1969

Calorimetry of room temperature deformed copper

George Juri Filatovs

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CALORIMETRY OF ROOM TEMPERATURE
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by

George Juri Filatovs 1941

A DISSERTATION
Presented to the Faculty of the Graduate School of the
UNIVERSITY OF MISSOURI-ROLLA

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in
METALLURGICAL ENGINEERING
1969

Respectfully submitted

[Signatures]

[Signature]
ABSTRACT

An adiabatic anisothermal differential calorimeter for the study of room temperature deformed 99.999% pure copper has been constructed. An annealed and a deformed specimen were heated at a constant rate in adiabatic surroundings and the differences in energy released between samples was obtained. The control circuits were automatic. Deformation was by elongation ranging from 12 to 40%, and the corresponding energy found was from 1.9 to 5.3 calories/gram-atom. No recovery energy was found. The results obtained generally agree with published results and, in particular, verify Gordon's isothermal annealing results.

It is proposed that the criteria for the presence of recovery energy in the annealing spectrum of room temperature deformed metals is a high stacking fault energy and/or the presence of impurities, and that the recovery energy is mainly due to the relaxation of dislocations from high energy configurations.
ACKNOWLEDGEMENTS

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CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>INTRODUCTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>HISTORICAL REVIEW</td>
<td>5</td>
</tr>
<tr>
<td>A.</td>
<td>DIFFERENTIAL METHODS</td>
<td>6</td>
</tr>
<tr>
<td>B.</td>
<td>DIRECT METHODS</td>
<td>7</td>
</tr>
<tr>
<td>C.</td>
<td>SOLUTION METHODS</td>
<td>10</td>
</tr>
<tr>
<td>D.</td>
<td>OTHER METHODS</td>
<td>10</td>
</tr>
<tr>
<td>E.</td>
<td>COMPARISON OF METHODS</td>
<td>11</td>
</tr>
<tr>
<td>III.</td>
<td>INFLUENCE OF VARIABLES</td>
<td>15</td>
</tr>
<tr>
<td>A.</td>
<td>BASE METAL</td>
<td>15</td>
</tr>
<tr>
<td>B.</td>
<td>IMPURITIES</td>
<td>17</td>
</tr>
<tr>
<td>C.</td>
<td>GRAIN SIZE</td>
<td>20</td>
</tr>
<tr>
<td>D.</td>
<td>MODE OF DEFORMATION</td>
<td>21</td>
</tr>
<tr>
<td>E.</td>
<td>TEMPERATURE</td>
<td>22</td>
</tr>
<tr>
<td>IV.</td>
<td>JUSTIFICATION FOR PRESENT INVESTIGATION</td>
<td>25</td>
</tr>
<tr>
<td>V.</td>
<td>CALORIMETER SYSTEM</td>
<td>28</td>
</tr>
<tr>
<td>A.</td>
<td>DESCRIPTION OF CALORIMETER</td>
<td>28</td>
</tr>
<tr>
<td>B.</td>
<td>HEAT TRANSFER IN CALORIMETER</td>
<td>38</td>
</tr>
<tr>
<td>VI.</td>
<td>MATERIAL AND SPECIMENS</td>
<td>43</td>
</tr>
<tr>
<td>A.</td>
<td>MATERIAL</td>
<td>43</td>
</tr>
<tr>
<td>B.</td>
<td>SPECIMENS</td>
<td>45</td>
</tr>
<tr>
<td>1.</td>
<td>DESCRIPTION</td>
<td>45</td>
</tr>
<tr>
<td>2.</td>
<td>FABRICATION</td>
<td>50</td>
</tr>
</tbody>
</table>
## CONTENTS - CON'T

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>VII. ELECTRONIC SYSTEMS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>SENSING AND CONTROL</td>
<td>52</td>
</tr>
<tr>
<td>B.</td>
<td>MEASURING CIRCUITS</td>
<td>57</td>
</tr>
<tr>
<td>C.</td>
<td>SIGNAL FLOW</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>1. SIGNAL AND CONTROL</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>2. MEASURING CIRCUITS</td>
<td>62</td>
</tr>
<tr>
<td>D.</td>
<td>CALIBRATION</td>
<td>64</td>
</tr>
<tr>
<td>VIII.</td>
<td>CONSTRUCTION DETAILS</td>
<td>66</td>
</tr>
<tr>
<td>A.</td>
<td>THERMOCOUPLES</td>
<td>66</td>
</tr>
<tr>
<td>B.</td>
<td>HEATERS</td>
<td>67</td>
</tr>
<tr>
<td>C.</td>
<td>CALORIMETER VESSEL</td>
<td>71</td>
</tr>
<tr>
<td>D.</td>
<td>VACUUM SYSTEM</td>
<td>73</td>
</tr>
<tr>
<td>IX.</td>
<td>ERRORS AND ACCURACY</td>
<td>76</td>
</tr>
<tr>
<td>A.</td>
<td>ERRORS</td>
<td>76</td>
</tr>
<tr>
<td>B.</td>
<td>ACCURACY</td>
<td>78</td>
</tr>
<tr>
<td>X.</td>
<td>TESTING PROCEDURE</td>
<td>81</td>
</tr>
<tr>
<td>XI.</td>
<td>EXPERIMENTAL RESULTS</td>
<td>87</td>
</tr>
<tr>
<td>XII.</td>
<td>DISCUSSION OF RESULTS</td>
<td>100</td>
</tr>
<tr>
<td>XIII.</td>
<td>CONCLUSION</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>116</td>
</tr>
<tr>
<td>APPENDIX</td>
<td>A. COMPUTER PROGRAM FOR RAW DATA</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>B. LEAST SQUARES COMPUTER PROGRAM</td>
<td>122</td>
</tr>
<tr>
<td>VITA</td>
<td></td>
<td>139</td>
</tr>
<tr>
<td>TABLE</td>
<td>TOTAL STORED ENERGY</td>
<td>PAGE</td>
</tr>
<tr>
<td>-------</td>
<td>---------------------</td>
<td>------</td>
</tr>
<tr>
<td>A.</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>B.</td>
<td>SELECTED EXPERIMENTAL RESULTS</td>
<td>109</td>
</tr>
<tr>
<td>FIGURE</td>
<td>DESCRIPTION</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>TYPICAL ENERGY RELEASE CURVES IN THE ISOTHERMAL AND ANISOThERMAL METHODS</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BLOCK DIAGRAM OF CALORIMETER</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CROSS-SECTION VIEW OF CALORIMETER</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>OVER-ALL VIEW OF CALORIMETER</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>INSIDE VIEW OF CALORIMETER VESSEL</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CALORIMETER VESSEL</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CROSS-SECTION VIEW OF CALORIMETER VESSEL</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>MICROGRAPH OF UNDEFORMED COPPER SAMPLE</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CALORIMETER SPECIMEN-DIMENSIONS</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CALORIMETER SPECIMEN</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>TENSILE SPECIMEN</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>TENSILE SPECIMEN-DIMENSIONS</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>SCHEMATIC OF CIRCUITS</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>ISOLATION CIRCUIT</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>SIGNAL FLOW CHART</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>THERMOCOUPLE CIRCUITS</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>SPECIMEN HEATER</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>VACUUM SYSTEM</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>ENERGY RELEASE OBTAINED FROM CHART</td>
<td></td>
</tr>
</tbody>
</table>

RECORDEr
FIGURES - CON'T

<table>
<thead>
<tr>
<th>FIGURE 20-27</th>
<th>EXPERIMENTAL RESULTS</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>12% ELONGATION-DATA RUN 1</td>
<td>88</td>
</tr>
<tr>
<td>21</td>
<td>12% ELONGATION-DATA RUN 2</td>
<td>89</td>
</tr>
<tr>
<td>22</td>
<td>20% ELONGATION-DATA RUN 1</td>
<td>90</td>
</tr>
<tr>
<td>23</td>
<td>20% ELONGATION-DATA RUN 2</td>
<td>91</td>
</tr>
<tr>
<td>24</td>
<td>30% ELONGATION-DATA RUN 1</td>
<td>92</td>
</tr>
<tr>
<td>25</td>
<td>30% ELONGATION-DATA RUN 2</td>
<td>93</td>
</tr>
<tr>
<td>26</td>
<td>40% ELONGATION-DATA RUN 1</td>
<td>94</td>
</tr>
<tr>
<td>27</td>
<td>40% ELONGATION-DATA RUN 2</td>
<td>95</td>
</tr>
<tr>
<td>28</td>
<td>GRAPHIC PRESENTATION OF DATA</td>
<td>99</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

It has been sixty two years since Hort\(^{(1)}\) introduced the study of the stored energy of deformation. Since that time, the scientific literature has regularly produced calorimetric investigations of the stored energy. There is a strong hope that if the stored energy spectrum and the kinetics of its release are known, then the role of point and line defects in deformation and subsequent recovery and recrystallization will be more clearly detailed, and the relationship between such quantities as the dislocation flow stress and work hardening will be verified. The delineation of the roles of point and line defects in deformation is helpful or necessary for the verification of many theories concerning the basic behaviour of metals.

Yet in spite of such inducements only the general patterns of stored energy release have been established. Even the value of the total stored energy can vary by a factor of four, as inspection of the published literature will show. The reasons for this are the very small amounts of energy involved and the subsequent difficulties in attempting to measure these small differences.

A 100 gram mass of Copper has a heat capacity of approximately 10 cal/C\(^\circ\). The stored energy of cold work for this mass is approximately 4 calories. If the mass was heated at a rate of 10 C\(^\circ\)/Hr, the heat release would be in
the range of 0.1 calories/hr. In the present experiment, it took about 10 watts to heat a 120-gram specimen at a rate of 6°C/min, while the energy released was in the order of 0.01-0.1 watts. These small amounts of energy mean small temperature differences and low signal levels, with all the subsequent difficulties that these imply.

It now is accepted by nearly everyone that the plastic deformation of a metal occurs by the movement of dislocations and that work hardening results from the increasing difficulty in moving the dislocations through the lattice of the deformed metal. After the metal has been cold worked (cold worked meaning deformed at temperatures low enough to prevent relief of internal stresses) a small amount of energy is stored in the metal. This energy is attributed to the movement of point defects away from equilibrium positions, dislocations in high-energy positions or configurations, and some elastic stresses. The elastic stresses result from the inhomogeneous stress distributions which remain in a metal after deformation takes place.

Thermodynamically, stored energy can be analysed in several ways, not all of them useful. There is a change in the configurational entropy which is usually assumed to be low enough to be neglected. The change in enthalpy at constant pressure is due to the internal energy change and the change in volume. Because of the small volume change the latter is usually ignored. As a result, the free energy is
usually taken to equal the internal energy of cold work. In the present experiment the sample is deformed, then the sample is returned to the lower energy state by annealing. Therefore, the enthalpy is assumed to equal the stored energy.

The stored energy of cold work is usually divided into two categories; the first is recovery energy and the second recrystallization energy. These terms refer to the process of annealing, and therefore the recovery energy is that which is released with no visible change occurring in the microstructure of the metal while recrystallization energy is that which is associated with the movement of large angle grain boundaries during recrystallization. At first, it was believed that recovery energy was the result of the movement of point defects and that recrystallization energy was due to the movement of dislocations. The view has been emerging, however, that recovery energy, in addition to point defect movement, may contain the relaxation of dislocation bundles. This relaxation is too small to be even seen with the electron microscope, but its presence is suspected through such a phenomenon as the decrease in hardness in the latter stages of recovery.

Recrystallization refers to the movement of dislocations to form high-angle grain boundaries which sweep across the deformed crystal. The dislocation arrays, which are assumed to exist in the deformed metal, arrange themselves into new
configurations which, on sweeping through the crystal, alter its crystal orientation. Much effort has been expended on the analysis of recrystallization. In particular, a mechanism is needed for the formation of the nuclei. It is known that nuclei form preferentially in regions where the local deformation is high. According to one of two theories the nuclei form by a process of cell growth or rotation and coalescence. That is, the dislocations are arranged in the crystal in small individual groups known as cells. These cells can combine during the nucleation period to form the larger nuclei for recrystallization. The method of their combination has been proposed to be either by rotation of the cells to coalesce with their neighbors or by a shift in orientation as the curved region grows so as to allow eventual merging with a neighboring cell.

Recovery and recrystallization, therefore, contain many processes, some of which overlap. The energy of cold work is the driving force for recovery and recrystallization and the two processes can be said to be competing for the same energy.
CHAPTER II

HISTORICAL REVIEW

The stored energy of cold work has been measured in a variety of ways. The techniques can be grouped in the following categories:

Differential Methods—These are called "single-step methods". The energy of cold work is taken to equal the difference in energy required to deform a specimen and in the energy which is immediately released in the form of heat.

Direct Methods—Also called "two-step methods". The specimen is first deformed, and the energy stored is measured as it is released from the sample. This method is composed of three techniques:

a) Anisothermal Anneal—The energy release is measured as the specimen is heated at a constant rate.

b) Isothermal Anneal—The energy release is measured as a function of time as the specimen is maintained at a constant temperature.

c) Solution Methods—The heats of solution of an annealed and a deformed specimen are compared. The difference is taken as the stored energy.

Each of the three above techniques can be sub-divided further. Some methods use only one specimen and make successive runs to obtain the stored energy while some use two specimens simultaneously. A brief description of the development of these methods is presented in the following sections.
A. Differential Methods

The differential method was used in the first experiment specifically designed to measure stored energy. Hort, in 1906, constructed a calorimeter which contained a tensile tester in a water bath. The values for stored energy that he obtained for iron and copper are more reasonable than those of much later investigators.

Farren and Taylor used a thermocouple to measure the temperature rise of a specimen deformed in tension, (1925). Recently, Williams has used the same technique utilizing modern instrumentation. In both cases there was scatter in the data. Rosenhain and Stott, in 1933, measured the temperature rise of a die in an oil calorimeter. They attempted to relate the stored energy with the amount of deformation. Taylor and Quinney, in 1934, used torsion to obtain cold working. The angle of twist plotted against the torque gave the energy expended while the temperature rise of the sample gave the energy release.

