A Method of Automatic Measurement of Specific Heat*

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Synopsis

An automatic recording apparatus for measuring specific heat of alloys and compounds was constructed. The specific heat could be computed from the recorded chart of the electric current of the feedback circuits for controlling the energy supply together with its rate of temperature rises of the samples under test. This apparatus has been used effectively for thermal analysis of various kinds of ferromagnetic compounds and binary supperlattice alloys.

I. Introduction

Numerous methods of measuring the specific heats of alloys or compounds together with their temperature dependence have hitherto been reported. According to the measuring principles these methods may be classified into two types, the adiabatic and the conduction methods(1). The method of Sykes(2) belongs to the former type and that of Smith(3) the latter. These methods have been employed adequately according to the character of the temperature dependence of the specific heat as well as the other thermal properties of the substance to be investigated. For the measurement of specific heat, it is claimed in general that temperature uniformity in the specimen must be highly guaranteed. For this reason the heating rate of the substance cannot be made too fast, and hence the thermal analysis, in general, requires a long time.

In the present paper, a new automatic method of recording the temperature dependence of the specific heat is described and some examples of recorded charts are shown. By using this apparatus, the lengthy and tedious labour for the thermal analysis for metallurgical purposes can be saved without losing the high accuracy of measurement.

II. Principle of the measurement

The apparatus for measuring the specific heat described below belongs to a kind of the adiabatic type proposed by Sykes. In this method the specimen material is packed into a container of a heating element, which is kept in a

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(1) See for example Handb. d. exp. Phys., Bd. 8 1-TEIL, 110.
(2) C. Sykes, Proc. Roy. Soc. A **148** (1935), p. 422.
(3) A. W. Smith, A. I. M. E. **137** (1936), p. 236.

radiationless condition. The impressed energy in the heating element during an unit temperature rise gives the specific heat of the specimen. The block diagram of the apparatus is shown in Fig. 1. The container E is inserted in a hollow

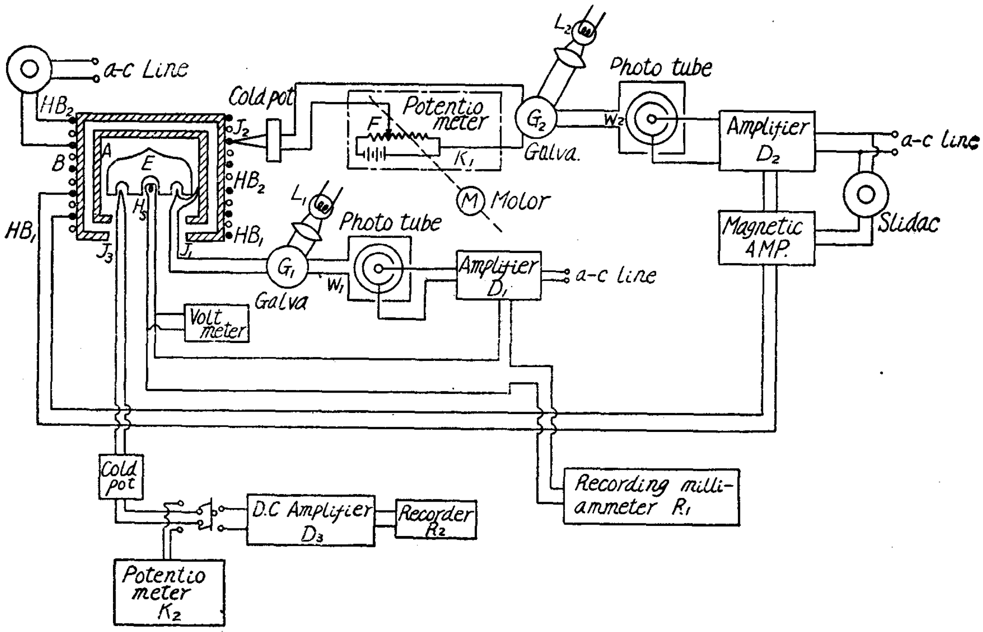

Fig. 1. Block diagram of the whole apparatus.

cylinder A, the temperature of which is raised at constant rate. The electric current in the heating element H_s is automatically regulated by a feedback control system in such a way as to remove temperature difference between the specimen and the cylinder A. This current in H_s is recorded by a recording milliammeter R_1. The specific heat of the specimen can be computed from the recorded chart of the heater current. The specific heat C_p is proportional to the square of the current and inversely proportional to the rate of temperature rise of the specimen. That is, C_p is given by

$$C_p = \frac{RI^2 \Delta t}{4.18 m \Delta T}$$

where, R, I is the mean electrical resistance and current strength of the H_s during a time interval Δt respectively. ΔT is temperature rising during Δt. m is the mass of the sample.

