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High-temperature specific heat by a pulse-heating method

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A pulse-heating method for measuring specific heat and electrical resistivity to high temperatures is described. This technique can be used for electrically conductive materials from room temperature to near 1300 K. As an example of this method, measurements of zirconium are presented.

INTRODUCTION

The measurement of specific heat at high temperatures is important in the understanding of the thermodynamic properties of materials. In particular, one can study phase stability and the energetics of phase transformations at these high temperatures. In many cases, a comparison can also be made of materials parameters measured at low temperatures and their values measured at high temperatures (e.g., γ and θ_D).

Several of the usual problems that arise in the measurement of properties at high temperatures can be circumvented by using transient pulse heating.^{1,2} In this technique, the problem of the sample reacting with imperfect vacuum is greatly reduced because the sample only stays at elevated temperatures for a short time. The correction for radiation losses is also greatly reduced because of the short duration of the experiment. Another advantage of the pulse-heating technique is that it can be used to study metastable materials for which the cooling rate of the sample is sufficient to retain the metastable phase. Lastly, the pulse-heating method, by its very nature, is well suited for studying the effects of heating rates on phase transformations.

We describe here a pulse-heating method for measuring specific heat and electrical resistivity of metallic samples at high temperatures. This method differs from that of Ref. 1 because we use thermocouples rather than optical pyrometry to measure the sample temperature. This allows us to measure from room temperature, but limits our highest temperatures of measurement. The method described in Ref. 2 resembles ours, but has somewhat slower heating rates that allow (and require) a measurement of the sample's emissivity, but require longer samples. Thus, our technique extends the method's applicability to brittle intermetallic compounds where long samples are difficult to make.

1. SPECIMEN PREPARATION

The specimens to be measured by this technique must be electrically conductive and formed into the shape of a long thin rod or wire. The specimen may be produced in this shape by a variety of methods including drawing, swaging, and vacuum casting.³ We have used all of these methods

with satisfactory results. In principle, specimens may also be formed by spark cutting from a large piece of the material to be studied. Since the specimen is resistively self-heated, it is important that it have uniform cross section along its length as well as being macroscopically homogeneous and free of voids.

The length of specimen necessary is determined by several parameters. The temperature profile for a resistively self-heated wire (clamped at both ends) is initially flat topped, but eventually becomes parabolic in the steady state.¹ Therefore, the important criterion that must be satisfied is that the thermal gradient end effects must not propagate into the center region of the sample, between the voltage leads, during the current pulse. To estimate this propagation time for a particular material, the temperature profile is calculated as a function of time by numerically solving the one-dimensional heat equation.⁴ Measured, estimated, or literature values of the electrical resistivity, thermal conductivity, and specific heat at room temperature are used as input parameters for this calculation. An example of a temperature profile for UAl_2 is shown in Fig. 1. It is clear from this model

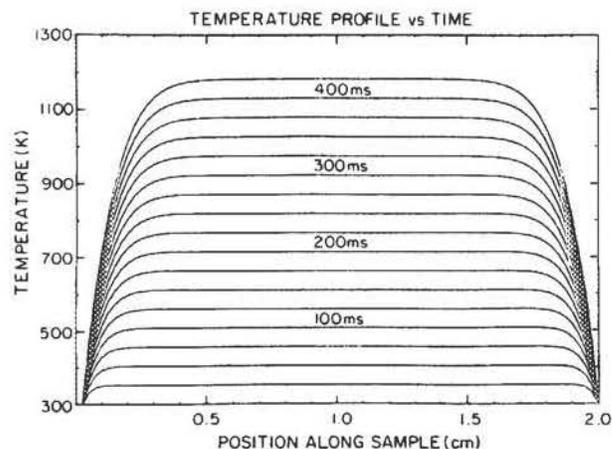


FIG. 1. Numerical simulation of the temperature profile vs time for UAl_2 . The parameters used during this calculation were: current through sample = 200 A, diameter = 0.202 cm, length = 2 cm, resistivity = 120 $\mu\Omega$ cm, specific heat = 3 R (Dulong-Petit law), thermal conductivity = 0.1 $W\ cm^{-1}\ K^{-1}$, and emissivity = 0.3.