A group of researchers at Tomst have used essentially the same method for obtaining stored energy. Kunin and Senilov (1936) compressed metals in stages, using the differences between the heat evolved and the energy of deformation as the stored energy. Fedorov (1941), Tiznova (1946), Studenok (1950), and Degtiarev (1950) used essentially the same method on a variety of metals and alloys. There is an unusually large scatter in the data of these experimenters which now is attributed to disregard of the impurity content
of the various test metals.

Among the latest work using the differential methods (11) is that of Williams (1963) who measured the energy stored in 99.999% pure copper by means of a phase change (12) calorimeter. A continuous measure of the heat evolved during a tensile test was obtained by measuring the amount of gas evaporated from a working fluid surrounding the test sample. This work will be discussed more fully later. It will be mentioned now, however, that Williams was able to measure a large energy release immediately following testing, which had not been measured by anyone else.

B. Direct Methods

Anisothermal (13)

Sato (1931) was apparently the first to use a differential method for stored energy determinations. He placed an annealed and a cold worked sample side by side inside a silver furnace, which was heated at a constant rate. A second run established the baseline. While Sato's method was basically correct, his calculations of the energy release curves were in error.

Quinney and Taylor (14) (1937) used a single specimen with an axial hole for a heater. Two runs were necessary; the first on the cold worked sample and the second on the same sample in the annealed state. They were the first to conduct their tests in a vacuum.

Suzuki, (15) in 1949, used a method similar to that of
Quinney and Taylor,\textsuperscript{(14)} as did Kanzaki\textsuperscript{(16)} in 1951. Nagasaki and Takagi\textsuperscript{(17)} (1948) used a slight variation of the technique. They used a special fixture which contained the monitoring thermocouples and the specimen heaters. This minimized handling of the specimen following cold-working. Both Suzuki and Kanzaki appear to have interpreted the results of their experiments incorrectly, as they assigned all of the measured energy to recovery.

Welber\textsuperscript{(18)} (1952) and Welber and Webeler\textsuperscript{(19)} (1953) used equipment similar to that of Quinney and Taylor,\textsuperscript{(14)} except that their specimen heating power could be more accurately controlled. The results of Welber and Webeler are highly suspicious since they found that specimens deformed in fatigue absorbed energy on heating.

In 1952 Clarebrough, Hargreaves, Mitchell, and West\textsuperscript{(20)} used refinements of many of the above techniques to determine values of stored energy. They placed two specimens, one annealed and one cold worked, inside of an evacuated guarding furnace which was heated at a constant rate. A differential wattmeter was used to determine the differences in power supplied to the copper specimens. The same equipment was used by Clarebrough, Hargreaves, and West\textsuperscript{(21)} in 1953 to measure stored energy release in nickel. In 1955 these same authors investigated the release of energy stored by a variety of processes in nickel and several purity grades of copper.\textsuperscript{(75)} Since then, a variety of experiments
have been carried out with the same apparatus.

A variation in the differential anisothermal annealing technique has been used by Bockstiegel, and Lucke\(^{(22)}\) (1951), Bihnenkamp, Lucke, and Masing\(^{(23)}\) (1955) and Riggs\(^{(24)}\) (1956). In this method either single wires or bundles of wires or small pieces of copper were placed in containers which were heated. One container enclosed cold worked specimens and the other the annealed reference samples, the energy release being measured as the two were heated at some constant rate.

**Isothermal**

The first stored energy measurements by the isothermal method were made by Borelius\(^{(25)}\) and Borelius, Berglund, and Sjoberg\(^{(26)}\) in 1952 using a microcalorimeter. Constant temperatures were obtained through the use of a vapor thermostat, and the tests were of long duration, up to 60 hours. A thermopile was used for temperature detection. Astrom\(^{(27)}\) (1955) used the same method, but employing isothermal stages of increasing temperature.

The best experimental work using the isothermal technique appears to be that of Gordon\(^{(48)}\) (1955) who used a calorimeter\(^{(28)}\) similar to that of Borelius, et al.\(^{(26)}\) Gordon claimed an accuracy of ±5% and a sensitivity of 0.003 calories/hour. Copper (99.999%) was deformed by elongation and annealed at various temperatures.
C. Solution Methods

A variety of solvents have been used. In general, aqueous solvents have been the least successful. Ticknor and Bever (1952) used liquid tin as the solvent and measured the energy stored in silver-gold alloys. This work was carried on by Bever and Ticknor (1953), Bever, Marshall, and Ticknor (1953), Leach, Loewen, and Bever, (1955), Greenfield, and Bever (1956), Averbach, Bever, Comerford, and Leach, (1956), Greenfield and Bever (1957), and Cohen and Bever. The basic method, dissolution in liquid tin, was varied from experiment to experiment by changes in types of samples or the addition of a gas or by changing the temperature of the sample.

D. Other Methods

Other techniques have been used to measure the stored energy. Since cold work is expected to change the corrosion rate this presents another method of estimating stored energy. The method, however, has not been successful.

Pulse heating techniques have been used with limited success. Usually, wires were deformed and then annealed with an electric pulse. A bridge was used to determine the temperature rise. Khotkevich, Chaikovskii, and Zashkvara used this method in 1954.
E. Comparison of the Various Techniques

Each of the above techniques has some disadvantages. As previously mentioned, the basic problem in stored energy measurements is the amounts of energy involved. If it is desired to observe the various steps in the energy release, it is necessary to spread the energy out, therefore necessitating even more accuracy. Conversely, those methods which give the best total values do not usually reveal the various processes participating.

The only satisfactory method for obtaining information about the kinetics of stored energy release come from isothermal investigations. A typical energy vs. time curve as obtained by Gordon (48) is shown in Figure 1. Due to the length of time over which the energy release is spread, from 10 to 60 hours depending on the annealing temperate and the amount of deformation, the energy release at any instant of time is small. Therefore, the instrument must have high sensitivity and stability over long periods of time.

In the isothermal method, the time to fully anneal the specimen is considerably shorter. However, the constant change in temperature makes kinetic interpretations difficult, and the benefit of an increased signal level is negated by the difficulties of attempting to keep several temperatures rising at the same rate. Figure 1 is an energy release curve as obtained by Clarebrough et al. (20) on less pure material. The reason for the differences
Typical heat evolution curve in the isothermal annealing method. 99.999% Cu, 30% elongation. (After Gordon(48))

Typical energy release curve in the anisothermal method. Commercial copper deformed 33% in elongation and heated at 6°C/minute. (After Clarebrough et al. (20))

Figure 1. Typical energy release curves in the isothermal and anisothermal methods.
will be discussed later, but it will be mentioned now that the total energy stored increases with impurity content. Thus, a very pure material is capable of storing much less energy than an alloy. This is the reason why solution methods have been limited to alloys. The solution method does not reveal anything about the kinetics of energy release. It can be used to obtain the total stored energy in cases where this energy is relatively high. Williams considers the accuracy of the solution methods to be 2 calories/mole, while the total energy stored in pure metals at low deformations is about the same amount.

The choice of whether to use a reference sample depends on the experiment. Having an annealed reference sample can cancel out radiation and conduction losses. Fluctuations in the calorimeter wall temperature and drift of the wall temperature would not register in the two-specimen method. The disadvantages are the increased difficulty in measuring extra temperatures and power, and, depending on the experiment, in maintaining another sample at the correct temperature.

The single specimen calorimeter has the advantages of simplicity of calorimeter design and elimination of the extra instrumentation. In most cases, the calorimeter wall is used as a high thermal inertia reference. It is usually necessary to make a second run to establish a back-
ground level. This is done in both single and two specimen arrangements.

When using differential methods for evaluating the stored energy there are difficulties in measuring the work expended. There must be corrections for thermoelastic cooling, friction, and heat losses. If these losses are not properly evaluated, the usefulness of the method is reduced.
CHAPTER III

INFLUENCE OF VARIABLES

In spite of the attention given to the problem of stored energy of cold work, many of the basic mechanisms involved have not yet been identified. It is generally agreed that recovery energy contains the contributions of point defects and the possible relaxation of high-energy dislocation arrangements, and that recrystallization involves mostly dislocation motion. The exact mechanisms involved, however, have not been identified and the theoretical models developed have not proven entirely satisfactory. In particular, the various species participating in the recovery energy are unidentified. It is probable that the species of defect depends on the temperature of deformation, the base metal, and the impurities present. The type of deformation also apparently has some effect. The influence of the various factors on the deformation energy and its release will be briefly discussed.

A. Base Metal

In general, the amount of energy stored in different metals which have been cold worked the same amount is proportional to the melting point. A material with a higher melting point stores more energy than one with a lower melting point. The manner in which this energy is
released, and therefore, the allocation of energy among the various defects, it is also altered by the nature of the base metal. The sketches below are schematic representations of the energy release in copper and nickel.

Energy release in Cu from present work.

Energy release in Ni, after Clarebrough et al. (21)
It is evident that there is a larger portion of energy released in the first stage for nickel than for copper. The possibility that this can partly be due to the increased role of point defects is supported by the values for energy formation of vacancies and stacking fault energies for copper and nickel, given below:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Formation energy for vacancies (ev)</th>
<th>Stacking fault energy (ergs/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.0 (49)</td>
<td>80 (38)</td>
</tr>
<tr>
<td>Ni</td>
<td>1.6 (50)</td>
<td>240 (38)</td>
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</tbody>
</table>

The migration energies for vacancies are also lower in copper than nickel at room temperature, about 1 ev (51) vs. 1.5 ev (52). Therefore, the presence of equal amounts of vacancies would contribute more energy in the case of nickel, and these vacancies would also persist to higher temperatures. The roles of vacancies and interstitials in deformations, however, have not been satisfactorily explained. This is in part due to the difficulty in separating out the various contributions of the line and point defects and in identifying exactly these defects.

B. Impurities

Both the amount and type of impurity have strong effects on the way the energy is stored and released. In general,
the less pure material always recrystallizes at a higher temperature and has larger amounts of recovery energy, and this recovery energy is liberated at lower temperatures. The influence of impurities on recrystallization is probably due to the anchoring of dislocations by impurity atmospheres. The increase in the recovery energy is not as easily explained. The sketch below illustrates the energy release curves as a function of impurity.

![Energy release for pure and impure copper, after Clarebrough et al.](image)

As can be seen, the recovery energy is spread out with increasing amounts of impurities. This suggests a range of activation energies, some of which may be associated with different processes. It is probable that impurities affect the motion of dislocations both during deformation and during annealing. During annealing, the
dislocations which have been anchored in high energy positions by impurities may relax, the impurities may diffuse to more stable positions, or there may be clustering or perhaps breakup of clusters. The exact identification of the mentioned processes has not yet been made. Impurities also increase the spectrum of recrystallization energies. This means that there also is a range of activation energies. In purer materials there is a smaller range which means that the recrystallization peak is narrower.

In alloys, which may be considered an extreme case of impurity content, the situation is even less clear. The total amount of energy which can be stored in alloys is several times that which is stored in pure metals. In part, this is probably due to the high dislocation density which may exist in an alloy. It is also likely that there is a return to short range order and the storing of energy in subboundary interfaces. The details of these mechanisms, however, still lack satisfactory explanation.
C. Grain Size

The sketch below illustrates the effect of the grain size on the stored energy. The material is 99.999\% copper deformed in compression.

Influence of grain size on stored energy. After Loretto and White. (40)
The reason for this behavior can be explained when the Petch equation is examined. This predicts that

\[ S_Y = S_i + K_y d^{-\frac{1}{2}} \]

where \( k_Y = S_D \frac{1}{2} \)

\( S_i \) = the shear stress resisting the movement of dislocations across the slip plane after unpinning

\( S_D \) = shear stress to unpin a dislocation from its atmosphere

\( l \) = the distance from piled-up dislocations at a boundary to the nearest Frank-Read source in the next grain.

\( S_Y \) = lower yield strength

\( 2d \) = grain diameter

This means that as the grain diameter gets smaller, the material gets stronger and higher dislocation densities occur. Usually the energy release for fine grained specimens shows a more rapid release than for coarse grained specimens. It has been found that at high strains the stored energy begins to be independent of the grain size.

D. Mode of Deformation

Increasing amounts of deformation result in increasing amounts of stored energy until a saturation limit is approached. Deformation methods which involve large amounts of shear, such as filing, result in higher values of stored energy. The energies stored by equal deformations in tension or compression are equal, \(^{(42)}\) and the total amount of energy which can be stored is less than some more
severe methods of deformation such as torsion. In general, only the amount of stored energy varies with the type of deformation, although methods which introduce inhomogeneous deformation, such as torsion, can affect the spectrum of release by spreading it out thus creating a range of activation energies. Fatigue increases the number of point defects in a metal and therefore increases recovery energy.\(^{(43)}\)

E. Temperature

Investigations on stored energy have been conducted at both room temperatures and at low temperatures. It can be concluded that the temperature of deformation affects both the way in which the energy is stored and in its later release.

Most of the previous discussion concerned deformation at room temperature. Temperatures below 200°C have not been extensively used for stored energy measurements; instead, most of the data has been concerned with resistivity and flow properties. The liquid nitrogen to room temperature region, however, has been thoroughly investigated.\(^{(44-46)}\) In general, deformation at low temperatures increases the total energy stored, and both the recovery and the recrystallization energies are increased. The recrystallization energy, even though it is released
at high temperatures, is greater than for comparable deformations at room temperature. The recovery energy shows up in an entirely different spectrum, all of it below room temperature, with none of the above-room temperature recovery spectrum being excited.

The figure below shows the energy release from 99.999% pure copper deformed at liquid nitrogen temperatures. Other investigators have obtained similar results.

