrangement Study

Further study of the rearrangement process was made by comparing two prints from sample Ni-B at time = 0 and 200 min and superimposing them to detect shifts in the compact. Examination of these photographs and the line drawing in Fig. 14 support qualitatively Exner et al.'s\textsuperscript{9} theory of localized sintering. The areas in the upper right hand corner and left central are more close-packed than the center. After only 10% overall shrinkage, pores in the close-packed areas have (or nearly have) closed and the two regions have moved apart. Also, the angle between three spheres in the upper central area has increased.

To clearly illustrate permanent particle shifts, a perimeter line connecting the ten points used in run Ni-B's 28 measurements was drawn on overlays of the two prints. The segments of the perimeter line are not measurement lines. The measurements were made across the figure and span at least one other point. To most perfectly match the time = 0 polygon, the 200 minute figure was enlarged approximately 8-1/4\% to cancel the shrinkage. Then the two polygons were superimposed as seen in Fig. 14.

From the overlay, considerable rearrangement can be seen, which would greatly affect shrinkage calculations. A photographic transparency of the superimposed polygons was projected to check alignment of the 28 measurements. On the 2 ft x 3 ft wall projection, measurements on the 200 minute polygon that matched within 1/2 in. of the time = 0 polygon were categorized as "good alignment". Measurements that were within about 2 in. were designated as "marginal alignment" and the remaining were categorized as "poor alignment". Three values for the
Fig. 14. Sphere rearrangement study of experiment Mi-B.

Line drawing of surface spheres

Time = 0 denoted by _______ on line drawing and time = 200 min by _______.

Overlay of time = 0 and 200 polygons

time = 0 min

time = 200 min
isothermal shrinkage rates were plotted using four "good alignment" measurements (Fig. 15a), the four "good" and eight "marginal alignment" measurements (Fig. 15b), and only the remaining 16 "poor alignment" measurements (Fig. 15c). Table V lists the slopes for comparison.

From the above analysis it is concluded that the selection of "good alignment" and "marginal alignment" measurements reduces the ΔL/L₀ deviations at later sintering times. The large deviation at initial sintering times implies that the measuring locations shift relative to each other in the first 20 min. By predetermined measurement selection, the slope is not greatly affected, but the slope deviation is reduced by eliminating locations that permanently shift. By eliminating the data corresponding to measuring locations that shift permanently, the initial period of erratic sintering which requires a time-length correction is eliminated.

Sintering data for compacts cannot reasonably be subjected to the above selective treatment for shrinkage rate determination if rigorous results are desired. A rigorous study of correlated effects should include statistical analysis of the movement of large numbers of particles. Or more simply, the effect of initial green density on initial stage sintering rates should be investigated as this probably plays a significant role in initial stage sintering.

C. Effect of Green Density on Non-Uniform Sintering

Intuitively, as green density of a compact approaches the density of ideally packed spheres, the rearrangement process during initial sintering will decrease. In a preliminary attempt to characterize the effect of green density on initial stage sintering of compacts, three experiments were run using identical heating rates.
Fig. 15a. Four good alignment measurements.

Fig. 15b. Four good and eight marginal alignment measurements.

Fig. 15c. Sixteen poor alignment measurements.

Fig. 15. Isothermal sintering graphs from selected measurements of experiment Ni-B.
Table V. Comparison of shrinkage rates for run Ni-B using selected measurements

<table>
<thead>
<tr>
<th>Measurements Used</th>
<th>Fig. No.</th>
<th>Slope (shrinkage rate)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>All 28</td>
<td>6a</td>
<td>0.663</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>0.818</td>
<td>0.074</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>0.742</td>
<td>0.059</td>
</tr>
<tr>
<td>4 &quot;good alignment&quot;</td>
<td>15a</td>
<td>0.624</td>
<td>0.045</td>
</tr>
<tr>
<td>4 &quot;good&quot; and 8 &quot;marginal alignment&quot;</td>
<td>15b</td>
<td>0.696</td>
<td>0.045</td>
</tr>
<tr>
<td>16 &quot;poor alignment&quot;</td>
<td>15c</td>
<td>0.718</td>
<td>0.059</td>
</tr>
</tbody>
</table>

