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E. A. Ryan and J. J. Jackson

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Calorimeter for Simultaneous Measurements of Stored Energy and Resistance*

E. A. RYAN† AND J. J. JACKSON
Argonne National Laboratory, Argonne, Illinois 60439
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An adiabatic calorimeter using digital data acquisition and programmed heating for measurement of stored energy in the range 350–1000 K is described. In addition to combining the advantages inherent in digital acquisition systems with the advantages of an adiabatic calorimeter, samples were heated by Joule heating permitting (1) simultaneous measurement of stored energy and resistance and (2) calibration of the system including losses. This arrangement, when applied to measure the stored energy and resistance associated with defects introduced in samples by quenching, plastic deformation, or radiation damage, has sufficient sensitivity not only to measure the total stored energy but also to yield a spectrum of the energy release as a function of temperature. Calibration data indicated that energy release rates as small as 10 μW could be measured. Measured losses which were nearly independent of temperature totaled approximately 5.5 μW. Resistance measurements were reproducible to better than 10 parts in 10.[6]

INTRODUCTION

THE calorimeter described in this paper was designed specifically to investigate the recovery, in the range 350–1000 K, of stored energy introduced into metals by quenching, radiation damage, or plastic deformation. In the development of calorimeters for this purpose, consideration must be given to the relatively small, gradual, and irreversible energy release. If this energy release takes place at temperatures where radiation losses are important the problems of design are greatly increased.[1] Although others[2–6] have taken the above into account in designing calorimeters, to the authors' knowledge none of the systems described in the literature combines the sensitivity and flexibility required by these applications.

Of the few designs for use above room temperature the system used here follows most closely that of Clarebrough *et al.*[7] Nevertheless, significant differences exist between the calorimeter described here and theirs. Although the calorimeter is adiabatic and uses a differential power analysis to measure stored energy, samples are heated by a technique[8] usually used in pulse calorimetry. Basically, the sample is maintained at the same temperature as a continuously heated surrounding shield. The difference in power required to heat the sample for two consecutive runs is simply related to the stored energy. Since samples used here are typically much smaller than those used by Clarebrough, the absolute sensitivity of the calorimeter must be greater. In order to increase the sensitivity the following steps were taken. First, samples were heated by passing direct current through them. The resistive heating was used in an automatic control loop to maintain the sample at the temperature of the shield. This had a number of advantages: (1) Simultaneous measurement of power and resistance was possible, (2) heater mass was eliminated, and (3) heating inhomogeneities and losses were reduced. Secondly, the differential technique using two matched samples was not used in the present system. Instead the stored energy is calculated from the power spectra of two consecutive runs on the same sample. It was found essential to heat the adiabatic shield in a precisely controlled, reproducible manner and that the differential technique offered no further improvement in obtaining useful data. Finally, the sensitive differential wattmeter used in the work of Clarebrough *et al.*[9] was replaced by a digital data acquisition system. This system is similar to that used by Kollie[10] to obtain precise measurement of the specific heat of iron in a pulse calorimeter. As with the majority of differential power analysis systems accurate measurements of absolute temperature were not necessary. After the sample is mounted in the calorimeter unattended operation is possible.

The degree to which the system met the design objectives was investigated by a calibration technique which consisted of adding precisely known amounts of energy and comparing these to the measured quantities produced by the system. In addition, the calibration procedure permitted evaluation of losses present. Based on the calibration results and preliminary measurements of the stored energy in quenched platinum a usable calorimeter with sufficient sensitivity to detect small energy release rates such as those associated with vacancy recovery in metals

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.
† Based in part on a thesis submitted by this author to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science.
[1] F. E. Karasz, Contemp. Phys. **4**, 321 (1963).
[2] P. Gordon, Rev. Sci. Instrum. **25**, 1173 (1954).
[3] W. DeSorbo, Phys. Rev. **117**, 444 (1960).
[4] A. L. Titchener and M. B. Bever, Progr. Metal Phys. **7**, 247 (1958).
[5] J. L. White and K. Koyama, Rev. Sci. Instrum. **34**, 1104 (1963).
[6] R. A. Arndt and R. E. Fujita, Rev. Sci. Instrum. **34**, 868 (1963).
[7] L. M. Clarebrough, M. E. Hargreaves, D. Michell, and G. W. West, Proc. Roy. Soc. (London) **A215**, 507 (1952).
[8] T. E. Popchapsky, Rev. Sci. Instrum. **25**, 238 (1954).
[9] L. M. Clarebrough, M. E. Hargreaves, D. Michell, and G. W. West, J. Sci. Instrum. **30**, 282 (1953).
[10] T. G. Kollie, Rev. Sci. Instrum. **38**, 1452 (1967).