Energy release from copper deformed 53% in compression at liquid nitrogen temperature. After van den Beukel. (46)

Evaluation of the activation energies for the defects has indicated that the activation energies for migrating defects can be as low as 0.1 ev. (47) This indicates an extremely fast moving defect, as can be seen from the annealing peaks above. Although tentative assignments of defects to the various peaks have been made, there has been no
confirmation that any of the assumptions are right. This essentially means that no point defect has been positively identified as a participant.
CHAPTER IV

JUSTIFICATION FOR PRESENT INVESTIGATION

The previous discussions have indicated the general trends of the influences of the various variables on the stored energy of cold work. It is obvious that the variables have such a large effect and compete so much for attention that comparison of results is almost impossible. In order to investigate specifically the process of deformation some variables must be controlled.

The material on which the most attention has been focused is copper. To minimize impurity effects the copper content should be at least 99.999%. Tensile or compressive deformation must be used for comparison. When all of the above criteria are satisfied, only three sets of data can be found. One of the sets of data, that of Loretto and White, gives only values of 30% elongation for only two specimens.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Total Energy Stored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loretto &amp; White (40)</td>
<td>0.085 cal/gram</td>
</tr>
<tr>
<td>Gordon (48)</td>
<td>0.079 cal/gram</td>
</tr>
<tr>
<td>Williams (11)</td>
<td>0.173 cal/gram</td>
</tr>
</tbody>
</table>

The disagreement, obviously, is unacceptable. Each of the authors, however, demonstrated satisfactory sensitivity and accuracy for his method, therefore, the methods themselves must also be investigated. The work of Williams (11)
must be closely examined. About one-half of the total energy was released within seven minutes following deformation. The allocation of this energy has not been satisfactorily made. It is possible that it involves dislocation relaxation or an unidentified species of defect.

Loretto and White (40) used the two specimen anisothermal method of Clarebrough et al, (20) while Gordon (28) used the single specimen isothermal method. In both cases considerable time passed between the deformation of the specimen and the testing. In Gordon's case, the specimen had to be heated to the annealing temperature, and energy could not be measured during this time. Also, in both cases there was considerable handling of the specimen following deformation, namely, the drilling of the axial hole for the specimen heater.

In view of the scarcity of data and the wide range in values therein, it seemed desirable to conduct an investigation with the following points in mind:

a) Obtain stored energy releases on the purest available copper.

b) Use a range of deformations.

c) Attempt to eliminate some of the difficulties inherent in the other experiments, such as eliminating the drilling of the axial heater hole following deformation, and eliminating the time between
testing and deformation.

d) Construct a calorimeter which would confirm or deny the results of the few other tests available.

e) If data is obtained, make some hypotheses concerning the deformation process.
CHAPTER V
CALORIMETER SYSTEM

A. General Description of the Calorimeter

The calorimeter system and its principle of operation will be discussed in this section. A more detailed description of the individual electronic and mechanical components and of the signal flow will be presented later.

A block diagram of the mechanical and electrical elements is shown in Figure 2. In operation, the system is closest to that of Clarebrough et al. (20) and can be said to be almost a direct descendent of it. The main differences are the automatic amplifier control of heat to the specimens and the design of the deformation specimens. It was felt that the use of fully automatic and continuous control of the power to the specimen heaters represent a sufficiently significant improvement from previous experiments to justify this experiment. In addition, there were many small improvements such as increased sensitivity in temperature measurement and the design of the specimens. The specimens are so designed as to allow the minimum elapse of time between deformation and testing. This was done by pre-machining the hole which was to contain the specimen heaters, so that all that remained after deformation was the removal of the deformed section by sawing. This sawing
Figure 2. Block Diagram of Calorimeter
operation did not introduce any measurable amount of stored energy as was found later. Due to the desire to improve accuracy by using the largest specimens possible it was decided to use tensile deformation, because it was difficult to get homogeneous compressive deformation in large samples.

The system can be called an adiabatic differential calorimeter. Two samples, one annealed and one containing energy of cold work, were placed in the calorimetric vessel which was then evacuated and heated at some constant rate. See Figure 3. Differential thermocouples between the annealed "dummy" specimen and the calorimeter wall, and dummy specimen and cold worked specimen sensed any temperature differences. These differences were noted by the control circuits which attempted to minimize them by applying power to the samples by means of the internal sample heater. Since the samples had identical masses and similar shapes, the cold worked sample, due to the release of internal energy, required less energy than the dummy specimen. Thus, the difference in applied energy could be said to equal the internal energy or stored energy of cold work.

Figure 4 is a photograph of the entire calorimeter system, showing the vacuum system, bell-jar in which the calorimeter operates, and various electronic components.
Figure 3. Cross-Section View of Calorimeter
Figure 4. Over-all View of Calorimeter
The console to the left of the calorimeter is the calorimeter wall power supply and control while the components in the background are various control and calibration devices for the specimen heaters.

Figures 5 and 6 are photographs of the calorimeter vessel, the former showing the inside of the calorimeter with the specimens in place and the latter with the cover in place. Figure 7 is a cross-section view of the calorimeter vessel.

The specimens sit on small rings cut from thin quartz tubing, and are located at approximately the foci of the elliptically shaped vessel. Thermocouples from the specimens and calorimeter wall, and lead-ins from the specimen heaters emerge through a slit in the cover. The calorimeter vessel contained a vacuum pumping port and had a cooling chamber as part of a double bottom.

The vessel was heated by wire spirally wound on refractory alumina supports. Power to the heater wire was supplied by a Leeds and Northrup cam-controlled c.a.t. Controllall power supply which was programmed to heat the calorimeter at 0.1°C/second.

To prevent heat transfer between specimens and oxidation of the specimens and calorimeter, the calorimeter was operated under vacuum in a bell jar. A heat shield prevented radiant heating the bell jar and baseplate,
Figure 5. Inside View of Calorimeter Vessel
Figure 6. Calorimeter Vessel
Figure 7. Cross-section View of Calorimeter Vessel
and a small fan, seen in Figure 3, cools the conduction heated baseplate.

In order to maintain a "clean" vacuum at the temperatures used it was necessary to be extremely careful about the types of materials used; otherwise the specimens would be coated with very thin films of impurities after heating. It was found that pure alumina was best for high temperature regions and that Mullite was satisfactory elsewhere.
B. Heat Transfer In The Calorimeter

Assume the specimen-calorimeter configuration shown below:

\[ Q \text{ dummy} \quad Q \text{ cold worked} \]

\[ Q \text{--------energy release in cold worked sample} \]

\[ Q_{cw}, Q_d \text{--------energy input into specimens from heaters} \]

\[ T_w, T_d, T_{cw} \text{-------temperatures of wall, dummy, and cold worked specimens} \]

\[ C_d, C_{cw} \text{-------heat capacities} \]

\[ K_{d-w}, K_{cw-w}, K_{d-cw} \text{---------interchange factors for the heat transfer between the specimens and wall. It includes such things as emissivity and shape factors for heat transfer by radiation.} \]

The subscripts \( d \) and \( cw \) indicate dummy or annealed specimen and cold worked specimen, respectively.
Balancing the change in the heat content against the various factors affecting that change gives:

\[ C_d \frac{dT_d}{dt} = K_{d-w} (T_w - T_d) + K_{d-cw} (T_d - T_{cw}) + Q_d \]

\[ C_{cw} \frac{dT_{cw}}{dt} = K_{cw-w} (T_w - T_{cw}) + K_{d-cw} (T_d - T_{cw}) + Q_{cw} + Q \]

Solving the above completely is difficult as it is practically impossible to evaluate such factors as the \( K \)'s, nor would a complete solution be particularly useful. It must be remembered that the operation of the calorimeter assumes two contradictory statements, namely, that there is enough of a temperature difference to create signals in the differential thermocouples but that the difference is small enough to neglect considering heat transfer. The equations show that as the temperature differences get smaller the approximation

\[ Q_d - Q_{cw} = Q \]

gets better. (This assuming that the specific heat in the cold worked sample is not altered as a result of the deformation.)

The assumption that there is a small difference in the wall-cold worked specimen-dummy specimen temperatures will not destroy the validity of the last equation. The term

\[ K_{d-cw} (T_d - T_{cw}) \]

appears in both equations and drops out. It can also be assumed that the differences in temperature between the
specimens and wall will remain more-or-less constant, even from test to test. This means that the effect due to the internal release of energy can be separated from other effects by making a second test immediately following the test run. That is, following a test run the samples are allowed to cool and a second test is run without disturbing the experimental arrangement. The first test will contain the summation of all factors on the specific heat, while the second will contain all the factors except Q.

The K's are also dependent on the geometry of the heater and on the position of the heater in the sample. The heat transfer from heater to sample can change if the thermal resistance is changed by a change in contact or geometry. Therefore, the only way of extracting Q is the two-run method which allows the subtraction of total energies and thus effectively cancels out the contributions due to the K's. For this assumption to be valid great care must be taken that nothing is disturbed from one run to another.

Examination of the block and circuit diagrams shows the power system to be essentially a feedback controlled amplifier, where the thermocouples are the feedback elements. In systems of this type there are occasionally problems due to "cycling" of the system; that is, the lag
due to the heating of the calorimeter by the external heater. The improvement which the opposite system offers depends on the ratio of the calorimeter/heater masses and on the sensitivity of the control systems. In the present system the mass of copper which had to be used in the calorimeter vessel in order to obtain satisfactory temperature distributions dictated the constant surroundings heating rate approach. The response of a mass in a temperature field can be expressed as

\[ \frac{dT}{dt} = \frac{K}{C_p} (\Delta T) \]

- \( T \) = temperature of sample
- \( K \) = heat transfer coefficient between field and mass
- \( C_p \) = heat capacity of mass
- \( \Delta T \) = temperature difference between field and mass

If the mass is contained in \( C_p \) then for maximum sensitivity the mass should be kept as small as possible. The \( K \) in this case is between the heater and sample and should be as large as possible. The previous is true for both specimens.

Maximum sensitivity means the quickness of response to change and therefore increased resistance to cycling. The other way to combat cycling is by increasing the mass to the point where damping occurs.

The main experimental difficulty centers on the large differences in magnitude between \( Q \) and \( Q_{cw} \) and \( Q_d \). The
latter two are such large numbers compared to the former, the average ratio is 1:100, that any error in measuring the heater currents or voltages can obliterate $Q$. This is the experimental difficulty which has been the main obstacle to reliable stored energy values and which has caused much of the previously published work to be in disagreement.
A. Material

The material used was 99.999% copper supplied by Jarrell-Ash. Available laboratory facilities did not allow a verification of such high purity or an identification of remaining impurities. The material was continuously cast in a one-inch diameter and was supplied in 12-inch lengths.

Through an unfortunate oversight the microstructure of the material was not checked prior to machining. After the structure was inspected it was discovered to have an irregular cast structure. The material was subsequently given two vacuum anneals in an effort to break up the structure; one at 350°C for one hour and another at 600°C for forty-five minutes. This succeeded in reducing the cast structure but left behind a rather irregular grain size. As can be seen in Figure 8 it is almost impossible to make any sort of grain size determination.

At first it was suspected that the polishing technique was at fault or that the sample was not completely annealed. Repeated polishing attempts, including electrolytic methods, however, did not change the appearance of the structure; nor did reheating the specimen at 800°C
Figure 8. Micrograph of Undeformed Copper Sample 100X
for several hours change the general inhomogeneous appearance. In the absence of any satisfactory alternative, the material had to be used with this irregular microstructure.

Comparison of the grain sizes of the specimens with standard tables and a check using the grain-intercept method indicated that the average size of the grains was roughly 0.2 mm. But although the average grain size from specimen to specimen was reasonably close, the variation within a specimen was too great for the grain size to be used in any quantitative way.

B. Specimens

1. Description

The dummy and cold-worked specimens which are used in the calorimeter are small cylinders 2 inches long with a 3/4-inch diameter and an axial hole 1/4-inch in diameter. Figure 9 shows a sketch of the specimens, and Figure 10 shows a photograph of a specimen. The photograph was included because it is of a dummy specimen which had been used in actual tests (about 4 data runs) and shows the excellent condition of the specimen, indicating a good high vacuum within the calorimeter.

The tensile specimens were fabricated according to the sketch shown in Figure 12. Figure 11 is a photograph of a finished tensile specimen. The 3/4-inch diameter for
Figure 9. Calorimeter Specimen-Dimensions
Figure 10. Calorimeter Specimen
Figure 11. Tensile Specimen
Figure 12. Tensile Specimen-Dimensions
the specimens was chosen because the necessity of threads to grip the specimen and a radius at the end of the specimen necessitated the unavoidable removal of approximately 1/4-inches of material from the diameter.

The cold-worked calorimeter specimens were fabricated from the deformed tensile specimen. Marks 2-inches apart were lightly scratched on the tensile specimen and served as guides when the section was removed after elongation.

The dummy and cold-worked specimens were matched as closely as possible in weight. All the specimens weighed between 121.61 and 121.65 grams and the weight of the specimens in calculations was taken at 121.6 grams.

2. Fabrication

The dummy and tensile specimens were fabricated with no lubricant used, to eliminate possibility of entrapment of lubricant in the surface of the metal. Machine work was done on a lathe with small finishing cuts employed. The axial holes were drilled with undersize bits and then reamed to size. After fabrication the specimens were given a light nitric acid etch and immediately cleaned with acetone and alcohol, annealed, and stored in an evacuated container.

As mentioned before, the cold-worked calorimetric specimens were cut from the deformed tensile specimens, with marks placed on the specimen prior to deformation to indicate the length of section to be removed. At
first, removal of the sections was by using a spark cutter under liquid nitrogen. This proved to be intolerably slow so that mechanical means had to be used. A special holder which had provisions for cooling the specimen and the cutting zone with ice water was used. The cutting tool was a fine bladed hacksaw which was guided by slits in the work holder. With practice it was possible to obtain specimens to within the desired weight tolerances.

The question arises, of course, as to whether or not the sectioning of the deformed specimen introduces further cold work. It is assumed that the maximum amount of cold work is introduced, assume some 20 cal/gram-atom, which is more than anyone has been able to store in copper, and if the affected volume of metal is narrow, which it probably is, then we can make the following conclusion: if the maximum amount of metal affected is 5 grams, and this has an energy of .32 cal/gram then the extra energy is 1.6 calories. This compares to an average value of 9.0 calories for the rest of the specimen. These are the worst conditions. Probably the amount of energy stored as a result of the cutting is much smaller.