The feedback control system works as follows. A differential thermo-junction J_1 between the specimen and inner wall of the cylinder A is connected to a galvanometer G_1. If the temperature of the specimen is higher or lower than that of A, then the galvanometer mirror deflects from its zero. A light beam L_1 of constant intensity is reflected by the galvanometer mirror and projected onto a window W_1 of a photoelectric-tube P_1, which is connected to an amplifier D_1. Thus the intensity of thermo-electromotive force of the differential thermojunction is converted into electric current. The output current of D_1 is inversely fed back to the heater H_s inserted in a hole of the specimen E. Consequently, the current in H_s decreases or increases according as the temperature of the specimen become slightly higher or lower than that of the cylinder A.

The method of heating the cylinder A at constant rate is due to another feedback control system. A cylinder B which encloses the cylinder A is heated at constant rate by heating coils HB_1 and HB_2. The temperature of A is raised by thermal radiation from the cylinder B. The reference signal, an emf increasing linearly with the lapse of time, is produced by rotating resistance drum F of a potentiometer K_1 which is connected in series with a galvanometer G_2 and thermojunction J_2 attached on the wall of the cylinder B. Thus the mirror of galvanometer G_2 is deflected by the error signal, the difference between the electromotive force of the junction J_2 and that of the emf terminals of the potentiometer K_1. Then the current of the heater HB_1 of the cylinder B is controlled in a similar manner as described above and hence the temperature of B is raised at constant rate. As the required input power of the heater HB_1 wound on the cylinder B is too great to be supplied directly from the output of the amplifier D_2, a magnetic amplifier M_A is used to feed the heater HB_1.

The temperature of the specimen is measured occasionally by using a potentiometer K_2 and for this purpose another thermo-junction J_3 is set in a hole of the specimen E. For the same purpose, emf of the junction J_3 is converted into a-c voltage and amplified by a feedback stabilized amplifier D_3, whose output current is recorded simultaneously with heater current of the specimen.

III. Details of the apparatus

a) Calorimeter: The detailed parts of the calorimeter used are shown Fig. 2. There are specimen holder D, specimen heater H_s, cylinder A, ordinary and differential thermo-junctions J_2, J_3 and J_1. These parts are surrounded by a brass cylinder C covered with a thermal insulator. This cylinder serves as a shield case to prevent thermal radiation loss. The total system of this calorimeter is enclosed by an evacuated bell-jar Q. The specimen* used in our case was in the form of powder of about 200 mesh. Such a specimen is packed in a telex glass capsule which has three holes; one of these holes contains the heater H_s and the other two small holes serve as containers of the ordinary and differential thermo-junction J_3

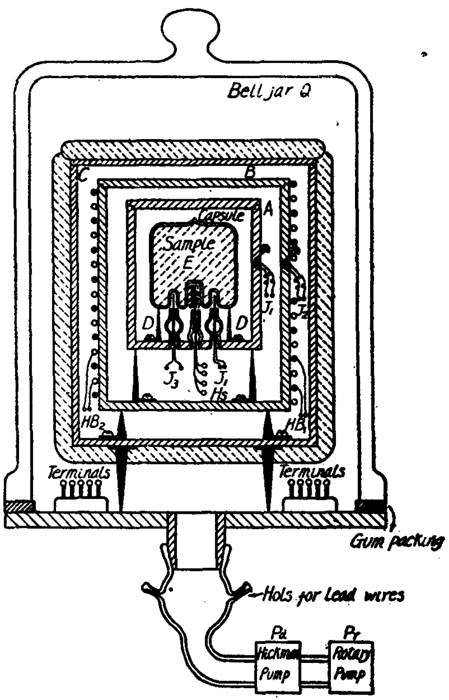

Fig. 2. Schematic view of the calorimeter.

* The specimen to be investigated in our laboratory are such as FeS, FeSe, etc. so that they must enclosed in vacuum container to prevent the variation of contents of the specimen at comparatively higher temperature.

and J_1, respectively. The sample holders D are made of steel needles of 1 mm diameter at the base with sharp points. The capsule E has dimension of 2.5 cm in diameter and 3 cm high and contains about 3 cc of the sample.