Tungsten microspheres were used to check the sensitivity of the hot stage SEM and the data measuring technique at temperatures below those required for rapid sintering. A maximum temperature of 1200°C was chosen, as 1200°C is only 0.4 the absolute melting temperature of tungsten and is well below the 0.7 value where measurable sintering occurs. Also, the thermal expansion coefficient of tungsten is 1/4 that of nickel. Although Fig. 16 indicates shrinkage, there is relative expansion from 800°C to 1200°C. Residual binder between spheres is believed to have caused contraction from room temperature to 800°C. A linear least squares slope through the experimental points shows an expansion of 0.16% over 400°C, versus the expected 0.21% calculated from the thermal expansion of tungsten. 12
Fig. 16. SEM hot stage sensitivity determination from the thermal expansion of tungsten. —— is the excepted expansion from thermal expansion values of tungsten,$^{12}$ ——— is a linear least square slope of the experimental values.
The same experiment was rerun using nickel spheres of the same 42% green density (run Ni-1). Figure 17a shows an expansion of 0.58% for run Ni-1 compared to an expected 0.83%.\textsuperscript{12} If the percent deviation in thermal expansion measured for tungsten can be expected in this type of experiment, then the results from run Ni-1 indicate that no shrinkage by sintering has occurred. However, experiment Ni-C, which was run at 1100°C, shows continual shrinkage after 7 min. Therefore, it is believed that undetectable non-uniform sintering was measured in Ni-1 as postulated by Exner, et al.\textsuperscript{9} and examplified in Fig. 1.

A distinct shrinkage was observed when the green density was increased to 50% (Fig. 17b). A contraction of 0.2% was observed from 800°C to 1200°C whereas an expansion of 0.83% was expected\textsuperscript{12} if the nickel did not sinter.

Despite the large scatter of data points in Figs. 16 and 17, it can be seen that higher green densities reduce the amount of non-uniform sintering.
Fig. 17. SEM hot stage thermal expansion of Nickel during non-uniform sintering. —— is the expected\textsuperscript{12} expansion if the nickel did not sinter and —— —— is a linear least squares slope of the experimental data.
V. CONCLUSIONS

The experimental confirmation of non-uniform sintering shows that attempts to distinguish between grain boundary or volume diffusion from shrinkage kinetics of real compacts lead to erroneous conclusions unless green density is considered. Time-length corrections made by many investigators appear to have been used to "bypass" what is now known to be spatial rearrangement. However, even if time-length corrections are made, localized sintering still occurs and this process will hamper accurate $\Delta L/L_0$ measurements in the 1% shrinkage range because of the constant shifting of particles. The study of particle rearrangement on the surface of compacts also shows that the two dimensional non-uniform sintering studies of Exner et al.\textsuperscript{9} hold true for real compacts. The present study shows qualitatively that increased green density reduces the extent of localized sintering.
APPENDIX A.