As a check on the above reasoning, an annealed but undeformed tensile specimen was sectioned using the saw and a calorimeter test made. There was no energy difference detected between the saw-deformed and annealed specimens.
CHAPTER VII

ELECTRONIC SYSTEMS

The electronic and electrical components of the block diagram in Figure 2 are shown in more detail in Figure 13. In this section, these components will be examined in greater detail. The signal flow will be examined in a later section.

A. Sensing and Control

The signals originate in the Chromel-Alumel thermocouples in the left hand side of Figure 13. These signals pass through ice junctions and switches - described in the section on thermocouples - and then are amplified by Preston floating differential amplifiers. These amplifiers are chopper stabilized DC amplifiers with a maximum gain of $10^3$ and an adjustable bandwidth. The bandwidth was set at its lowest value, 10 Hz, and this effectively eliminated pick-up by the thermocouples from the 60 Hz calorimeter wall heater and the 400 Hz specimen heaters.

The signal emitted from the top amplifier has a constant DC voltage added to it. This voltage is supplied by a regulated transistor power supply, for the purpose of raising the specimen heater voltages to the appropriate level for best radiant heat transfer and for approximately the correct heating rate. A 10K ten-turn potentiometer is used for control of this voltage.
Figure 13. Schematic of Circuits

A1, A2, A3: Floating differential amplifiers
DVM: Digital voltmeter connections
The DC signals are now converted to AC by a DPDT instrument chopper, that is, both signals are converted simultaneously by two mechanically linked single pole choppers. As can be seen in the diagram, transformers are used with the chopper to do this. The outputs from the chopper transformers are slightly rounded square waves which then are smoothed to sine waves by 400 Hz narrow band-pass filters. The filters have a bandwidth of 12 Hz, thereby further reducing transients and noise.

The smooth sine wave signals are the control inputs for the specimen heater power amplifiers. The input from the calorimeter wall-cold worked specimen thermocouple goes to both specimen heater power amplifiers while the input from the cold-worked specimen dummy specimen side is added to the dummy specimen heater amplifier.

In order to add the input signals of the dummy specimen heater amplifier without cross interference it was necessary to employ a separate addition circuit. Figure 14 shows this circuit. Two 2N2926 transistors are used in an emitter follower configuration which eliminated any influence of one input signal on the other amplifier. The circuit was added as part of one of the power amplifiers and obtained 5 volts from the amplifier.
Figure 14. Isolation Circuit
The power amplifiers were modified 32 watt high-fidelity amplifiers. As noted above, one of the modifications was the addition of an emitter follower circuit to one of the amplifiers. Other changes included the substitutions of ten-turn potentiometers in gain controls and changes in the internal power supplies and feedback loops. Although not having as high quality as really desired the modified power amplifiers performed fairly satisfactorily, especially after they were allowed to stabilize, that is, allowed to run continually. For this reason, bypass resistors were installed so that they could be switched in whenever the specimen heaters were turned off.

The specimen heaters are described elsewhere. The connection between heaters and amplifiers was by a single strand heavy gage copper wire. In series with each heater was a 0.051-ohm instrument shunt for measuring the current and across each heater were tap points for measuring the voltage. The signals to the various stages and to the heaters were continually monitored on an oscilloscope, while frequency stability was monitored with a frequency counter.

A Stabiline voltage regulator supplied voltage to all the components except the differential floating amplifiers which had internal regulated supplies. The
Stabiline regulator had good long time regulation but was not especially effective on transients. For this reason it was necessary to conduct the experiment at hours in which the line voltage was freest of transients. Unfortunately, these times turned out to be in the earliest hours of the mornings and on weekends.

B. Measuring Circuits

The measuring circuits were concerned with obtaining the power difference supplied to the individual heater currents and voltages.

The voltages across the heaters were obtained by putting the primaries of 1:2 ratio transformers in parallel with the heaters. The secondaries were then wired as shown in the schematic to give the sum of these voltages.

The currents were obtained by passing the current to the heaters through the primaries of 2:12,000 ratio transformers and then connecting the secondaries as shown in the schematic to give the current difference. This transformer ratio was used because it gives a high enough secondary voltage without adding any appreciable resistance to the primary side. Since transformers with this ratio were not commercially available they had to be produced in the laboratory. This was done by winding the primary on top of the primary of a 9,000:12,000 ratio transformer and omitting the transformer primary.
After the output from the secondaries was rectified it passed through a balancing circuit. The purpose of this balancing circuit was to make certain that the current difference was zero when both heaters had identical voltages across them. That is, when the same voltage from a signal generator was placed across both heaters, the balancing circuit was adjusted to show the voltage difference from the secondaries to be zero. All of the potentiometers shown in the schematic had 10-turns as high resolution was found to be necessary for acceptable accuracy.

The amplifier following the balancing stage had a gain of one and was used for isolation and filtering. It was the same kind as the DC floating differential amplifiers used to amplify the thermocouple signals.

The signals from the current subtracting and voltage summing stages were next multiplied by a servo-multiplier. The servo-multiplier was made from a balancing motor from a Minneapolis-Honeywell strip-chart recorder, two 360-degree rotation potentiometers, and a transistorized regulated DC power supply. Multiplication was accomplished by applying the current-difference signal across a 1K-ohm potentiometer whose shaft was turned by the balancing servo-motor. The value of this pot was changed when the servo-motor balances against the change in voltage caused by the voltage summing stage. The power supply provided a standard voltage against which the voltage changes
were balanced. The servo-multiplier system, then, worked as follows: The current differences of the heaters were applied across a potentiometer, the value of which was varied by the sum of the voltages across the heaters. The product of these values was plotted on a strip recorder.

C. Signal Flow

This discussion will be concerned with an analysis of the signal, control, and measuring voltages. A signal flow chart of these voltages is presented in Figure 15.

1. Sensing and control circuits.

The voltage originated in the differential thermocouples. Differences in temperatures between the calorimeter wall and the cold worked specimen created a DC signal designated as X and differences in temperature between the cold-worked specimen and dummy specimen created a DC signal designated as Y. Both these signals were amplified 1,000 times by separate amplifiers and the signals became $10^3X$ and $10^3Y$. The $10^3X$ signal now had added to it an additional voltage $X'$ so that the signal on that side becomes $10^3X + X'$. This biasing voltage was necessary to raise the over-all voltage level to the heaters high enough to attain the heating rate desired. This could be done by amplifying the X signal more but would have resulted in a degrading of the signal-to-noise-ratio.
Figure 15. Signal Flow Chart
The $X'$ signal then, was approximately the signal necessary to provide the correct voltage to the cold worked specimen while the DC signal $X$ provided the difference.

The two sets of signals were then converted to AC by means of 400 Hz choppers.

The $10^3X + X'$ signal was now the input to two different amplifiers. One was the power amplifier for the cold-worked specimens, and the signal was amplified to $(10^3X + X')10^2$ and was applied to the cold-worked specimen heater. The other input was a summing amplifier. It received the $10^3X + X'$ and $10^3Y$ signals and added them. The power amplifier took this summed signal, amplified it by $10^2$ and applied it to the dummy specimen heater. Depending on the signal $Y$ one of two things happened.

The differential thermocouples could produce either positive or negative signals, depending on the temperature relationships of the specimens and wall. Since the specimens were to follow the calorimeter wall temperature, and the heating rate of the wall was high, it was expected that the cold-worked specimen temperature would never exceed the wall temperature and thus the signal $X$ would always be positive. But due to the release of internal energy by the cold-worked sample, the dummy specimen could find itself either above or below the cold-worked specimen temperature. Under normal conditions it was
expected that the dummy specimen was at a lower temperature than the cold-worked specimen. High thermal resistance between the cold-worked specimen heater and specimen could result in an inversion of the expected temperature relationship. (It should be pointed out that the temperature differences mentioned here were small. That, after all, was the function of the control circuits.)

The two possibilities at the input of the dummy specimen power amplifier will now be considered.

Case 1 - The dummy specimen temperature is below the cold-worked specimen temperature. The two AC signals coming into the summing amplifier are in phase and the signal to the heater is 

$$((10^3 x + x') + 10^3 y) 10^2$$

Case 2 - The dummy specimen temperature is above the cold-worked specimen temperature. The two AC signals are out of phase and the signal is 

$$((10^3 x + x') - 10^3 y) 10^2$$.

2. Measuring Circuits

The signals into the measuring circuits will now be analyzed. Assume the following definitions:

$$V_x$$ - voltage across the cold-worked specimen heater

$$V_y$$ - voltage across the dummy specimen heater

$$R_x$$ - resistance of cold-worked specimen heater

$$R_y$$ - resistance of dummy specimen heater
The voltages across the specimen heaters were summed while the currents flowing through the heaters were subtracted. The values were $V_x + V_y$ and $V_x/R_x - V_y/R_y$, respectively. These two signals were then multiplied by the servo-multiplier so that the signal becomes

$$(V_x/R_x - V_y/R_y) \cdot (V_x + V_y)$$

If this multiplication is carried out the signal is seen to actually be

$$(V_x/R_x - V_y/R_y) + (V_xV_y/R_x - V_yV_x/R_y)$$

The first term in the above expression is the true power difference between the specimen heaters. The second term can be further rearranged to give

$$V_xV_y(R_y - R_x/R_xR_y)$$

If the difference in heater resistance are small the above term can be neglected. If the differences in resistance are not small, the above term will only add in a constant value, at least in the range of differences encountered. It is not implied that the values of $R_x$ and $R_y$ were constants. Indeed, they changed by nearly a factor of three between room and operating temperature. If the resistances of both heaters change by the same amount, however, the second term will be constant, and when multiplied signal is plotted out by the recorder only the variation in the first term would be seen.
D. Calibration

For proper operation of the calorimeter it was necessary that the two differential thermocouple circuits must be balanced. Small errors in amplification by the two circuits could be neglected since the power to the specimens was measured at the specimens and a second run was made to cancel out any circuit or heater differences. It was desirable, however, to minimize differences as much as possible since they could affect the speed of response of the circuits.

The power circuits were balanced by supplying the differential thermocouples with the same temperature and then adjusting the gains of the differential thermocouple amplifiers until the inputs to the power amplifiers were equal. Since there were inevitable differences in the heaters, it was best to balance the power amplifiers. This was done for each set of heaters to be used. The heaters were attached to the power amplifiers and were heated to operating levels (about 10 volts). Using the digital voltmeter as a monitor the gains of the power amplifiers were adjusted to give equal power input to the heaters.

The readout circuits were balanced by putting identical AC voltages across the primaries of the 2:12,000 transformers and using the adjustable 10K resistor to balance
the difference to zero. The 50K adjustable resistor was used to adjust the pen on the recorder.

The chart was calibrated by calculating the power difference to the heaters from the digital voltmeter readings. As will be pointed out later, the chart recorder was not used in actual data taking but it was helpful in balancing the calorimeter as it could be used to determine any unbalance or non-linearity in the power circuits.

As mentioned previously, a cam controlled Leeds and Northrup c.a.t. Controllall powered the calorimeter heater windings. Originally a cam was cut to provide a heating rate of $0.1^\circ\text{C/sec}$, but the best accuracy which could be obtained was $\pm15\%$. In attempting to better this it was found that manually adjusting the unit gave much better results. The method used was to connect a chart recorder to the calorimeter wall thermocouple and to mark a line on the chart with the slope of the desired heating rate. Trial and error then gave the settings necessary to duplicate the given line. The settings were noted at the corresponding times on the chart and the chart was used on subsequent runs. It was found necessary to perform a calibration run for each set of heater windings used.
CHAPTER VIII
CONSTRUCTION DETAILS

A. Thermocouples

Chromel-Alumel thermocouples were used. Choice of the thermocouple material was biased by the need for a thermocouple which would produce a strong signal and which had low and high temperature capabilities. Due to the low signal levels in the differential thermocouples, a high signal voltage was necessary to produce a favorable signal-to-noise ratio. In addition, the material must be fairly inexpensive as large amounts of it were needed. The Chromel-Alumel was found to be fairly satisfactory. It tended to get brittle with use in a vacuum, but this was not much of a problem since the thermocouples were replaced for each test.

The thermocouples were 0.013 inches in diameter and were sheathed in Mullite tubing. After the thermocouples were made up and the ends welded to form a bead, they were annealed at red heat to remove any stresses which might lead to spurious emf's. Attachment to the samples was by "peening". This consists of drilling a small hole in the sample, placing the thermocouple bead in the hole, and then lightly deforming the metal around the hole to anchor the bead. This method gave the best contact between the thermocouple and surface and eliminated convection and radiation effects.
The thermocouple circuitry is as shown in Figure 16. There were three Chromel-Alumel thermocouples, to the calorimeter wall, dummy specimen, and cold-worked specimen. The circuit was such that individual temperatures could be obtained through the ten-position low-noise switch and read on the digital voltmeter. The wall thermocouple was connected to the Controlall which heats the calorimeter, while the dummy and cold-worked specimen thermocouples were connected to recorders. Reversing switches were needed for the recorders because of the inversion of the voltage at the ice-point temperature.

The individual thermocouples were so attached that the differential temperatures between the calorimeter wall and dummy specimen, and dummy specimen and cold-worked specimen were obtained. These signals were the ones which were supplied to the differential floating amplifiers. The input to the amplifiers was also connected to the ten-position switch and could be read on the digital voltmeter. An ice junction was used.

B. Specimen and Calorimeter Heaters

Both specimen and calorimeter vessel heaters were made from Tantalum wire. Originally Nichrome was used. It was discovered, however, that the Nichrome was not stable in a vacuum at high temperatures in that the chromium would be vacuum deposited over all the components. After examination of the vapor pressure curves it was decided that
Figure 16. Thermocouple Circuits
tantalum and tungsten would be satisfactory. Since the calorimeter would be subjected to frequent handling and tungsten tends to become brittle with high temperature use, tantalum was chosen. The tantalum proved satisfactory with the exception that it tended to sag badly with use. This necessitated the replacement of the heater wires after each six runs.