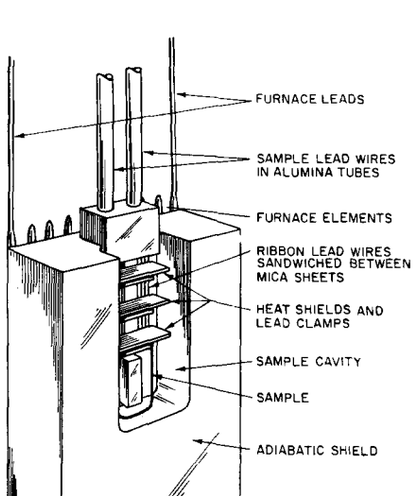

FIG. 1. Adiabatic shield and sample cavity.

has been developed. The apparatus will be used to study recovery of stored energy and Matthiessen's rule deviations. Although the system described here is particularly tailored to fit the requirements above, the basic techniques of measurement and sample heating are adaptable to other situations such as recovery of samples irradiated at low temperatures.

DESIGN AND CONSTRUCTION DETAILS

A. Adiabatic Shield

In order to reduce gaseous conduction losses to negligible values for both the sample and surrounding shields, the entire calorimeter and shields are placed within in a vacuum system. The pressure in this system measured during operation did not exceed 3×10^{-6} Torr. Radiation losses from the adiabatic shield are reduced by outer shielding consisting of five layers of aluminum foil. Electrical feedthroughs bring potential, current, and differential thermocouple leads into the calorimeter. Spot welded joints and thermocouple grade continuous wires were used to reduce thermal effects.

The adiabatic shield is made from two nearly identical sections bolted together to form the sample cavity. One of these sections is shown in Fig. 1. They are constructed of OFHC copper plate and measure $10.2\times20.4\times1.6$ cm with a sample cavity $3.5\times5.7\times0.8$ cm. Size was dictated by the samples used and by the need to reduce thermal gradients. Grooves cut into the outside surface accommodate the sheathed conductor heater elements[11] which were brazed to the shield with a gold slurry to insure good thermal contact. The entire system was gold plated to reduce metallic migration and corrosion. The electrical circuitry used to control the heating rate is shown in Fig. 2, and is similar to that suggested by various experimenters.[12,13] The output of a Chromel–Alumel thermocouple is matched to that of a motor driven set point.[14] The set point was modified in two ways: (1) The range control was changed to permit the heating rate to be varied and (2) the motor driven potentiometer used for programming the heating rate is of the continuously variable variety eliminating steps in the control which were apparent with conventional wire wound potentiometers.

The degree to which the temperature difference between the sample and shield remains reproducible for consecutive runs determines to a large extent the success or failure of the system. When the heating rate was not closely reproduced from one run to another the energy required to heat the sample varied enough to mask the stored energy release. This masking of the energy release was attributed to irreproducible changes in conduction losses resulting from changes in the heating rate. Using the shield and circuitry described above a typical set of runs yields heating rates reproducible to better than 5 parts in 10^4 with temperature control within 30×10^{-3}C° of the set point output throughout the usable range.

B. Sample Cavity

In the design of the sample cavity, reduction of thermal gradients and heat losses is again important. Radiation and conduction losses were reduced by keeping the temperature difference between the sample and adiabatic shield as small as possible and by careful thermal grounding of leads. Where possible lead wires with small cross sectional area and low thermal conductivity were used. Samples are spot welded to the lead wires. If the samples are of uniform cross section within the cavity, shape is not critical. Changes in cross section would lead to inhomogeneous heating.

In the region connecting the sample cavity to just outside the adiabatic shield the lead wires were rolled to a ribbon shape of uniform thickness and sandwiched between two layers of thin cleaved mica sheet. To insure good thermal grounding, small L-shaped gold plated

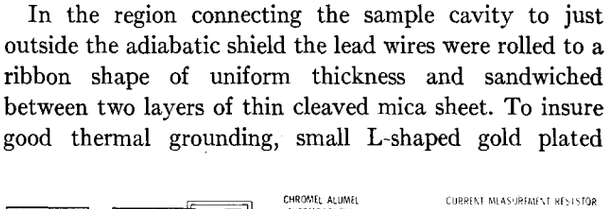

FIG. 2. Block schematic of electrical control circuits.

[11] Thermocouple Product Co., Villa Park, Ill.