Computer Program for Isothermal Sintering Experiment Calculations

The computer program used the time, normalizing factors, and length measurements to calculate $\Delta L / L_0$'s and slopes, and make time-length corrections and Cal Comp plots. The program was run on the Lawrence Berkeley Laboratory's Control Data Corporation 6600 computer, and includes the printout for experiment Ni-C.

```plaintext
C DATA DECK ORDER
C CARD 1 = RUN DESIGNATION, FULL CARD FIELD (FIRST 48 ON CAL COMP)
C NUM OF DATA PTS/PHOTO AND NUM OF PHOTOS (IN 21 FIELDS 10 WIDE
   ## 3  FMT = INPUT FORMAT (STARTING IN COL 1)
   ## 4  FMT = PRINT FORMAT OF INPUT DATA
   ## 5  FMT = PRINT FORMAT FOR NORMALIZED AND CALCULATED ARRAYS
   ## 6  TIME (FMT FORMAT)
   ## 7  NORMALIZING DATA (FMT)
   ## 8  THRU N+4 DATA (FMT)
C
PROGRAM SHACK (INPUT: OUTPUT: PLOT: IUP=256: TMAX=10:1)
DIMENSION TV(20),DIM(100,20),STAN(100,20),LO(100,20)
10LL(100,20):FMT(5), FAT(5), FRT(5),TMT(20)
COMMAND A(20), LOGT(20), SHB(1), RUN(12), TIME(20), SIG(20), AVG(20)
IT(20)
REAL LOGT, LOGT(20), JAVY(20)
INTEGER M
C TMT = THE CORRECTED BASE TIME WHERE THE FIRST SHRINKAGE OCCURS
C TLOG = THE ALOG10 OF TMT
C
C INPUT
C READ(I,): RUN
21 FORMAT(24X)
   READ 2X (N=0)
   FORMAT (24X)
   READ 3X, (FMT(J)+J=1,5)
   FORMAT (556)
   READ 3X, (FRT(J)+J=1,5)
   FORMAT (456)
   READ 3X, (FRT(J)+J=1,5)
   FORMAT (556)
   READ FMT, (TIME(J)+J=1,0)
   READ FMT, (TV(J)+J=1,0)
   READ FMT, (XIMS(I)+I=1,M)+1
C PRINTING OF THE INPUT DATA
C PRINT 56, RUN
56 FORMAT (24X)
   PRINT 51
   FORMAT (+/+ T = +)
   PRINT FRT, (TIME(J)+J=1,0)
   PRINT 5
   FORMAT (+/+/NORMALIZATION DATA+)
   PRINT FRT, (TV(J)+J=1,0)
   PRINT 7
   FORMAT (+/+/ RAW DATA MEASUREMENT+)
   PRINT FRT, (XIMS(I)+I=1,M)+1
C NORMALIZATION AND PRINT
   DO 100 J=1,0
   DO 100 I=1,N
   STAN(I,J) = DIMS(I,J) / TV(J)
   100 CONTINUE
C PRINT 75
75 FORMAT (+/+/ NORMALIZED DATA+)
   PRINT FRT, (STAN(I,J)+J=1,O)+11,N)
C DELTA L AND DELTA L/L SUB ZERO
C PRINT 73
73 FORMAT (+/+/SHRINKAGE CALCULATIONS WITH BASE LINE TIME = 0+)
   L = 1
980 LL = L+1
   DO 110 J=1,LL
   LOGT(J) = ALOG10(TIME(J))
```
TIM(j) = TIME(j) = TIME(L)
LD0(j) = ALOG10(TIM(j))
DO 110 I = 1,N
DL(I+j) = STA(I,j) - STA(I+L)
DLS(I+j) = DL(I+j) / STA(I+L)
110 CONTINUE
DO 114 K = 1,L
DO 115 I = 1,N
NL(I+K) = 0.0
DLS(I+K) = 0.0
114 CONTINUE
PRINT 776