The calorimeter heater was made from 0.013 tantalum wire wound on support rods of high-purity alumina which were supported by a welded copper framework. Heater and framework can be seen in Figures 5 and 6. In addition to the spirally wound heater around the calorimeter body, a smaller heating spiral was placed on the cover. The number of turns in this coil were those which experiments determined to give the closest temperature to that of the body.

The specimen heaters were of 0.007 inch diameter wire wound on 0.086-inch diameter Vitreosil tubing. A larger 0.175-inch diameter Vitreosil tube is used as the outer sheath for the heater. Figure 17 presents a photograph of the specimen heater.

Current was delivered to the heater through 0.02-inch diameter copper wire which was mechanically attached to the tantalum wire. The copper wire as well as the tantalum-copper joint were sheathed in Mullite thermocouple sheathing. The lead-in wires also functioned as the supports
Figure 17. Specimen Heater
for the heaters.

In making the heaters, great care was taken to match the resistances of all of the specimen heaters. The reason for this was not that a mismatch would affect the accuracy of the test, since the control circuits deliver power until the thermocouple difference is minimized, but because mismatch would contribute a cycling effect of its own. The only error which could enter here was that the heater lead-ins were of different resistances, and that there was considerable loss in the lead-ins. This means that the losses would occur outside of the specimen and that any energy difference in losses would directly contribute errors in the total energy. Relative energy, however, would still be unaffected.

In making the heaters, therefore, care was taken to match both heater and heater lead-in resistances. Using a Wheatstone bridge, the resistances could be matched to 0.0005 ohms.

C. Calorimeter Vessel

The calorimeter vessel may be seen in Figures 5 and 6, while Figure 7 is a brief summary of the dimensions. The vessel was about 5½-inches tall and, as can be seen, was elliptical in shape. This shape was chosen because if the specimens are placed at the foci of the ellipse there is a more symmetric placement of the specimens in relation to
the calorimeter walls than there might be in a square or round chamber. This may be an imagined advantage as it proved impossible to calculate any advantage for this geometry.

The bottom of the calorimeter contained one-inch vacuum port and was actually a double bottom. The two sections of bottom, the vacuum port, and the vessel walls formed a compartment through which liquid nitrogen was passed to cool the calorimeter.

The vessel was fabricated from commercially pure copper sheet of 1/4-inch thickness. The body was shaped on a wooden form, following which the cover, bottoms, and vacuum port were machined to size.

To insure uniformity of heat flow through the vessel all parts were carefully welded together to form the finished configuration. In order to allow introduction of liquid nitrogen into the cooling chamber, stainless steel fittings were welded into openings to the bottom. These fittings allowed stainless steel tubing to be connected from the calorimeter vessel to pass-throughs in the baseplate.

The calorimeter was heated by a spirally wound tantalum wire which was supported by alumina rods. The heater and support assembly can be seen in Figures 5 and 6. The alumina rods were supported on a removable framework made of formed copper rods. The framework was welded together after the
rods had been shaped to fit the calorimeter.

The heater material itself will be discussed later along with the specimen heaters.

D. Vacuum System

A photograph of the vacuum system is shown in Figure 18. As can be seen it was basically a mechanical-diffusion pump system. The calorimeter rested on a baseplate and was covered by a bell jar and shatter shield. The bell jar and shield were raised and lowered by means of a counter-weighted pulley arrangement. The baseplate rested on a small metal table. Around the inner circumference of the baseplate were eight tapped holes. These may be seen in Figure 5. Some of these holes contained thermocouples and ionization gauges, while others were fitted with Conax pass-throughs for the specimen and calorimeter heaters and for various thermocouples. In the center of the baseplate was a 4-inch vacuum port. Attached to the vacuum port by means of a spool piece was a NRC 4-inch manifold valve. The manifold valve contained a 4-inch high vacuum valve and two one-inch valves. These three valves allowed a variety of pumping possibilities between the vacuum chamber, mechanical, and diffusion pump. A CVC four-inch pump was bolted to the bottom flange of the manifold valve. Rubber hoses connected the one-inch valves to the foreline of the diffusion pump and to a high-capacity mechanical pump. An additional valve on the spool piece allowed air to be bled into the bell jar.
Figure 18. Vacuum System
Pressures in the system were monitored by a ionization gauge and a thermocouple gauge, both reading into the bell jar. The gauges were connected to a CVC ionization readout.

In normal operation the system was always kept under vacuum. When it was necessary to work inside the bell jar the diffusion pump was blanked off but kept hot. As a result, a fairly low vacuum for this type of system could be reached. After long periods of operation pressures of \(10^{-7}\) torr could be attained, although normal operating pressures were of the order of \(10^{-5}\) torr, even with the specimen and calorimeter heaters operating.

When any attempt was made to use the liquid nitrogen cooling, however, the vacuum would drop drastically. Repeated attempts to correct this flaw were not successful in the least. It is suspected that expansion-contraction of some sealing part was at fault giving rise to leaks.
A. Errors

There were a number of factors which could increase the error in a differential calorimeter.

a) The thermocouples could give erroneous readings. This can be caused by resistance in the thermocouple wires, stress caused by handling, or poor contact. Poor contact can be eliminated by peening the thermocouples into a small drilled hole. The resistances can be matched using a resistance bridge. After a set of thermocouples were made up, they were annealed in a vacuum by passing a current through them and heating to red heat.

b) The heaters could be mismatched. In a differential method this was not too serious. Mismatch in lead or heater resistance caused different amounts of power to be dissipated. It was possible for two heaters to dissipate the same wattage, yet due to this fact one heater would be operating at a higher temperature and therefore transfer heat more effectively. This effect should be cancelled out in the differential method if a second run was made to establish the baseline. The following effect, however, could occur.

c) Reinsertion effect. If a specimen was disturbed there was a change in the relationship of the specimen to the heater and to its surroundings. As a result, there will
be changes in the amount of energy delivered to each specimen from run to run. While great care was taken not to disturb the specimen following the data run, some change always resulted on the subsequent baseline run. It was possible that natural changes occurred in the heater due to operating temperatures and pressures, and it was also possible that the changes in heaters were not equal. However, these changes can be allowed for provided there were no changes during any single run. To minimize these changes, a new set of heaters and thermocouples were used for every set of specimens.

d) Differences in specimen mass. These would be subtractive in the two runs and will cancel. All sample masses were found to be within 0.05 grams of each other. This weight difference is out of a total specimen weight of 120 grams. The worst effect that a mismatching of weights could have was a slight curving of the baseline.

e) The linearity of the two circuits could be different. Again, the differential method cancelled this error out.

f) Non-adiabatic conditions. While the differential method was expected to cancel this out, any large differences in specimen-to-specimen and specimen-to-wall temperatures could result in unsymmetric heat losses which could change from run to run. This effect was not observed, however, it was possible that there was some non-adiabaticity during
the time that energy was released from the cold worked sample.

B. Accuracy

As with any research equipment, it was desirable to know the reproducibility and accuracy of the calorimeter. The absolute accuracy of the calorimeter was checked by using specific heats. The specific heat of a mass of material is given by

\[ C_p = \frac{\Delta E_I \Delta t}{M \Delta T} \]

\( \Delta E_I = \) power applied in the time interval \( \Delta t \)

\( \Delta T = \) temperature rise during the interval \( \Delta t \)

\( M = \) mass of the specimen

The above could be adapted to a differential calorimeter by using two specimens which have a mass difference of \( M \). \( \Delta E_I \) then becomes the power difference necessary to heat two specimens at the same rate through the interval \( \Delta T \).

Two pure copper specimens with a mass difference of 20 grams were used. The specimens were of course of different size but heat transfer due to this difference could be neglected.

The specimens were heated at a rate of approximately 6°C/minute and the time interval was 12 minutes. The time was obtained from an electric timer while the digital voltmeter was used to obtain \( \Delta E_I \). Specific heat values for four temperatures were made, the values being averages of
approximately four runs for each temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Cp (joules/gm·°C)</th>
<th>Cp (Wright)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>.410</td>
<td>.4047</td>
</tr>
<tr>
<td>200</td>
<td>.415</td>
<td>.4093</td>
</tr>
<tr>
<td>300</td>
<td>.424</td>
<td>.4195</td>
</tr>
<tr>
<td>400</td>
<td>.433</td>
<td>.4285</td>
</tr>
</tbody>
</table>

The values on the right are those obtained by J.W. Wright (50) at the University of Tennessee as part of his investigation on the specific heat of metals. As can be seen, the values obtained with the present equipment are extremely close to and follow the trend of Wright's data. While it is possible that a constant error in the equipment was in the favorable direction, certainly the trend of the values is correct. Therefore, one is forced to conclude that the calorimeter probably has sufficient absolute accuracy for the purpose intended.

Relative accuracy was checked by using two samples of equal mass, both in the annealed condition, and attempting to measure any difference in power applied as the samples were heated at .1°C/second. The largest variation observed was about .0015 calories/second. The magnitude of this can be seen by turning to any of the data plots and observing the variation of the energy relative to the baseline following the recrystallization peak. This variation was entirely acceptable considering that maximum energy releases could be as high as .04 calories/second.
In the light of the foregoing discussion and considering errors which can occur, it seems not unreasonable to claim an accuracy of at least ±10%. For most runs the accuracy was considerably better, in the range of ±5%.
Prior to conducting a test the calorimeter had to be balanced according to the procedure outlined previously. The thermocouples had to be made, matched, and annealed for every set of specimens. New heaters were also used for every test, therefore, it was necessary to match each set of heaters and then to balance the power amplifiers as outlined previously. Following the balancing of the electrical system the specimen heaters were switched for a pair of bypass resistors until the test was begun. Usually the system was allowed to stabilize for at least four hours prior to a test, in most cases the system was kept on continually.

The test specimens were removed from the vacuum dis­sicator and washed with ethyl alcohol. Testing proceeded immediately. A Baldwin 60,000 lb. tensile tester was used to induce deformation at a strain rate of .1 in./in./min. All mechanical deformation was done at room temperature. Immediately following deformation the specimens were quenched in ice water, where they remained through subsequent handling until they were placed in the calorimeter.

In order to know the length of deformed section to be removed from the tensil specimen, it was necessary to scribe thin lines on the undeformed specimen. These lines after
deformation showed where the specimen was to be cut.

Sectioning of the deformed section was by a fine toothed hacksaw, using a special jig which guided the saw blade and which circulated ice water on the specimen and into the saw cut. It was believed that no significant heating took place during sawing.

Following sawing the deformed specimen mass was matched to a standard dummy mass using a beam balance. Due to inaccuracies in sawing and moisture collecting on the chilled specimen it was not possible to match masses closer than 0.05 grams. Since the average specimen weighed 121.6 grams this error is not considered serious.

The next step was to attach the thermocouples. This was done by inserting the thermocouple bead into a small drilled hole and deforming the metal around the thermocouple in order to anchor it. If done carefully this procedure gave the best method of obtaining maximum heat transfer from specimen to thermocouple.

Following attachment of the thermocouple the specimen was inserted in the calorimeter and positioned on its rings. The thermocouple which had a matched chromel-alumel male connector plug, was joined to the pass-through thermocouple wire by means of a male plug. The heater was then inserted into the axial hole of the specimen and the calorimeter vessel top was placed in position. The heat shield and bell jar were positioned and the system was roughed out
using the mechanical pump. When the pressure was about 50 microns the diffusion pump was cut in and the system pumped to approximately $10^{-5}$ microns, following which the test began.

The above procedures take about 20 minutes from the end of the tension test to the time operating pressures are reached. The dummy specimen had its thermocouples and heater placed in position prior to the test. While 20 minutes might seem long (it is a much shorter time interval that required by Gordon and Clarebrough et al.), it was found impossible to decrease this time. In addition, there were some ten more minutes which the equipment required to stabilize.

It should be pointed out that the dummy and cold worked specimens must be at the same temperature at the beginning of the test as the equipment was unable to cope with large temperature differences. This was accomplished by keeping the dummy specimen in ice water during the preparations and by inserting it at the same time as the cold worked specimen.

Once operating pressures were reached the bypass resistors are switched to the heaters and some ten minutes allowed for the system to stabilize.

Unfortunately, the operation of the system was not satisfactory in all modes. The operation of the system was as intended and Figure 19 is an energy release curve
Figure 19. Energy Release Obtained From Chart Recorder
as obtained on the chart recorder. The power difference sensing circuits were so sensitive that it was impossible to screen them from extraneous signals. These signals came from equipment operating elsewhere in the building or from nearby radio and television stations. The affect of these spurious signals was to cause wild oscillation of the recorder pen. The power control circuits, however, were more insensitive to the external signals and were relatively stable in their operation, provided a suitable time of day was chosen. All of the tests were made late at night or early in the morning to take advantage of lower spurious signal levels.

Therefore, although the sensing circuits could be used for monitoring the test and for alignment purposes, they were of little value in obtaining quantitative data. This difficulty was circumvented by taking data directly with a digital voltmeter. Readings of the voltage to each heater and of the voltage across the instrument shunts were made every ten degrees during the course of a test run. This data was transferred to computer punch cards and was converted to power difference values in joules/second by means of the computer program in the Appendix.

During the course of a test run calibration was checked by momentarily turning off the dummy specimen—cold worked specimen thermocouple amplifier and reading the difference in signal inputs to the power amplifiers. The
difference in this case should of course be zero. In case drift had occurred and the value was not zero, the gains of the power amplifiers were adjusted so that the power to the two specimens was equal. The frequency meter and oscilloscope were also used to monitor the signals during tests. Chart recorders were used to monitor the temperature and heating rate of the specimens and calorimeter wall and to use as guides in trimming the calorimeter heating rate.