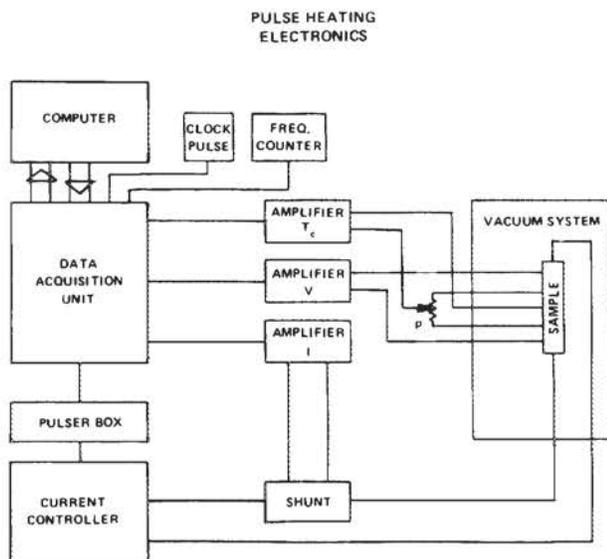


FIG. 2. Block diagram of the pulse-heating electronics. The outside thermocouple wires are of the same type with the center wire being its complement.

that for voltage leads with a separation less than 0.8 cm, and a pulse length less than 400 ms, thermal gradient end effects do not affect the measurement.

II. APPARATUS DESIGN

The specimen holder is built with two high-current leads, two voltage leads, and three thermocouple leads. The specimen is mounted into the sample holder by clamping it between the two current leads. The clamps holding the specimen are either copper or molybdenum strips held together with 0–80 (1.5-mm o.d.) stainless-steel screws. Because the measurements are done in a high vacuum (100 μ Pa), all of the components of the sample holder must be high vacuum compatible. The voltage leads are 50.8- μ m (2 mil) wire chosen of a material to minimize reaction with the sample at high temperatures. The thermocouples used were either 12.7 μ m (0.5 mil) Chromel–Alumel or Chromel–Constantan. Since the response time of a thermocouple is proportional to its cross-sectional area, it is important to have the thermocouple wires as small as possible. Because it is not possible to attach two thermocouple leads in exactly the same position along the sample, a three-wire technique is used. In this technique, the voltage drop due to current flowing in the specimen can be adjusted to zero with an external potentiometer (p in Fig. 2).

The electronics used in this measurement are shown schematically in Fig. 2. The current flowing through the sample is controlled by the pulser which is triggered by a TTL edge from the data-acquisition unit. This current pulse is variable from 0–1 s and 0–300 A. The amount of current flowing during a pulse is held constant by a current controller which has six 50-A current drivers in parallel. The power source for the large current is a standard automotive-type 12-V battery.

The data-acquisition system we used was fabricated at UCSD, but commercial systems are now available that are adequate for this application. The minimum requirements

for the data-acquisition unit are: 12-bit resolution, three simultaneous input channels, 5000 readings/s in each channel, variable data-acquisition rate, computer interfaceable, and capable of taking 1000 datapoints/channel in each pulse.

Each channel going into our data-acquisition unit goes through an amplifier to bring all of the signals to the same level. These amplifiers must have truly differential input with a high common mode rejection ratio and be fast enough to not change the signal shape (dc to 30-kHz frequency response is adequate).⁵ The computer used for the data acquisition and analysis was a HP9825 desktop computer and the data were taken in real time in direct memory access mode. The data-acquisition rate was established with an external frequency generator and measured with a frequency counter accurate to 1 Hz.