776 FORMAT (// DELTA L * )
PRINT 777
777 FORMAT (// DELTA L , L SUB ZERO * )
C
C STD OF V AND SIGMA
IF (L,N,E,I) GO TO 213
PRINT 12
GO TO 313
213 PRINT 413
GO TO 313
313 DO 140 J = LL,0
SUMA = 0.0
DO 150 I = 1,N
SUMA = SUMA + A(I)
150 CONTINUE
AVG(J) = SUMA/N
Y = ABS(DLS(I+J)) - AVG(J)
Z = Y**2
SUMR = SUMR + Z
140 CONTINUE
S10(J) = SQRT(SUMR/(N-1))
IF (L,N,E,I) GO TO 207
PRINT 134 (TIME(J),AVG(J),S10(J))
GO TO 144
207 PRINT 134 (TIM(J), AVG(J), S10(J))
144 CONTINUE
12 FORMAT (//20X,*TIME*,5X,*AVERAGE DELTA L/L SUBZERO AND STD DEVIATION*)
13 FORMAT (F25.1,2F25.6)
143 FORMAT (//10X,*AVERAGED TIME*, *AVERAGE DELTA L/L SUB ZERO AND 1ST DEVIATION*)
C
C LOG PFR CENT SHRINKAGE (EXPANSION AND LESS THAN 8.1 THROW OUT) AND
C
C PRINT
PRINT 132
AV = 0.0
DO 120 J = LL,0
AV = AVG(J) = 100.0
IF (AV) 120,122,122
121 AV = AV + 0.1
IF (AV) 214,221,222
221 AV = 0.0
LOGL(J) = ALOG10(AV)
IF (L,N,E,I) GO TO 513
PRINT 114 (TIME(J),LOGL(J))
GO TO 124
122 PRINT 132,TIME(J)
GOTO 120
222 PRINT 134,TIME(J)
124 CONTINUE
132 FORMAT (//20X,*TIME*,18X,*LOG TIME*,10X,*LOG PERCENTAGE SHRINKAGE*)
134 FORMAT (1F25.1,2F25.6)
136 FORMAT (1F25.1,10X,*LESS THAN 8.1 PER CENT SHRINKAGE*)
C
C PLOT THROUGH ALL SHRINKAGE POINTS
IF (L,N,E,I) GO TO 6
DO 437 J = 1,N
T = ABS(AVG(J))
NT = T - AVG(J)
IF (NT*NT) 437,493,493
437 CONTINUE
929 LOG = L - I
IF (LOG) 494,495,499
990 LOG = Q = -1
DO AS J = LL, LD
IF (AVG(J) <= B8) A8
JA(J) = AVG(J) - AVG(J + 1)
IF (JA(J)) B5, B9, B8
A8 CONTINUE
B8 IF (J, EQ, LL) 60 TO 69
IF (LL = EQ, 9) GO TO 273
CALL CEXIT
C GRAPH IF THERE ARE EXPANSION POINTS
MS = J
MU = MS + 1
CALL LINLSQ(LOGX, LOGY, MS, 10, SIGMA, SA, SB)
PRINT 60, TIME(MS)
FORMAT (1, 3X, H10.2, 1X, H10.2, 1X, H10.2)
PRINT 60, A(2), SB
PRINT 61, A(1), SA
TIL = TIME(L)
TM = TIME(MS)
CALL GRAPH (L, LL, G, N, MS, TIL, TM)
L = J
PRINT 60, TIME(J)
FORMAT (1, 3X, H10.2, 1X, H10.2, 1X, H10.2)
CALL CEXIT
G0 TO 999
999 MS = J
MU = MS + 1
CALL LINLSQ(LOGX, LOGY, MU, 10, SIGMA, SA, SB)
PRINT 60, A(2), SB
PRINT 61, A(1), SA
6A FORMAT (H10.2, 1X, H10.2, 1X, H10.2, 1X, H10.2)
FORMAT (1, 3X, H12.2, 1X, H12.2, 1X, H12.2)
CALL CEXIT
G0 TO 1
CALL CCEND
G0 TO 1
CALL LINLSQ(LOGL, LOGY, LL + 1, SIGMA, SA, SB)
PRINT 60, A(2), SB
PRINT 61, A(1), SA
TIL = TIME(L)
TM = TIME(MS)
CALL GRAPH (L, LL, G, N, MS, TIL, TM)
CALL CCEND
G0 TO 1
CALL CCEND
NO COMMENT
STOP
END