Following completion of a test run, in all cases 400°C, the calorimeter and specimens were allowed to cool to room temperature. Great care was taken that nothing was disturbed during cooling. As soon as room temperature was reached a second test was made. In the absence of any stored energy the data points obtained in this test represent the reference baseline for the first run, and the area bounded by the two curves represents the stored energy of cold work.
CHAPTER XI

EXPERIMENTAL RESULTS

The data is presented graphically in Figures 20 through 27. There are two sets of curves on each graph. The discrete points are values of the energy release obtained from the rough data by means of the computer program included in the appendix. The straight line represents the baseline, the experimental run made immediately following the data run and with presumably no further energy release from the cold worked specimen. This baseline is displaced from zero depending on differences in resistance of the specimen heater wire, the thermal resistances of the heater sheath, the conductive and radiant heat transfer coefficients of the specimens, and the mass differences of the heater and specimens. The baseline represents an equation of the form $y = mx + b$ which was fitted by computer through the baseline data points. These points are omitted on the graph. The vertical displacement and slant of the baseline are not important since the zero energy release point for any temperature is the baseline.

The set of discrete points on the graph are the data points. These are fitted with a least squares curve, the program for which is also included in the appendix. Because of the scarcity of points in the peaks, the least squares smoothing is not altogether satisfactory. As no
Figure 20. 12% Elongation-Data Run 1
Figure 21. 12% Elongation-Data Run 2
Figure 22. 20% Elongation - Data Run 1
Figure 23. 20% Elongation-Data Run 2
Figure 24. 30% Elongation-Data Run 1
Figure 25. 30% Elongation-Data Run 2
Figure 26. 40% Elongation - Data Run 1
Figure 27. 40% Elongation-Data Run 2
satisfactory smoothing procedure could be found, the curve was drawn to include the data points in the peaks.

The curves were integrated to obtain the total energy release from the specimens. Table A gives the values of the total energies. The values of total energy for individual tests at each elongation differ by at most 8% from each other. This is of the same order of differences as found by Gordon (48) and is within the previously stated accuracy of the apparatus.

Most of the energy is released in one peak, which is assumed to be the recrystallization peak. The height of this peak and the temperature at which it occurs are functions of the amount of deformation. The greater the elongation the higher the peak and lower the recrystallization temperature. This has been observed on numerous previous occasions. The samples which were deformed 40% have the peak occurring at approximately 220°C, and the energy release in the peak reaches a value of almost 0.04 cal./sec. The samples deformed 12% have their peak at about 335°C and their maximum energy release rate is just below 0.02 cal./sec. The other sets of results fall between these values.

The energy release peaks are sharp and well defined. It is possible that, due to the sharpness of the peaks and the resultant scarcity of data points, some of the energy in the peaks is underestimated. The magnitude of this
**TABLE A**

Total stored energy as obtained by graphic integration.

<table>
<thead>
<tr>
<th>Total Energy cal/gram-atom</th>
<th>Elongation %</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.89</td>
<td>12</td>
<td>12-1</td>
</tr>
<tr>
<td>1.90</td>
<td>12</td>
<td>12-2</td>
</tr>
<tr>
<td>3.40</td>
<td>20</td>
<td>20-1</td>
</tr>
<tr>
<td>3.28</td>
<td>20</td>
<td>20-2</td>
</tr>
<tr>
<td>4.25</td>
<td>30</td>
<td>30-1</td>
</tr>
<tr>
<td>3.97</td>
<td>30</td>
<td>30-2</td>
</tr>
<tr>
<td>5.36</td>
<td>40</td>
<td>40-1</td>
</tr>
<tr>
<td>5.20</td>
<td>40</td>
<td>40-2</td>
</tr>
</tbody>
</table>
loss can be estimated by extending the sides of the peaks as straight lines until they cross. This gives a maximum value of about 0.2 cal/gram-atom, a value which does not affect the total energy greatly.

In the 30 and 40% elongation curves there is an indication of lower temperature recovery. This energy is so low, below 0.001 cal/second, that it is barely within the resolution of the calorimeter. The energy is released at temperatures under 100°C, the approximate range where recovery energy had been found in other experiments. Due to the low amounts of this energy, however, it can be assumed that any major recovery energy has annealed out within the 30 minutes it took to initiate a run following deformation, or, there was no recovery energy present.

Figure 28 presents the total stored energy as a function of elongation. There is no strong indication that the total energy saturates at some value of elongation. The maximum amount of deformation, however, was only 40%. It is expected that at higher deformations the energy vs. % deformation curve will level off, as has been observed in other investigations. Elongation was limited to 40% in the present experiment due to necking. In other methods, such as compression or torsion, larger deformations are possible.
Figure 28. Total energy released as a function of per-cent elongation on 99.999% Cu.
CHAPTER XII

DISCUSSION OF RESULTS

Examination of the individual curves indicates that most of the energy is released in a single peak, following which there is no further energy release. It is certain that this peak corresponds to the point at which recrystallization takes place and that the energy under the peak is the driving force for recrystallization. This type of peak has been correlated to the recrystallization process through grain size studies\(^{(21)}\) and resistivity and hardness measurements.\(^{(39)}\) Bailey,\(^{(53)}\) using electron microscopy, definitely assigned this type of peak to recrystallization:

As previously noted, there is little or no energy release of the type associated with recovery. The sharpness of the peaks also indicates that the energy release is rapid and therefore, probably depends on a single mechanism. That is, there does not appear to be a spectrum of energy releases. This does not mean that there is only one source, but rather implies that the various sources may be connected with one release mechanism.

In spite of the large amount of activity in the measurement of stored energy, only Gordon,\(^{(48)}\) Williams,\(^{(11)}\) and Loretto and White\(^{(40)}\) have published what seem to be reasonable data for the stored energy of room temperature deformation of high-purity copper. Loretto and White\(^{(40)}\) are the only ones to employ a method similar to the one
used in the present work. Unfortunately, they obtained data for only two samples, both deformed 30% in tension. Their value of the stored energy of 99.999% copper compares with the present work as follows:

<table>
<thead>
<tr>
<th>Source</th>
<th>Total Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>0.069 cal/gram</td>
</tr>
<tr>
<td>Loretto &amp; White (40)</td>
<td>0.085 cal/gram</td>
</tr>
</tbody>
</table>

The agreement appears to be reasonably close. The energy release curves are similar in appearance and no recovery energy was detected by Loretto and White.

The experiment of Loretto and White was carried out using the equipment of Clarebrough et al. (20) Since Clarebrough et al. have published large amounts of data using a method similar to the present work and heating rates are the same as in the present work, (0.1°C/second), some comparison should be made. In general, the curves have approximately the same features. In the present results the recrystallization peaks fall 30 to 70°C lower than for Clarebrough et al. and the peak heights are considerably lower. However, agreement can be considered satisfactory when the differences in purity (99.96 for Clarebrough et al. as opposed to 99.999%) and homogeneity in grain size are considered. As pointed out earlier, there was considerable recovery energy in some of the results of Clarebrough et al.
The values of Williams\textsuperscript{(11)} are almost twice those of the present work. Williams' apparatus was capable of measuring the energy release immediately following deformation. The next shortest time between deformation and testing among the various experiments is the 30 minutes of the present experiment. The next shortest time is the three hours of Clarebrough et al. Williams allocated one-half of his total energy to recrystallization and the remaining portion to point defects and strain rate effects. Therefore, as far as the recrystallization energies are concerned, there is agreement.

The only other extensive energy measurement on room temperature deformed 99.999\% purity copper, using the two-step method, are those of Gordon,\textsuperscript{(48)} who used isothermal annealing. Gordon's values, along with those of the present work, are given as a function of elongation in Figure 28. The values are total values, and included, in the case of Gordon, 6 to 10\% recovery energy. The curves show good agreement. The rise in energy as a function of elongation is roughly parallel, and differs on the average by 20\%. This could be caused by systematic errors and differences in grain size. Williams\textsuperscript{(11)} found that in going from a grain size of about 0.02 to about 0.6 mm, the stored energy had a decrease of 15\%. However, there probably is some unaccountable error.
in the data because the grain size energy difference should be less at higher strains, whereas it is about constant in the present data.

Nevertheless, it can be concluded that in general the present data agree with previous work. And since all methods used to obtain stored energy have demonstrated reasonable accuracy, any differences in results must lie with the method of testing or the material used.

Recovery has been assumed to consist of one or more of the following: annealing out of point defects, break-up of point defect aggregates, small movements and relaxation of dislocations and dislocation groups. Recrystallization is characterized by the movement of high angle boundaries through the rearrangement and annihilation of dislocations. The assignment of the recovery energy to point defects needs close examination. Cahn, in his analysis of work by Clarebrough et al., attributes the lack of recovery energy to the diffusing out of vacancies. Other workers, too, usually attribute the recovery energy of room temperature metals to point defects, usually vacancies.

It is known that vacancies are produced in quenching, and it is fairly certain that they are produced in deformation. Oliver and Girifalco observed the formation of voids in 99.99% silver deformed at temperatures from 680 to 1097 K. It took from 20 to 80 minutes under strain for voids to be observed. Although there are more vacancies
present at high temperatures, this at least confirms the formation and annealing of vacancies in deformation at high temperatures. The formation of vacancies with room temperature deformation has not been definitely proven, although there is no theoretical reason why they should not be. If vacancies are formed, then their rate of jumping at room temperature can be roughly estimated by

\[ J = K \exp \left( -\frac{Q_m}{RT} \right) \]

- \( J \) = jumps/second
- \( K \) = a constant containing the Debye frequency and the coordination number
- \( Q_m \) = the sum of the jump energy and entropy
- \( R \) = universal gas constant
- \( T \) = absolute temperature

The value of \( K \) for copper is approximately \( 10^{15} \) (56), the energy \( Q_m \), 29,000 cal/gram-atom. At a temperature of \( 300^\circ K \), approximately room temperature,

\[ J = 10^{-6} \] jumps/second

This means that \( 10^6 \) seconds occur between jumps. Therefore, there is practically no movement of vacancies at room temperature.

This conclusion is supported by quenching studies on copper and gold. Clarebrough et al. (39) deformed 99.9% purity gold and found that the energy was evolved in a single high temperature peak. Bauerle and Koehler (58) quenched gold to \( 40^\circ C \) and found that it required 49 hours
to anneal out one-half of the quenched resistance. If vacancies have been produced, and were mobile, they should have been detected by Clarebrough et al. (39). Likewise, Airoldi et al. (59) found that quenched copper annealed at 346°C recovered only 30% of its normal resistivity after 100 minutes.

The above indicate that if vacancies are produced in room temperature deformation, they would probably not be annealed out prior to measuring for the stored energy. If this is the case, however, then there remains the problem of explaining the presence of the recovery energy found by other experimenters, as opposed to those results in which no recovery energy was found.

The other obvious point defect, the interstitial, could be a participant. The calculated activation energies for creation and movement of point defects in copper are

<table>
<thead>
<tr>
<th>Defect</th>
<th>Energy for Formation</th>
<th>Energy for Movement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial</td>
<td>3.5 ev. (60)</td>
<td>0.50 ev. (62)</td>
</tr>
<tr>
<td>Monovalency</td>
<td>1.3 ev. (63)</td>
<td>1.3 ev. (61)</td>
</tr>
</tbody>
</table>

The above value would indicate that vacancies are more easily produced than interstitials. However, in deformation the energy of formation is supplied by the deformation forces and therefore energy is equally available to form both vacancies and interstitials.
There is a great deal of theoretical uncertainty as to whether vacancies, interstitials, or both are produced in plastic deformation, and in what proportions. The important theoretical efforts can be summarized thus:

Seeger (1958)\(^{(64)}\) -- Predicted equal probability for vacancies and interstitials.

Cottrell (1957)\(^{(65)}\) -- Jogs would form interstitials only.

Mott (1960)\(^{(66)}\) -- Predicted both vacancies and interstitials would be produced.

Hirsch (1962)\(^{(67)}\) -- Calculated that large jogs would form vacancies but not interstitials.

Weertman (1963)\(^{(68)}\) -- Reworked Hirsch's theory and predicted both vacancies and interstitials.

The theoretical picture can therefore be summed up as unpromising. If the presence of interstitials is accepted, it is still hard to predict their rate of movement. If an equation of the same form as that used for vacancy motion is used,

\[ J = A \exp \left(-\frac{Q_m}{RT}\right) \]

using a value of 0.5 ev for \(Q_m\) gives a jump rate of a few jumps per second at room temperature, too low to allow movement. However, the movement of the interstitial is probably too complex to be treated in this fashion. Birnbaum,\(^{(69)}\) for example, has shown that interstitials in copper at low temperatures have to be treated as crowdions with one-dimensional walk. Balluffi et al.\(^{(47)}\) have
pointed out that a variety of interstitial geometries are possible in which the energies are not greatly different. As a result, the configuration and movement of the interstitial is not at all certain. It is probable, however, that at low temperatures there is production of interstitials by plastic deformation. In particular, some of the numerous low temperature deformation annealing peaks have been assigned to interstitials.\(^{(45)}\)\(^{(46)}\)

At room temperature and above, however, only a few peaks are present in the annealing curve, and only the dislocation peak\(^{(53)}\) has been assigned with any certainty. If the interstitial has the calculated activation energy, however, it is hard to see how room temperature annealing could remove all the interstitials within the time observed by Williams. Moreover, it is hard to see how such large amounts of energy can be stored by point defects.

It should be pointed out that the presence of dislocations, which can act as vacancy sinks, may increase the rate of point defect annealing. Kuhlman-Wilsdorf et al.\(^{(70)}\) have suggested that as a sink for point defects the presence of fresh dislocations is much more effective than dislocations already present. It implies that any vacancies produced would have to be immediately drawn to the dislocations and not released during the first stages of annealing. If these trapped point defects are released,
they are released during the recrystallization peak, or after prolonged heating at high temperatures.

Examination of the previous investigations suggests that recovery energy is present in metals which have one or both of the following criteria:

a) presence of impurities
b) high stacking fault energy

An incomplete survey of the experiments relevant to the above point are presented in Table B. Other factors, such as type and amount of deformation can also effect the distribution of the annealing spectrum.