III. MEASUREMENT PROCEDURE

For the measurement the sample is mounted in the sample holder and the voltage and thermocouple leads are attached by spot welding. The thermocouple wires, e.g., two Chromel and one Alumel, are connected to the sample making sure that the Alumel wire is between the two Chromel wires and that all three wires are as close together as possible. The sample holder is then placed into a high-vacuum chamber and pumped to $\sim 100 \mu$ Pa.

The potentiometer for the thermocouple, p in Fig. 2, is coarsely adjusted by passing a small ac current through the sample and adjusting the potentiometer to give a null or minimum ac signal on the output of the amplifier that reads the thermocouple. Fine adjustments are made during preliminary pulses by minimizing the offset that occurs when the current pulse stops.

The sample is then “pulsed up” to temperature by sending pulses of successively larger energy through the sample. The temperature that a given sample can be “pulsed up” to is usually determined by the temperature at which the leads react with the sample or the sample melts (or breaks). During each pulse, voltage, current, and temperature are monitored as a function of time and this data set is recorded. In the “pulse up” process, the gains of the amplifiers are adjusted to keep the signal levels between 33% and 100% of full scale. Successive pulses are not started until the sample has returned to room temperature.

IV. DATA REDUCTION AND RESULTS

The measured quantities $T(t)$, $V(t)$, and $I(t)$ are then related to the specific heat (per formula weight) of a sample of circular cross section by

$$C_p = M \frac{IV - 2\pi r l \epsilon \sigma (T^4 - T_a^4)}{l\rho(dT/dt)}, \quad (1)$$

where r is the radius of the sample, l is the distance between the voltage leads, ϵ is the emissivity of the sample, σ is the Stefan–Boltzmann constant, T_a is room temperature during the measurement, M is the formula weight of the sample, and ρ is the mass per unit length of the sample. The second term in Eq. (1) is a radiation correction, where a value for ϵ is usually estimated.⁶ To reduce the relative size of the radi-

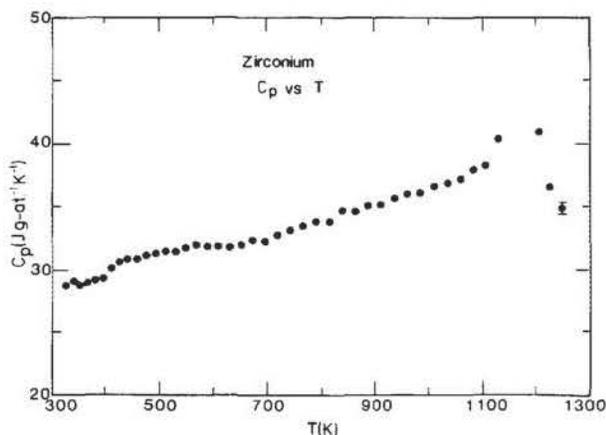


FIG. 3. Specific heat of Zr measured by a pulse-heating technique. These data were averaged over 18 datapoints. The error bar represents a $\pm 1\%$ error.

ation correction, we keep the pulse length short and the volume-to-surface ratio of the specimen large. For pulse lengths of 0.5 s this term usually amounts to a 2% correction at 1300 K and, therefore, it is of little importance to know ϵ well. The assumption is made here that the temperature of the surface of the sample (as measured by the thermocouple) is the same as at the center of the sample. Since the radiation correction is small and the power is uniformly dissipated throughout the sample, we feel that this assumption is reasonable.

The derivative in Eq. (1) was taken numerically by a ratio of differences method and is thus the major source of random error in the C_p calculations. To reduce the noise introduced by taking this derivative, we have averaged the data over 5–20 points. An example of the specific heat of Zr measured by this method is shown in Fig. 3. The peak in these data at ~ 1130 K is the $\alpha \rightarrow \beta$ phase transformation. We see the scatter in the data using this averaging is $\pm 1\%$.