SUBROUTINE LINLSQ(X, Y, MS, SIGMA, SA, SB)
A(2) IS THE SLOPE, A(1) IS THE INTERCEPT
SB IS THE DEV OF SLOPE, SA IS DEV OF INTERCEPT
SIGMA IS RMS DEV

DIMENSION X(MS), Y(MS), A(2)
NOT THE STANDARD LINLSQ = CHANGED 50 RIGHT NUMBER PT
FN = (N-1)!1
SUMX = 0
SUMYSQ = 0
SUMY = 0
SUMYSQ = 0
SUMXDEV = 0
DO 12 J = 1, MS
SUMX = SUMX + X(I)
SUMY = SUMY + Y(I)
SUMXSQ = SUMXSQ + X(I)*Y(I)
SUMYSQ = SUMYSQ + X(I)*Y(I)
SUMY = SUMY + X(I)*Y(I)
SUMXDEV = SUMXDEV + X(I)*Y(I)
12 CONTINUE
A(2) = (SUMY * SUMX * SUMXDEV) / (SUMY * SUMX + SUMXDEV)
A(1) = (SUMY * A(2) - SUMX) / FN
SIGMA = SQRT((SUMXSQ - A(1)*SUMX + SUMY) / (FN - 1)))
SA = SIGMA * SQRT(FN / (FN - 1))
SB = SIGMA * SQRT(FN * (SUMXSQ - SUMX * SUMX))
RETURN
END
SUBROUTINE GRAPH (L1, LL, N, MS, TIL, TIM)
COMMON A(2), LOST(2), SB(1), RUN(12), TIME(28), S10(20), AVX(20)
T1Q0(120)
DIMENSION GRIDX(2), GRIDY(2), X(2), Y(2)
REAL LOST
INTEGER 0
COMMON/CPOOL/KMIN, XMAX, YMIN, YMAX, CCMIN, CCMAX, CCYMIN, CCYMAX
COMMON/CFACT/FACTOR
FACTOR = 1


THEN THE SLOPE WHICH WAS CALCULATED IN THE LINREG SUBROUTINE IS PLT.


THE LAST GRAPH WILL ALWAYS BE PLOTTED WITH THE FIRST SHRINKAGE ADJUSTED TO THE BASE LINE TIME WITH THE SLOPE ADJUSTED TOO.

SIZE OF THE PLOT
CCMIN = 200
CCMAX = 300
CCYMIN = 200
CCYMAX = 300
XMIN = -0.5
XMAX = 2.05
YMIN = -1.6
YMAX = 0.6

BOTTOM TICK MARKS
CALL CCLCDT (1, 6, HOLDS, 51)
GRIDX(1) = -1.0
GRIDY(2) = -0.9
DO 108 I = 1, 6
GRIDX(I) = (I*0.5) - 0.5
GRIDY(2) = GRIDY(1)
CALL CCLCDT (GRIDX, GRIDY, 2, 4, JOIN)
CONTINUE

RIGHT SIDE TICK MARKS
GRIDX(1) = 2.75
GRIDX(2) = 0.9
DO 109 I = 1, 4
GRIDY(I) = (I*0.5) - 1.0
GRIDY(2) = (I*0.5) - 1.0
CALL CCLCDT (GRIDX, GRIDY, 2, 4, JOIN)
CONTINUE

TOP TICK MARKS
GRIDX(1) = 3.0
GRIDX(2) = 1.0
DO 110 I = 1, 4
GRIDX(I) = (I*0.5) - 0.5
GRIDY(I) = GRIDY(1)
CALL CCLCDT (GRIDX, GRIDY, 2, 4, JOIN)
CONTINUE

LEFT SIDE TICK MARKS
GRIDX(1) = -0.15
GRIDX(2) = -0.05
DO 111 I = 1, 3
GRIDY(I) = (I*0.5) - 1.0
GRIDY(I) = (I*0.5) - 1.0
CALL CCLCDT (GRIDX, GRIDY, 2, 4, JOIN)
CONTINUE