The table suggests that the type of impurity may also be important. Arsenic, for example, is known to influence the stored energy more than other impurities in copper. Copper and gold both have low stacking fault energies and show no recovery energy in the pure state. Aluminum has a high stacking fault energy and shows considerable recovery energy.

If the stacking fault energy of a metal is low, the dislocations have difficulty in climbing out of the glide planes. This means that in these metals the dislocations can relax without the recrystallization process occurring.

The dislocations can be trapped in high energy configurations by other dislocations, such as in dislocation forests, by vacancies and vacancy clusters, or by impurities. Even in the purest materials used, the impurity concentra-
<table>
<thead>
<tr>
<th>Material</th>
<th>Purity</th>
<th>Recovery Energy (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>99.999</td>
<td>0</td>
<td>Filatovs</td>
</tr>
<tr>
<td></td>
<td>99.999</td>
<td>0</td>
<td>Loretto &amp; White (40)</td>
</tr>
<tr>
<td></td>
<td>99.98 (arsenic</td>
<td>50</td>
<td>Clarebrough et al. (39)</td>
</tr>
<tr>
<td></td>
<td>impurity)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>99.999</td>
<td>40</td>
<td>Gordon and Vandermeer (71)</td>
</tr>
<tr>
<td></td>
<td>99.998</td>
<td>50</td>
<td>Clarebrough et al. (39)</td>
</tr>
<tr>
<td>Ni</td>
<td>99.85</td>
<td>30</td>
<td>Clarebrough et al. (20)</td>
</tr>
<tr>
<td>Au</td>
<td>99.9</td>
<td>0</td>
<td>Clarebrough et al. (20)</td>
</tr>
<tr>
<td>Ag</td>
<td>99.99</td>
<td>37</td>
<td>Bailey (53)</td>
</tr>
</tbody>
</table>
tions are usually higher than the room temperature equilibrium concentrations of vacancies.

How dislocations can be trapped in high energy configurations can be understood by considering the configuration below.

The dislocations are piled up along a single slip plane. The force causing the pile-up was supplied by the deformation force and the dislocations are prevented from relaxing by one of the obstacles mentioned above. The force holding the dislocation pile up is approximately given by the expression

\[ F = nGb/k \]

\( n \) = number of dislocations in the pile up

\( G \) = shear modulus

\( b \) = Burgers vector

\( k = 1 \) for screw dislocations, \((1 - \nu)\) for edge dislocations

\( \nu \) = Poisson's ratio
When the force $F$ is overcome the dislocations can relax. If the anchoring is by an impurity atom the dislocations may be able to carry the impurity along. The process would be thermally activated and sensitive to temperatures if diffusion were required for motion of the solute atom. Perhaps stress assisted diffusion of the atom also occurs. If the obstacle could not be moved the dislocations could only move through the process of climb. As pointed out earlier, the stacking fault energy is an indicator of how easily dislocations can climb. In materials with high stacking fault energies some relaxation of dislocation pile-ups can occur, with resultant release of recovery energy. This relaxation may require very small amounts of climb and would thus not be observable even in the electron microscope. It is known that in materials with high stacking fault energies the dislocations tend to form cellular substructures which are very sharply defined, while in materials with low stacking fault energies the cellular substructures, if they are formed, are not very well defined. Therefore, one part of a cell wall can trap another part into a high-energy configuration, from which escape of partial relaxation can occur by climb.

Aluminum, which has a high stacking fault energy, is known to have a sharp cell structure. Astrom found that there was an energy release which corresponded
to structure changes occurring before recrystallization, and indicated that this was probably polygonization. Gay et al. \(^{(73)}\) used x-ray microbeam techniques to find that recovery was composed of dislocation rearrangement in the subgrains. While aluminum has several stages for recovery, and is an extreme case since it polygonizes at room temperature, this at least shows that climb can be associated with part of the recovery process in a high stacking fault metal.

Impurities can affect recovery in several ways. It has long been known that the rate of recrystallization decreases with the addition of impurities. Vandermeer and Gordon \(^{(74)}\) have shown that in aluminum the recrystallization process is retarded more than the recovery. Therefore, the presence of impurities would tend to reduce any overlap in the recovery and recrystallization. The impurities could also anchor the fresh dislocations present after the deformation into high energy configurations. Relaxation could occur only if the impurity could be dragged along or if it could diffuse away, possibly by stress assisted diffusion. In any case, the presence of impurities would enhance the amount of recovery energy.

Any conclusions concerning the annealing process must recognize that there may be present different mechanisms in both the storing and release of energy depending on the base material, impurity content and type,
temperature, and the method of deformation. The general process of annealing of room temperature deformed metals as discussed in this chapter can be summarized as follows:

1) Recovery results from the relaxation of dislocations from high energy configurations. This relaxation would not be visible in the electron microscope.

2) High energy configurations of dislocations are encouraged by the presence of a high stacking fault energy and the presence of impurities.

3) It is unlikely that there is a large contribution by point defects to the recovery energy, although no definite conclusions can be made at this time, especially about the interstitial.

4) Recrystallization is the large scale rearrangement of dislocations. Any excess vacancies produced by deformation are used up during this time.

The presence of more recovery energy in the results of Gordon (48) than in the present work may be due to differences in the experimental method. Gordon used the isothermal method which required at least an hour to release the recovery energy, while in the present work all of the energy usually was released in this time. It is possible that the isothermal method allows the observation of the recovery energy by allowing enough time to separate the recovery and recrystallization processes, while the continuous heating method does not.
As for large recovery energy found by Williams, the speed of its release suggests that diffusion processes are not participating, although a quick moving interstitial could be present. It is possibly caused by immediate recombination of close Frenkel pairs and the immediate relaxation of dislocation bundles. Most likely, the latter contributes most of the energy.

In the present work then, all of the energy measured is assumed to be associated with the recrystallization process. The type of peaks found in this work have been correlated with the recrystallization process with sufficient certainty. The lack of recovery energy can be explained by the simultaneous presence of a pure base material with a low stacking fault energy. This prevented those high energy configurations which did not relax immediately following deformation from relaxing until the recrystallization process occurs.
CHAPTER XIII

CONCLUSIONS

1) An anisothermal calorimeter capable of measuring 0.0015 calories/second has been constructed and operated.

2) The stored energy remaining 30 minutes after room temperature deformation of 99.999% purity copper has been obtained. Deformation by elongation was 12% to 40% while corresponding energy values ranged from 1.9 to 5.3 calories/gram-atom.

3) The values of stored energy in general conform to those previously published. In particular, the values obtained by Gordon using the isothermal method have been verified.

4) No recovery energy was found.

5) It is proposed that it is unlikely that the recovery energy of room temperature deformation found by other workers is due to vacancies. It is possible that interstitials take part, but it is more likely that relaxation of high-energy dislocation configurations is involved.

6) It is also proposed that the criteria for the presence of recovery energy in the spectrum of room temperature deformed metals is a high stacking fault energy and/or the presence of impurities.
REFERENCES

3. Williams, R.O.; Acta. Met. 12 (1964) 745
22. Bockstiegel, G. and Lucke, K.; Z. Metallkunde 42 (1951) 225
26. Borelius, G. Berglund, S. and Sjoberg, S.; Ark. Fys. 6 (1952) 143
27. Astrom, H.U.; Acta. Met. 3 (1955) 508
34. Averbach, B.L., Bever, M.B., Comerford, M.F. and Leach, J.S.; Acta. Met. 4 (1956) 477
36. Cohen, J. B. and Bever, M.B.; Progress in Metal Phys. 7 (1958) 269
38. Dobson, P.S., Goodhew, P.J., and Smallman, R.; Phil. Mag. 16 (1967) 9


42. Williams, R.O.; Acta Met. 13 (1965) 163


45. Manintveld, J.A.; Nature, 169 (1950) 690

46. Van den Beukel, A.; Physical 27 (1961) 603


53. Bailey, J.E.; Phil. Mag. 8 (1963) 223

54. Cahn, R.W.; Physical Metallurgy- North Holland (1965)


56. Takamura, J.; Physical Metallurgy-North Holland (1965)


60. Bennemann, K.H.; Phys Rev. 124 (1961) 669

61. Damask, A.C., Dienes, G.J. and Weizer V.G.; Phys. Rev. 113 (1959) 781


63. Huntington, H.B.; Phys. Rev. 61 (1942) 325

64. Seeger, A.; Proc. of 2nd Int. Conf. on Peaceful Uses of Atomic Energy 6 (1958) 260

65. Cottrell, A.H.; Dislocations and Mechanical Properties of Crystals—Wiley (1957) 361


67. Hirsch, P.B.; Phil. Mag. 7 (1962) 67

68. Weertman, J.; Phil. Mag. 8 (1963) 967


72. Astrom, H.U.; Arkiv. Fysik, 10 (1955) 197


APPENDIX A

REDUCTION OF RAW DATA

The values of energy release in calories/second were obtained from the current and voltage data of the specimen heaters by means of the following program:
**FORTRAN IV G LEVEL 1, MOD 2**

**MAIN**

**DATE = 68354**

**PAGE 0001**

---

**0001** REAL MW

**0002** INTEGER PAGE(20), NODATA/******/*, BLANK/** */

**0004** 1 READ (1,100) PAGE

**0005** IF(PAGE(1) .EQ. BLANK) GO TO 20

**0006** 100 FORMAT(20A4)

**0007** WRITE (3,200) PAGE

**0008** 200 FORMAT(11*,20A4//)

**0009** WRITE (3,201)

**0010** 201 FORMAT(7X,TEMPERATURE, 5X,ENERGY RELEASE*)

**0011** WRITE (3,202)

**0012** 202 FORMAT(8X,DEGREES C., 8X,CAL./SEC.*)

**0013** 2 READ (1,102) TEMP,V1,V2,V1P,V2P,NODATA

**0014** 102 FORMAT(7F9.4)

**0015** IF(NODATA .EQ. NODATA) WRITE (2,205) NODATA

**0016** 205 FORMAT(76X4)

**0017** IF(NODATA .EQ. NODATA) GO TO 1

**0018** MW = (V1*V1P - V2*V2P)/.213486

**0019** WRITE (3,203) TEMP, MW

**0020** 203 FORMAT(10X,F5.0,9X,F12.8)

**0021** WRITE (3,204) TEMP, MW

**0022** 204 FORMAT(2E15.8)

**0023** GO TO 2

**0024** 20 RETURN

**0025** END
APPENDIX B

MODIFIED LEAST SQUARES METHOD

The data points were smoothed by a least squares method which was provided by Mr. R. Nash, U.S. Bureau of Mines Research Station, Rolla, Mo.
DO 8 4 = 1, KC

6 PY(J) = AO + 41 + PX(J)

SUM = C + 4

GO TO 4

SY(J) = AO + 41 + PX(J)

RES(J) = NS(Y(J)) - ABS(Y(J))

7 SUM = SUM + RES(J)**2

STF = SQRT(SUM/(PY-1, 11)

DO 7 J = 1, NP

10 IF(PY(J) .LT. XMIN) PX(J) = XMIN

DO 10 J = 1, NP

11 IF(PX(J) .GT. XMAX) PX(J) = XMAX

DO 11 J = 1, NP

60 CONTINUE

9 CALL ARFREAD(A, 3, 4)

91 VV = 0.0

92 DO 91 J = 1, IP

93 CM(1) = CM(1) + VV

94 CM(2) = CM(2) + VV*J

95 CM(3) = CM(3) + VV*J**2

96 CM(4) = CM(4) + VV*J**3

97

98 CALL ARFREAD(A, 3, 4)

99 RX = CM(2, 4) / CM(1)**2

100 CALL ARFREAD(A, 3, 4)

101 IF(RX .LT. 0.0) GO TO 1

102 AO = AR(1, 1)

103 A1 = AR(2, 4)

104 A2 = AR(3, 4)

105 H = (X(MP) - X(1)) / (MP - 1)

106 H2 = H**2

107 KC = 3 + HP

108 PX(1) = YJ(1) - H2

109 IF(PX(1) .LT. XMIN) PX(1) = XMIN

110 IF(PX(1) .GT. XMAX) PX(1) = XMAX

111 DO 111 J = 1, HP

112 PY(J) = AO + A1*PX(J) + A2*PX(J)**2

113 SUM = SUM + PY(J)**2

114 IF(J = 1, HP)

115 EY(J) = AO + A1*PX(J) + A2*PX(J)**2

116 RES(J) = ABS(EY(J)) - ABS(Y(J))

117 SUM = SUM + RES(J)**2

118 IF(J = 1, HP)
FORTAN IV G LEVEL 1, MOD 2

MAI N

DATE = 68365 19/5/47

PAGE 0004

0164 605 WTVI = AC + A1*X(J1) + A2*Y(J1)+2
0165 \*E11 LT. 2 OR, L GE. (NP-1) GO TO 626
0166 G0 TO 482
0167 466 SIV = C, 0
0168 607 JCl, NP
0169 607 SUM = SUM + (ABS(Y(J1)) - ABS(Y(J1))/X(J1)+2
0170 \*SIV = SORT(SUM/PW)
0171 GO TO 482 JCI, NP
0172 606 FIV(J1) = WTVI
0173 \*M = NY + 1
0174 IF(MY, GT, 10) GO TO 610
0175 IF(MS, LE, 60) WN = 10
0176 GO TO 611
0177 610 CALL SMOOTH(WY, W, NP, 11
0178 SUM = C, 0
0179 GO TO 481 YC1, NP
0180 YF = Y(J1)
0181 FIV(J1) = FIV(YE(J1), WY, YC, H, NP)
0182 FEIV(J1) = ABS(YE(J1)) - ABS(Y(J1))
0183 SUM = SUM + FEIV(J1)+2
0184 SF = SRT(SUM)/(PW-1.1)
0185 CR = J1 - 1, KC
0186 613 FY(J1) = X(Y(J1))
0187 IF(KL, LT, 1) GO TO 614
0188 614 Y(J1) = WY(J1) - 7/MV
0189 X(J1) = WY(J1) - 7/INV
0190 GO TO 611
0191 690 Y(J1) = Y(J1) - 7/INV
0192 GO TO 481 YC1, NP
0193 611 Y(J1) = EX(J1) - 7/INV
0194 6P(B2) = S*Y(J1)+1+2*Y(J1)) + (68453)*A2
0195 466 KFC = KC-1
0196 GO TO 481 JCl, NP
0197 696 YV(J1) = Y(I(J1)) + 0.1
0198 APEX = SIMP(YV, CC, H2)
0199 AREA = AREA - APEX
0200 614 WRITE (13, 621) NAME
0201 WRITE (13, 621) NAME
0202 IF (TYPE, EQ, BLANK) GO TO 615
0203 TYPE = BLANK
0204 WRITE (3, 624) STE
0205 264 (FERT8) STANDARD EPR2(1, E15, 2)
0206 700 CALL DEP(1, Y, EY, RES, STD, OBS, NP1
0207 CALL DEPL1D(Y, Y, YL, WP, PX, PY, KC, XM, YM, XM, YM, XM, YM, PLT8L, 1
0208 IF (TYPE, EQ, BLANK) GO TO 614
0209 GO TO 1
0210 615 WRITE (3, 620)
0211 205 IF (TYPE, EQ, BLANK) GO TO 615
0212 WRITE (3, 206) H
0213 206 FOR Y(J1) X INCREME T= 1, E15, 3/1
0214 WRITE (3, 207)
0215 207 IF (X, EQ, Y(J1)) GO TO 615
0216 GO TO 620 JCl, NP
0217 620 WRITE (3, 209) WTVI, FY(J1)
FORTRAN IV G LEVEL 1, MOD 2