In a similar manner, the enthalpy can be calculated from the data. The enthalpy is given by

$$H(T) = \frac{M}{l\rho} \int [IV - 2\pi r l \epsilon \sigma (T^4 - T_a^4)] dt, \quad (2)$$

where we choose $H(T_a) = 0$. The enthalpy is most useful in

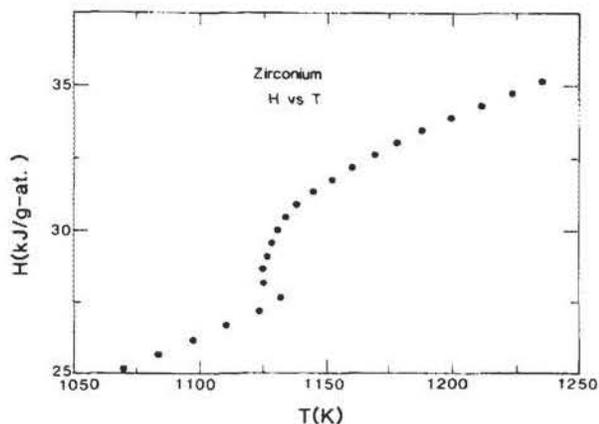


FIG. 4. Enthalpy of Zr near the $\alpha \rightarrow \beta$ transformation. These data were averaged over six datapoints. We believe that the overshoot at the beginning of the transformation is due to a slight superheating of the transformation.

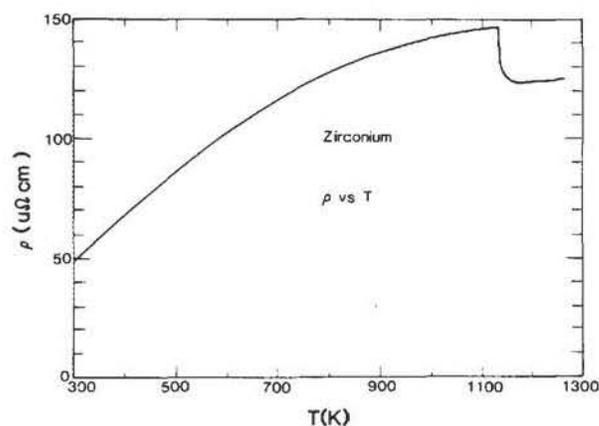


FIG. 5. Electrical resistivity of Zr vs temperature.

extracting the latent heat of a transformation. Shown in Fig. 4 is the enthalpy of Zr near the $\alpha \rightarrow \beta$ transformation. An extrapolation to the midpoint of the transformation gives $L_{\alpha \rightarrow \beta} = 4.0$ kJ/g-at. and $T = 1125$ K for Zr in good agreement with the accepted values of 3.9 and 1136.⁷ Since the enthalpy does not contain the derivative of the temperature, it does not have the noise problems of the specific heat. The integral in Eq. (2) was approximated as a sum with step size equal to the time between data points.

The high-temperature resistivity is given by

$$\rho = \frac{\pi r^2 V}{II}. \quad (3)$$

In this case the resistivity is a ratio of two raw data channels normalized by the proper geometrical factor. Shown in Fig. 5 is the resistivity of Zr. The drop in the resistivity at high temperature is caused by the $\alpha \rightarrow \beta$ transformation.

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⁶Schematic diagrams of the pulser, current controller, and amplifier circuits are given in M. S. Wire, Ph.D. thesis, University of California, San Diego, 1984; Los Alamos Report No. LA-10199-T, 1985.

⁷For most metals ϵ can vary from 0.1 to almost 1 depending on the surface conditions. A typical value of 0.3 is usually used for our smooth, clean but not polished surfaces. See, for example, *Handbook of Chemistry and Physics*, 55th ed., edited by Robert C. Weast (Chemical Rubber, Cleveland, 1974), p. E-228.

⁸See, for example, C. B. Alcock, K. T. Jacob, and S. Zador, in *Zirconium: Physico-Chemical Properties of its Compounds and Alloys*, edited by O. Kubaschewski (International Atomic Energy Agency, Vienna, 1976), pp. 8–10.