[12] T. M. Gayle and W. T. Berg, Rev. Sci. Instrum. **37**, 1740 (1966).
[13] D. McSweeney, P. W. Levy, and P. D. Townsend, Rev. Sci. Instrum. **36**, 1324 (1965).
[14] Honeywell, Philadelphia, Pa., model 62-R-100-D.

brackets were used to clamp these leads to the adiabatic shield. Furthermore, these brackets were placed to reduce radiation losses from the sample cavity and to permit evacuation (see Fig. 1). The differential thermocouple connecting the adiabatic shield and sample is spot welded directly to the sample to eliminate gradients caused by any electrically insulating layers. Beryllia washers used to insure good thermal contact and electrical insulation at the reference junction in the adiabatic shield avoid the problem of electrical insulation at the sample. Wires 0.05 mm diam of Au+40% Pd vs Pt+10% Rh were chosen for the differential thermocouple because of their low thermal conductivity and large difference in thermoelectric power ($\sim 50\ \mu V/C^\circ$ @ 300°C).[15]

The electrical apparatus for sample heating shown in Fig. 2 is similar to that used for control of the adiabatic shield except that (1) the difference in output between the thermocouple and set point is replaced with the differential thermocouple output, and (2) the SCR used to heat the shield is replaced with a programmable dc power supply.[16] Of a number of deviation amplifiers tried for the differential thermocouple the choice of a Honeywell (model 687293) was based mainly on its isolated input–output configuration. Although this amplifier's sensitivity is not as high as some more sophisticated devices, sample control was within $10\times10^{-3}C^\circ$ throughout the complete run. Moreover, the control as recorded from the amplifier's output was quite reproducible from run to run and followed that of the shield.

MEASUREMENTS

If measurements of resistance are made simultaneously with measurements of stored energy a continuous relation between resistance recovery and energy recovery can be obtained. A resolution of approximately 10 parts in 10^6 is necessary to detect resistance changes due to annealing of defects because of the large contribution to resistance from phonon scattering at high temperatures. The calorimeter described here measures the stored energy by measuring the power required to heat the sample for a specific time interval. Since the power is calculated from measurements of the sample current and voltage, resistance follows immediately. The power and temperature measurements yield a relation which can be analyzed to give the energy release as a function of time and therefore the total stored energy. Because of the programmed heating, a simple reproducible relationship exists between temperature and time.

The concentration of defects introduced by quenching is typically appreciably smaller than those introduced by radiation damage or plastic deformation. For quenched samples the stored energy associated with these defects is of the order of 0.3 J/g.[17] One would like the sensitivity of the calorimeter to be sufficient not only to measure the total stored energy release but also to resolve the temperature dependence of this release.

A prepackaged data acquisition[18] system capable of rapid measurement of voltages with high accuracy and resolution was used. Its high resolution is ideally suited for measurements of resistance as stated above, while the rapid rate at which data are taken permits quasicontinuous measurements of the power applied to the sample. It has a resolution of 1 part in 10^6 at scanning rates of five channels/sec. Under normal operating conditions one measures all three sample parameters (voltage, current, and temperature) every 0.6 sec ($\sim 50\times10^{-3}$ C°). To permit precise measurement of the current a 0.1 Ω standard resistor was placed in series with the sample and the voltage drop across this measured. The energy supplied to the sample for a fixed time interval $t_f - t_i$ is given by

$$Q=\int_{t_i}^{t_f} E(t)I(t)dt=\sum_{j=1}^{M}\int_{t_i+(j-1)\Delta t}^{t_i+j\Delta t} E(t)I(t)dt, \qquad (1)$$

where $E(t)$ is the voltage across the sample and $I(t)$ is the current through the sample. This can be broken down into M intervals of duration Δt, providing t_f, t_i, and Δt are chosen such that $M=(t_f-t_i)/\Delta t$ where M is an integer. Ideally, $E(t)$ and $I(t)$ should be measured simultaneously and continuously as in the work of Karasz and O'Reilly[19] but this method is not readily adaptable to digital techniques and computer analysis. In the analysis presented here the stored energy is calculated by summing the average values for each interval. These calculations use computer techniques to handle the large amounts of data accumulated by the quasicontinuous monitoring of the power supplied to the sample.