MAIN

DATE = 68365 19/58/47  PAGE 0005

0219  230 FORMAT (E2E, 91)  WRITE (15, 2501) AREA
0221  250 FORMAT (TOTAL AREA UNDER CURVE = *E15.8)
0222  GO TO 1
0223  1000 CALL LSTPLT
0224  RETURN
0224  END
**FORTRAN IV G LEVEL 1, MOD 2**

<table>
<thead>
<tr>
<th>LINE</th>
<th>CODE</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>6001</td>
<td>SUBROUTINE ARZERO (A, M)</td>
<td></td>
</tr>
<tr>
<td>6003</td>
<td>DO IC J=1,M</td>
<td></td>
</tr>
<tr>
<td>6004</td>
<td>DO IC J=1,M</td>
<td></td>
</tr>
<tr>
<td>6005</td>
<td>IC M1, M= 0.0</td>
<td></td>
</tr>
<tr>
<td>6007</td>
<td>END</td>
<td></td>
</tr>
</tbody>
</table>
SUBROUTINE ARSUM (A, C, M, N)
REAL M, N, A(M, N)
DO 10 I = 1, M
    DO 10 J = 1, N
    A(I, J) = A(I, J) + C(I) * C(J)
10 CONTINUE
END
FORTRAN IV LEVEL 1, MOD 2

SUBROUTINE GNASH(A,N,M,KZ)

REAL A(N,N),W(1)

DIMENSION Y(1)

DATE = 68365 19/58/47

PAGE 0001

DO 10 I=1,N
10 A(I,I) = W(I)

DO 20 J=1,N
20 W(J) = Y(J)

IF (L4) 63,63,62

63 Y(1) = Y(J)

IF (L4) 907,907,907

907 IF (L4) 63,63,62

908 IF (L4) 63,63,62

909 A(I,J) = A(I,I)

910 A(I,J) = A(I,J) + A(I,J)

911 A(I,J) = A(I,J)

912 A(I,J) = A(I,J)

913 A(I,J) = A(I,J)

914 A(I,J) = A(I,J)

915 A(I,J) = A(I,J)

916 A(I,J) = A(I,J)

917 A(I,J) = A(I,J)

918 A(I,J) = A(I,J)

919 A(I,J) = A(I,J)

920 A(I,J) = A(I,J)

921 A(I,J) = A(I,J)

922 A(I,J) = A(I,J)

923 A(I,J) = A(I,J)

924 A(I,J) = A(I,J)

925 A(I,J) = A(I,J)

926 A(I,J) = A(I,J)

927 A(I,J) = A(I,J)

928 A(I,J) = A(I,J)

929 A(I,J) = A(I,J)

930 A(I,J) = A(I,J)

931 A(I,J) = A(I,J)

932 A(I,J) = A(I,J)

933 A(I,J) = A(I,J)

934 A(I,J) = A(I,J)

935 A(I,J) = A(I,J)

936 A(I,J) = A(I,J)

937 A(I,J) = A(I,J)

938 A(I,J) = A(I,J)

939 RETURN

END
SUBROUTINE ARANGE(X, Y, N)

I = 1
J = 1

IF(X(I), .LE., Y(J)) GO TO 10

T = X(I)
Y(I) = Y(J)
Y(J) = T

10 CONTINUE

RETURN
END
FORTAN IV LEVEL 1, MOD 2  OUTPUT  DATE = 68365  19/58/47  PAGE 0001

CC01  SUBROUTINE OUTPUT(X, Y, EY, RES, STD, OBS, NP)
      REAL X(NP), Y(NP), EY(NP), RES(NP), STD(NP)
CC03  INTEGER OBS(NP)
CC05  WRITE (3,300)
CC05  300 FORMAT(1X,'OBSERVED',12X,'ESTIMATED',12X,'RESIDUAL',9X)
CC06  WRITE (3,301)
CC07  301 FORMAT(1X,'VALUE OF X',10X,'VALUE OF Y',10X,'VALUE OF Y',10X,'VALUE OF Y',10X,'VALUE OF Y',10X)
CC08  C0 16 X=1,16
CC10  WRITE (3,302) X(J), Y(J), EY(J), RES(J), STD(J), OBS(J)
CC11  302 FORMAT(5F20.1,17)
CC12  RETURN
FOKTRAN IV 6 LEVEL 1, MTD 2

AVERG

DATE = 69365 19/58/47 PAGE 0001

C0211 SUPPORT FOR AVERG(AX,AY,K,X,Y,YL,STD,ORS,MP)
C0212
C0213 N
C0214 N1 = 0
C0215 NP = 4
C0216 N = X
C0217 5 IF(M2 .GT. K) GO TO 6
C0218 IF(X(N1) .LT. AX(N2)) GO TO 6
C0219 M2 = M2 + 1
C0220 GO TO 6
C0221 6 NP = NP + 1
C0222 Y(NP) = AX(N1)
C0223 OBS(NP) = N2 - N1
C0224 THE OBS(NP)
C0225 1 IF(OBS(NP) .GT. 11) GO TO 4
C0226 Y(NP) = AX(N1)
C0227 Y(NP) = AX(N1)
C0228 Y(NP) = AX(N1)
C0229 STD(NP) = 0.0
C0230 GO TO 10
C0231 4 NN = N2 - 1
C0232 SUM = C.0
C0233 DO 7 J = N1, NN
C0234 7 SUM = SUM + AX(J)
C0235 Y(NP) = SUM/NN
C0236 SUM = SUM
C0237 DO 7 J = N1, NN
C0238 SUM = SUM + ABS(Y(NP)) - ABS(Y(J)) ** 2
C0239 8 CONTINUE
C0240 STD(NP) = SQRT(SUM/NP + 1.0)
C0241 Y(NP) = Y(NP) + STD(NP)
C0242 Y(NP) = Y(NP) - STD(NP)
C0243 N1 = N1 + 1
C0244 N2 = N2 + 1
C0245 IF(N1 .EQ. K) GO TO 5
C0246 50 RETURN
C0247 END
FORTRAN IV G LEVEL 1, VRT 2          SMOOTH          DATE = 68365          19/58/47          PAGE 0001

0001       SUBROUTINE SMOOTH(Y,VEC,N,M)
0003                     (N=1,Y(1)),VEC[1]
0004                     
0005                     L=1,J=1
0006                     DO 2 J=1,N
0007                     10 VEC(J) = (-3.*Y(J-2) + 12.*Y(J-1) + 17.*Y(J) + 12.*Y(J+1) 
0008                       * -3.*Y(J+2)) / 35.
0009                     VEC(1) = Y(1) +(3.*Y(5)-5.*Y(4)-3.*Y(3)+9.*Y(2)-4.*Y(1))/35.
0010                     VEC(2) = Y(2) +5.*Y(5)+6.*Y(4)+12.*Y(3)-22.*Y(2)+9.*Y(1)/35.
0011                     VEC(N-1) = Y(N-1) + (5.*Y(N)-22.*Y(N-1)+12.*Y(N-2) 
0012                       * +6.*Y(N-3) - 5.*Y(N-4))/35.
0013                     VEC(N) = Y(N) + (-4.*Y(N) + 9.*Y(N-1) - 3.*Y(N-2) 
0014                       * -5.*Y(N-3) + 3.*Y(N-4))/35.
0015                     DO 2 J=1,N
0016                     20 Y(J) = VEC(J)
0017                     RETURN
0018                     END
FUNCTION FINDYE (X,Y,E,H,N)
D1= X(1), Y(1)
F= (X-E=1.7)
I= (X-E= X(1)+3, 2, 10)
Y(J)= Y(J)
RETURN
J=1
U = (X-E=Y(J))/H
F1 = HI*(E-1.1)/2.
F2 = (E-(E)-1.1)*(E-2.1)/6.
YE = Y(J)+ E1.*(Y(J+1)-Y(J)) + E2.*(Y(J+2)-2.*Y(J+1)+Y(J)) +
E3.*(Y(J+3)-3.*Y(J+2)+3.*Y(J+1)-Y(J))
RETURN
L = A-1
ON 2C K=2.1
IF YE = X(X1+4, 5, 70)
YE = Y(J)
FINDYE = YE
RETURN
J=1
U = (X-E=Y(J))/ 4
F1 = HI*(E-1.1)/6.
F2 = HI*(E-1.1)*HI*(E-2.1)/8.
YE = U*(X(J+1)+Y(J) + E1.*(Y(J+1)-2.*Y(J+1)+Y(J+2)) -
E2.*(Y(J+2)-2.*Y(J+1)+Y(J+1))
RETURN
RETURN
2C CONTINUE
IF YE = X(X1+3,7,30)
Y(J)= Y(J)
FINDYE = YE
RETURN
U = (X-E=Y(N))/ 4
F1 = HI*(E-1.1)/2.
F2 = HI*(E-1.1)*HI*(E-2.1)/8.
YE = Y(N)+ E1.*(Y(N)-Y(N-1)+Y(N-2)) +
E2.*(Y(N)-3.*Y(N-1)+3.*Y(N-2)-Y(N-3))
RETURN
RETURN
END
INTEGER HND, BLANK
CALL MOVEIT(1,2,4,11.0)
CALL ORIGIN(XR,YR)
CALL XSCALE(1,1,1.0)
CALL YSCALE(YR,1,1.0)
CALL VPUT(YP,YP,1,0.0)
RETURN
CALL MOVEIT(YP,YP,1,1.0)
DO 19 J=1,9
YP(1)=YP(J)
YP(2)=YP(J)
YP(3)=YP(J)
YP(4)=YP(J)
IF(YP(J).LT.0.5,1,3)
GO TO 19
X=0.5/XY
Y=7.0/XY
CALL XSIS(0X)
CALL XSCALE(0X)
CALL MOVEIT(1,2,0,11.0)
CALL ORIGIN(0.0,0.0)
CALL XSCALE(0.0,0.0)
CALL VPUT(0.0,0.0,0.0)
CALL VSCALE(0.0,0.0)
DO 23 J=1,9
XM=9.0/XY
YM=7.0/XY
CALL XSIS(MX)
CALL XSCALE(MX)
CALL MOVEIT(1,2,0,11.0)
CALL ORIGIN(MX,MY)
CALL XSCALE(MX,MY)
CALL VPUT(MX,MY,0.0)
CALL VSCALE(MX,MY)
DO 27 J=1,9
XM=9.0/XY
YM=7.0/XY
CALL XSIS(MX)
CALL XSCALE(MX)
CALL MOVEIT(1,2,0,11.0)
CALL ORIGIN(MX,MY)
CALL XSCALE(MX,MY)
CALL VPUT(MX,MY,0.0)
CALL VSCALE(MX,MY)
DO 31 J=1,9
XM=9.0/XY
YM=7.0/XY
CALL XSIS(MX)
CALL XSCALE(MX)
CALL MOVEIT(1,2,0,11.0)
CALL ORIGIN(MX,MY)
CALL XSCALE(MX,MY)
CALL VPUT(MX,MY,0.0)
CALL VSCALE(MX,MY)
DO 35 J=1,9
XM=9.0/XY
YM=7.0/XY
CALL XSIS(MX)
CALL XSCALE(MX)
CALL MOVEIT(1,2,0,11.0)
CALL ORIGIN(MX,MY)
CALL XSCALE(MX,MY)
CALL VPUT(MX,MY,0.0)
CALL VSCALE(MX,MY)
DO 58 IN = 1, NV
      IF (IN.LE.J) THEN
        C* = XSVNY(J,IN)
        CALL XXNY(IN,**,96,**,C*,0,0,NDY)
      END IF
      J = J + 1
      JY = JY + 1
      X = Y / J

END
VITA

George Juri Filatovs was born in Vilnius, Latvia, March 29, 1941. He received a Bachelor of Science degree in Mechanical Engineering from Washington University (St. Louis, Mo.) in June 1963. From June 1963 to January 1965 he was employed at McDonnell Aircraft Corporation, St. Louis, Mo. In January 1965 he enrolled in the University of Missouri at Rolla as a candidate for a Doctor of Philosophy degree with a major in Metallurgical Engineering. He was a Teaching Assistant during the year 1965-1966 and held a U.S. Bureau of Mines Fellowship from June 1966 to January 1969, under terms of which he performed his dissertation research at the U.S. Bureau of Mines Research Station, Rolla, Mo. Since January 1969 he has been an Assistant Professor in the Department of Metallurgical Engineering at Youngstown State University, Youngstown, Ohio.