LABELING
CALL CCLTR (410, -168, 1, 3, 14, TIME (MIN), 10)
CALL CCLTR (120, -188, 1, 13, 13, SHRINKAGE (PER CENT), 26)
CALL CCLTR (210, -710, 0, 3, 8, SLOPE = 8)
CALL CCLTR (655, 715, 0, 2, 10, STD DEI = 10)
PRINT OF SLOPE, STD DEI, AND RUN INFO
WRITE (94, 96) A(2)
FORMAT (195, 3)
CALL CCLTR (340, -710, 0, 3)
WRITE (94, 91) SB
FORMAT (195, 3)
CALL CCLU(172, 718, 0, 0)
WRITE (94, 92) RUN
92 FORMAT (64) 
CALL CCLU(196, 509, 3, 0)
CALL CCLU(210, 750, 0, 0, IXHRA = MIN, T0)
PRINT OF BASELINE TIME
WRITE (94, 91) TIL
91 FORMAT (15F5, 2)
CALL CCLU(426, 750, 0, 0)
CALL CCLU(495, 750, 0, 0, 15MSLOPE BASE TIME, 15)
WRITE (94, 96) TIM
96 FORMAT (15F5, 2)
CALL CCLU(898, 750, 0, 0)
C
C C X AXIS LETTERING
CALL CCLU(536, 180, 6, 2, 1H1S)
CALL CCLU(355, 180, 6, 2, 1H3S)
CALL CCLU(176, 180, 6, 2, 2H1S)
CALL CCLU(106, 180, 6, 2, 2H3S)
CALL CCLU(720, 180, 0, 0, 2, 3H1S)
CALL CCLU(845, 180, 0, 0, 2, 3H3S)
C
C C Y AXIS LETTERING
CALL CCLU(596, 192, 0, 0, 2, 2MS, 1, 3)
CALL CCLU(180, 318, 0, 0, 2, 3H0S, 3, 3)
CALL CCLU(106, 443, 0, 0, 2, 1H1S, 1)
CALL CCLU(856, 568, 0, 0, 2, 1H3S, 1)
CALL CCLU(172, 663, 0, 0, 2, 2H1S, 2)
C
C C PLOT OF EXPERIMENTAL POINTS AND THE ERROR BARS
DO 416 J = 1, 20
IF (LME(J)) GO TO 446
Y(J) = LME(J)
GO TO 466
496 X(J) = TLOG(J)
466 X(J) = X(J)
C
C C PLOT OF AVG IF GREATER THAN 0.1 PER CENT
IF (AVG(J)) 141, 151
141 AVG(J) = AVG(J) + 0.01
IF (AVG(J)) 241, 241, 251
241 AVG(J) = AVG(J) + 0.01
Y(J) = ALOG10(AVG(J))
Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 6, 1)
GO TO 551
C
C C PLOT OF EXPANSION POINT
151 Y(1) = -3.5
Y(2) = Y(1)
Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 237, 1)
GO TO 551
C
C C PLOT OF SHRINKAGE POINT LESS THAN 0.1 PER CENT
251 Y(1) = -3.5
Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 9, 1)
GO TO 551
C
C C SET UP OF TOP ERROR BAR IF GREATER THAN 0.1 PER CENT SHRINKAGE
451 STDH = AVG(J) - 0.01
STDH = STDH
STDH = STDH
STDH = STDH
IF (STSH > 50) GO TO 448
448 IF (STSH > 100) GO TO 449
449 Y(2) = Y(1)
Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 8, 1)
GO TO 248
449 Y(1) = 3.2
Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 9, 1)
GO TO 248
C
C C ERROR BAR TICK PLOT - TOP ANG BOTOM
851 SL = ABS(STD(J)) + 0.01
Y(2) = ALOG10(SL)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 2, 1)
GO TO 889
C
C C TOP ERROR BAR TICK IF LOWER GOES LESS THAN 0.1 PERCENT
931 Y(2) = Y(1)
CALL CCLPLOT (X, Y, 1, 6MNOJOIN, 2, 1)
Y(2) = -3.5
GO TO 889
889 CALL CCLPLOT (X, Y, 2, 4MNOJOIN, 5, 2)
PLOT OF EXPANSION OR LESS THAN .1 P/C LOWER TICK
Y1 = Y(2)
IF (STDL) 789, 790, A99
680 CALL CCPLT (X1, Y1, 1, 6MNOJOIN, 239, 1)
GO TO 144
789 IF (STLL) 142, 589, 589
580 CALL CCPLT (X1, Y1, 1, 6MNOJOIN, 97)
GO TO 144
144 CONTINUE
C
C STRAIGHT LINE SLOPE FROM THE LINLSU SUBROUTINE
C IF (LNSU>1) GO TO 619
Y(2) = A(1) * LOGT(1) + A(1)
X(2) = LOGT(1)
GO TO 618
619 Y(1) = A(2) * LOGT(1) + A(1)
X(1) = LOGT(1)
618 IF (MS>NSU) GO TO 620
Y(1) = A(1)
X(1) = 0
GO TO 625
620 Y(1) = A(2) * LOGT(MS) + A(1)
X(1) = LOGT(MS)
GO TO 625
C
CHECK TO ASURE ENDS OF SLOPE ARE ON GRAPH.
C LBL= NOT JUST REALITY, DATA.
625 IF (Y(1) > T1 + 0.5) GO TO 623
Y(1) = (1.5 - A(1)) / A(2)
X(1) = 0
623 IF (Y(1) < T1 - 0.5) GO TO 622
Y(1) = -1.5
X(1) = (-1.5 - A(1)) / A(2)
622 CALL CCPLT (XY+, 1MNOJOIN)
C
RETURN
END