Equation (1) can be replaced with

$$Q=\sum_{j=1}^{M}\bar{P}_j\Delta t, \quad \text{where} \quad \langle\bar{P}_j\rangle=\frac{1}{J}\sum_{i=1}^{J}E_iI_i \qquad (2)$$

and E_i and I_i are the digital sample voltage and current measured J times in the jth interval. $\langle\bar{P}_j\rangle$ is the average power supplied to the sample during the jth interval. Similarly the average resistance of the sample during the jth interval is calculated from

$$\langle\bar{R}_j\rangle=\frac{1}{J}\sum_{i=1}^{J}(E_i/I_i). \qquad (3)$$

Typically at heating rates of 5 C°/min, J is approximately

[15] E. D. West, Rev. Sci. Instrum. **31**, 896 (1960).
[16] Kepco, Inc. Flushing, New York, model ck-36-1.5M.
[17] J. J. Jackson, in *Lattice Defects in Quenched Metals*, R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii, Eds. (Academic Press Inc., New York, 1965), p. 479.
[18] Vidar Corp. Mountain View, Calif. series 5202.
[19] F. E. Karasz and J. M. O'Reilly, Rev. Sci. Instrum. **37**, 255 (1966).

100. Since the peak-to-peak variation in the readings of voltage and current does not exceed 5%, the error in replacing the integral with the product of elapsed time and the average value of the power is likely to be small. More rapid measurements were tried without any noticeable changes in the data, giving further support to the use of an average value. During a complete run nearly 8000 separate measurements of the sample parameters are made.

The program, which was written[20] to reject erroneous data points, divides the data into intervals and calculates the values of $\langle \bar{P}_j \rangle$ and $\langle \bar{R}_j \rangle$ by taking the appropriate averages resulted in approximately 0.3% loss in the number of measured parameters. The measurement of the time Δt to complete each interval is determined by counting the number of measurements made in that interval. Scanning rates of the data acquisition system were reproducible to better than 0.2%.

CALIBRATION

An electrical method to simulate stored energy release was devised to evaluate the performance of the calorimeter. Many experimenters[5,21] have used calibration procedures, a common form of which consists of determining the heat of fusion, or some other step type energy release. This form of calibration does not compare favorably with the gradual release encountered in the measurement of stored energy. The electrical method used here simulates this gradual release. Data acquisition and calculations similar to those used for stored energy yield precisely measured amounts of calibration energy. In Fig. 3 data are presented which compare the calibration power to the difference between the total power and control power. An external power supply was connected in parallel with the sample and existing control circuitry to supply the calibration power. Five channels of the data system were used to read sample voltage, control current, calibration current, total current, and temperature. Because of the time constants involved in the control circuitry, reading these three currents was not redundant. The total power for any interval was nearly constant whether the calibration circuit was connected, disconnected, or supplying energy indicating interactions between the two power supplies were not significant. Energy levels between 1×10^{-3} and 60×10^{-3} J were supplied by the calibration circuit during time intervals between 1 and 2 min. With any of the power levels used, deviations in temperature were very small and the normal control mode was always established within 10 sec after application of these powers. Furthermore, the deviations did not affect the results as tested

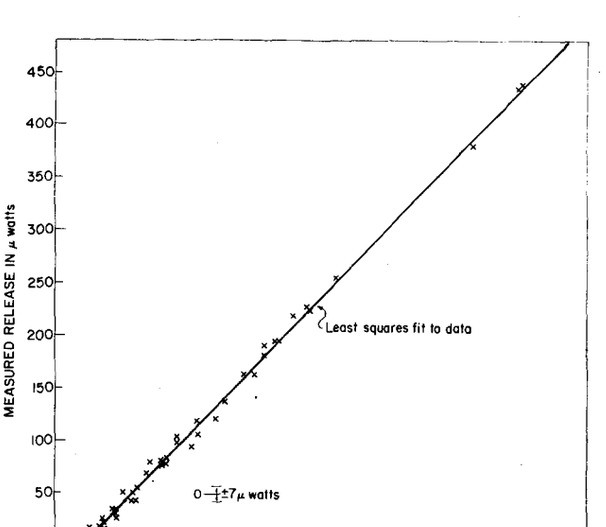

FIG. 3. Calibration data.

by one calibration run in which data were taken only after normal control was established. Although energy was still supplied in a step-like fashion, the time over which the power is applied is much larger than in systems using latent heats of melting and is to a large extent at the discretion of the experimenter. Preliminary data for platinum indicate release rates up to 450 μW might be encountered.[22] Measurements were taken throughout the range 350–800 K and power levels of 15–450 μW. The linear response of the calorimeter is obvious from the data presented in Fig. 3. In fact, the slope of the line fitted to the data by the method of least squares differs only 1% from that of the ideal system.