K-20 U 20-30 U 1110 C 40P10D TVP/N MOVIE DUPL

I = 0.0
  1.50  3.00  6.00  10.00  20.00  45.00  100.00  140.00

MEANALYSIS DATA

DATA MEASUREMENTS
17.41  17.50  17.53  17.25  17.46  17.44  17.28  17.28  17.17
17.25  17.23  17.30  17.16  17.27  17.04  17.23  17.04  17.00
12.83  12.73  12.68  12.73  12.60  12.73  12.66  12.70
22.65  22.57  22.98  22.91  22.69  22.44  22.59  22.45  22.30
20.85  20.76  20.72  20.69  20.84  20.79  20.61  20.50  20.45
20.35  20.25  20.33  20.25  20.38  20.34  20.27  20.09  20.01
20.77  20.68  20.72  20.64  20.81  20.80  20.72  20.63  20.51
20.61  20.53  20.60  20.48  20.62  20.61  20.58  20.38  20.29
16.30  16.22  16.18  16.30  16.27  16.08  16.02  15.98
17.75  17.75  17.62  17.64  17.66  17.70  17.66  17.46  17.30

MEANALYZED DATA
.86081  .86358  .86791  .87519  .87695  .87550  .86878  .86464  .86022
1.07331  1.07321  1.07497  1.07103  1.06831  1.06677  1.06687  1.05603  1.04659
.87209  .87595  .87639  .87662  .87670  .87542  .86626  .85243  .84570
.68069  .68733  .68793  .68926  .69706  .69620  .68707  .66333  .66483
.73256  .73157  .72594  .72958  .72627  .72289  .71996  .70935  .71343
.64463  .64718  .64235  .64587  .64289  .63906  .64002  .63332  .63627
1.14510  1.14763  1.14387  1.14206  1.13963  1.13655  1.13774  1.13006  1.12124
1.05410  1.05561  1.04965  1.04972  1.04671  1.04367  1.03620  1.02551  1.02455
.99748  .99449  .99493  .99290  .99297  .98996  .98692  .97549  .97094
### Shrinkage Calculations with Base Line Time = 0

#### Delta L

<table>
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#### Delta L / L Sub Zero

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#### Average Delta L / L Sub Zero and Std Dev

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#### Time Log Time Log Percentage Shrinkage

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#### Slope is .045568 Std Dev of Slope is .000002

#### Intercept is -.178703 Std Dev of Intercept is .000001

Summary: Base time but without points below 6.0

---

**Slape is .64129 Std Dev of Slope is .005794**

**Intercept is -.93239 Std Dev of Inter is .00676**
### Delta L

| J+ | 0. | 0. | 0. | -0.0176 | -0.0031 | -0.0041 | -0.01076 | -0.01497 |
| J+ | 0. | 0. | 0. | -0.00272 | -0.00426 | -0.00416 | -0.01900 | -0.02444 |
| J+ | 0. | 0. | 0. | -0.00322 | -0.01520 | -0.00436 | -0.01820 | -0.01892 |
| J+ | 0. | 0. | 0. | -0.00466 | -0.00771 | -0.01624 | -0.02259 | -0.02209 |
| J+ | 0. | 0. | 0. | -0.00331 | -0.00669 | -0.00962 | -0.02022 | -0.01615 |
| J+ | 0. | 0. | 0. | -0.00297 | -0.00681 | -0.00584 | -0.01255 | -0.00959 |
| J+ | 0. | 0. | 0. | -0.00243 | -0.00551 | -0.00832 | -0.01900 | -0.02082 |
| J+ | 0. | 0. | 0. | -0.00301 | -0.00605 | -0.01352 | -0.02421 | -0.02517 |
| J+ | 0. | 0. | 0. | -0.00007 | -0.00294 | -0.00798 | -0.01741 | -0.02196 |
| J+ | 0. | 0. | 0. | -0.00379 | -0.00631 | -0.00829 | -0.02239 | -0.02489 |
| J+ | 0. | 0. | 0. | -0.00198 | -0.00301 | -0.00945 | -0.01517 | -0.01963 |
| J+ | 0. | 0. | 0. | -0.00341 | -0.00443 | -0.00438 | -0.01956 | -0.02253 |
| J+ | 0. | 0. | 0. | -0.00222 | -0.00414 | -0.01246 | -0.01950 | -0.02030 |
| J+ | 0. | 0. | 0. | -0.00269 | -0.00764 | -0.00433 | -0.01415 | -0.01187 |
| J+ | 0. | 0. | 0. | -0.00699 | -0.00945 | -0.01816 | -0.03056 | -0.03026 |
| J+ | 0. | 0. | 0. | -0.00041 | -0.00396 | -0.00541 | -0.01394 | -0.01089 |

### Delta L / L Sub Zero

| J+ | 0. | 0. | 0. | -0.0201 | -0.0036 | -0.00733 | -0.01229 | -0.01710 |
| J+ | 0. | 0. | 0. | -0.00254 | -0.00398 | -0.00389 | -0.01774 | -0.02282 |
| J+ | 0. | 0. | 0. | -0.00370 | -0.01746 | -0.00501 | -0.02090 | -0.02173 |
| J+ | 0. | 0. | 0. | -0.00711 | -0.01128 | -0.02375 | -0.03302 | -0.03230 |
| J+ | 0. | 0. | 0. | -0.00654 | -0.00917 | -0.01318 | -0.02772 | -0.02214 |
| J+ | 0. | 0. | 0. | -0.00460 | -0.01054 | -0.00905 | -0.01944 | -0.01485 |
| J+ | 0. | 0. | 0. | -0.00213 | -0.00443 | -0.00729 | -0.01664 | -0.01823 |
| J+ | 0. | 0. | 0. | -0.00287 | -0.00576 | -0.01288 | -0.02306 | -0.02398 |
| J+ | 0. | 0. | 0. | -0.00007 | -0.00296 | -0.00084 | -0.00753 | -0.00231 |
| J+ | 0. | 0. | 0. | -0.00369 | -0.00614 | -0.00007 | -0.02180 | -0.02423 |
| J+ | 0. | 0. | 0. | -0.00189 | -0.00287 | -0.00521 | -0.01448 | -0.01874 |
| J+ | 0. | 0. | 0. | -0.00328 | -0.00426 | -0.00421 | -0.01882 | -0.02169 |
| J+ | 0. | 0. | 0. | -0.00270 | -0.00504 | -0.01517 | -0.02376 | -0.02473 |
| J+ | 0. | 0. | 0. | -0.00310 | -0.00881 | -0.00499 | -0.01631 | -0.01368 |
| J+ | 0. | 0. | 0. | -0.00780 | -0.01054 | -0.02027 | -0.03411 | -0.03377 |
| J+ | 0. | 0. | 0. | -0.00058 | -0.00599 | -0.00763 | -0.01965 | -0.01535 |

### Adjusted Time, Average Delta L/L Sub Zero and STD Dev

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### Time, Log Time, Log Percentage Shrinkage

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### Slope

- Slope IS: 0.7661
  - STD Dev of Slope IS: 0.03743

### Intercept

- Intercept IS: -0.86732
  - STD Dev of Intercept IS: 0.05949
ACKNOWLEDGMENTS

With appreciation, this work was completed under the guidance and suggestions of Professor Richard M. Fulrath. Special thanks are paid to fellow graduate student, Joseph Masaryk, for his Graflex camera idea and his assistance with the computer program.

This work was done under the auspices of the United States Atomic Energy Commission.
REFERENCES

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