Since all the measured powers are less than the corresponding powers supplied by the calibration circuit, losses are present. Careful analysis of the data places these losses at 5–6 μW independent of power added or of the temperature at which the addition took place. After making this correction this system is capable of measuring power levels of approximately 10 μW.

DISCUSSION

Because of the use of the data system measurement errors are rather small and insignificant, ~0.02%. At present the largest measurement error is associated with the duration of the intervals used for determining the energy release spectra. This is approximately 0.2% and is the present limit in the precision of the measurement of specific heat of the samples.

Gaseous conduction losses can be estimated using the

[20] More details can be found in E. A. Ryan, M. S. thesis, Illinois Institute of Technology, 1969.

[21] R. W. Attree, R. L. Cushing, J. A. Ladd, and J. J. Pieroni, Rev. Sci. Instrum. **29**, 491 (1958).

[22] Data will be submitted for publication when a sufficient amount has been accrued to allow a meaningful interpretation of the results.

formula given by Swift.[23] This loss may be neglected since it is smaller by an order of magnitude than the measured losses. Conduction losses due to calorimeter leads for heaters have been studied previously.[24,25] Since the heat generated per unit length is constant for our sample wires, estimates of the actual gradients down these leads are difficult. Simple estimates place an upper limit of 2 μW on this loss. Other conduction losses resulting from the differential thermocouple and potential leads could account for an additional 10 μW loss. These losses result from the gradients developed in these wires due to the dynamic nature of the calorimeter and are dependent upon the heating rate. Since radiation losses increase by nearly an order of magnitude in the temperature range used here, there is a strong indication that most of the losses in this calorimeter are due to conduction. The measured losses of 5–6 μW independent of temperature are in rough agreement with the estimates of conduction losses given above.

[23] J. D. Swift, *Handbook of Vacuum Physics*, A. H. Beck, Ed. (Pergamon Press, Inc., New York, 1966), Vol. I, Pt. 5, p. 287.
[24] J. E. Neighbor, Rev. Sci. Instrum. **37**, 497 (1966).
[25] D. C. Ginnings and E. D. West, Rev. Sci. Instrum. **35**, 965 (1964).

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Writing Speed Determination of Sweeping Image Cameras Using a Photomultiplier Tube Calibrator

S. P. MARSH*
Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544
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A photomultiplier tube was used to detect light from an image sweeping over slits distributed across the image plane of the camera. The time interval between photomultiplier signals was measured using a Tektronix 545 oscilloscope. The resulting writing speed was determined with an error of less than 0.15% and showed a $\sec^2\theta$ variation over the image plane.

A Q-SWITCHED ruby laser in conjunction with a delay produced by the velocity of light has been used to determine the writing speed of a sweeping image camera.[1] Because of uncertainty in emission time of the laser, variation of writing speed across the image plane could not be determined.

A technique has been developed for measuring the writing speed of a sweeping image camera across the image plane. Because the length of the writing arm of our camera varies as an image moves across the film plane, the writing speed of the camera must be determined at many precise locations across the plate. Hence it is required that image transit times be accurately measured over small distances compared to the size of the photographic plate.

The device used for this calibration is shown in Fig. 1. The image of an object slit is swept over a multislit plate mounted within 0.3 mm of the image plane of the camera at the normal operating angular velocity of the rotating mirror. The widths of the slit image and the slits in the multislit plate were 0.1 mm. As the image passes each slit in the multislit plate, light is detected by the photomultiplier. Mirrors mounted in the calibrator housing increase the light seen by the detector. An aperture of 2.5 cm diameter is taped to the end of the tube so that the peripheral area of the cathode, which has the most signal delay, is excluded.

The output of the photomultiplier was fed to a Tektronix 545 oscilloscope. The slit image was accurately focused on the multislit plate by peaking the photomultiplier signal output when the object slit position was varied.

Uneven slit spaces were used to facilitate their identification on the oscilloscope. The 'scope sweep was triggered by the signal from the first slit. By means of the delayed sweep and horizontal sweep speed of the 'scope, each adjacent pair of slit signals was examined in turn. They were expanded horizontally to fill a large fraction of the 'scope face. This image was photographed and an oven-controlled Tektronix 184 time-mark generator signal of 50 MHz was photographed superimposed on it at the same sweep, thus allowing a measurement of the time interval between pairs of slit signals (see Fig. 2).

The distances between centers of the slits on the multislit plate were measured to an accuracy of 0.01 mm per-

* Work performed under the auspices of the Atomic Energy Commission.
[1] A. B. Christensen and W. M. Isbell, Rev. Sci. Instrum. **37**, 559 (1966).