The heater H_s for the specimen is made of 0.14 mm diameter constantan wire formed into a double spiral with diameters 1.2 mm and 8 mm respectively and its resistance is about 60 Ohms. This heater is supported by the lead wires which are fixed on the bottom plate of the cylinder A through silica pipes of 2 mm in diameter. The heater H_s is then inserted in a heater hole of the capsule E. The thermo-junction J_3 for the measurement of the temperature of the specimen is made of 0.06 mm diameter copper and 0.14 mm constantan wires. Both ends of this junction make a pair of cold terminals outside the evacuated bell-jar Q. The cylinder A is made of copper having dimensions of 4 cm in diameter, 7 cm in length and 0.3 cm in thickness. The differential thermo-junction J_1 is made of the same wires as mentioned before and the intermediate part is made of constantan. The copper leads of this junction are connected to enameled copper wires of 0.2 mm diameter in the bell-jar for the purpose of decreasing the circuit resistance.

b) Temperature controlling apparatus for the specimen: As can be seen Fig. 3 the differential thermo-junction between the specimen and the cylinder A is connected to the galvanometer G_1 (volt sensibility; 2×10^{-8} volt/mm) and G_3 in parallel and the light beam from the source L_1 is reflected by the mirror of the galvanometer G_1 and then projected on the photo-tube P_1 as stated above. The

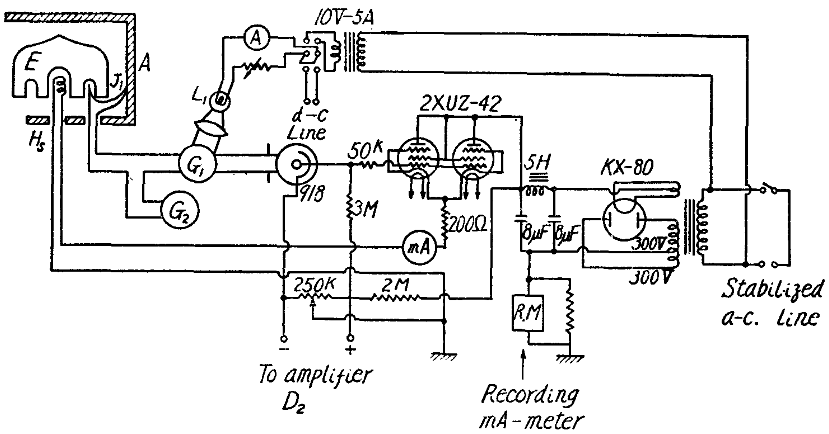

Fig. 3. Temperature controlling device for the sample.

galvanometer G_3 serves as a monitor of the said temperature difference. The light source L_1 is a talkie exciter lamp connected to a battery or a stabilized a-c line. The light beam from L_1 is collected on the mirror of the galvanometer G_1 by a convex lens of 8 cm diameter and 15 cm focal length, and then projected on the photo-tube window W_1 of 3 cm diameter. The optical path is about 50 cm. If the temperature difference exists between specimen and cylinder A, the image of light source L_1 moves in or out of photo-tube window. A stopper was necessary for the mirror of galvanometer G_1 to prevent the light image from escaping outside of the photo-tube window. By this arrangement the current of the heater H_s is adjusted so that specimen and cylinder A lay in same temperature. The type 918 photo-tube and two type 42 power tubes in parallel connection are used. The maximum and minimum plate currents corresponding to the minimum and maximum incident light beam on the photo tube are about 10 and 90 ma respectively. The maximum current of the photo amplifier is limited by the series resistance of 50,000 ohms in the grid circuit of two 42-type tubes which act as cathode-follower amplifier, so that the fluctuation of the plate voltage makes only a small effect on the plate current, i.e. the current of the heater H_s. The a-c 100 volts power source is regulated by a stabilizer. Slow change in the voltage of the a-c source does not give serious effects on the recorded chart because of the nature of the feedback control system. However, when remarkable voltage change of a-c line occurs suddenly, a damped osillation is observed on the recorded chart; but this oscillation died out very quickly and its period is decided by the time constant of the heat conduction from the heater to the differntial junction J_1 through the specimen itself. Therefore no special voltage stabilizer is used when voltage fluctuation of the a-c line is comparatively slow and small. The current of H_s was recorded by a recording milli-ammeter of 10 ma full range with suitable shunt resistance. This recording milli-ammeter had an oil damper in order to record the mean current alone without small fluctuations of the plate current due to the automatic balancing.

Fig. 4 shows a circuit of the apparatus of heating the cylinder A at constant rate. A function of this apparatus was described in previous section and is similar to that of controlling apparatus of H_s, then detailed description on it is omitted here. The rate of temperature rising must be chosen a suitable value according to the heat capacity and the thermal conductivity of the sample, and it was performed by changing the rotating speed of the resistance drum F or

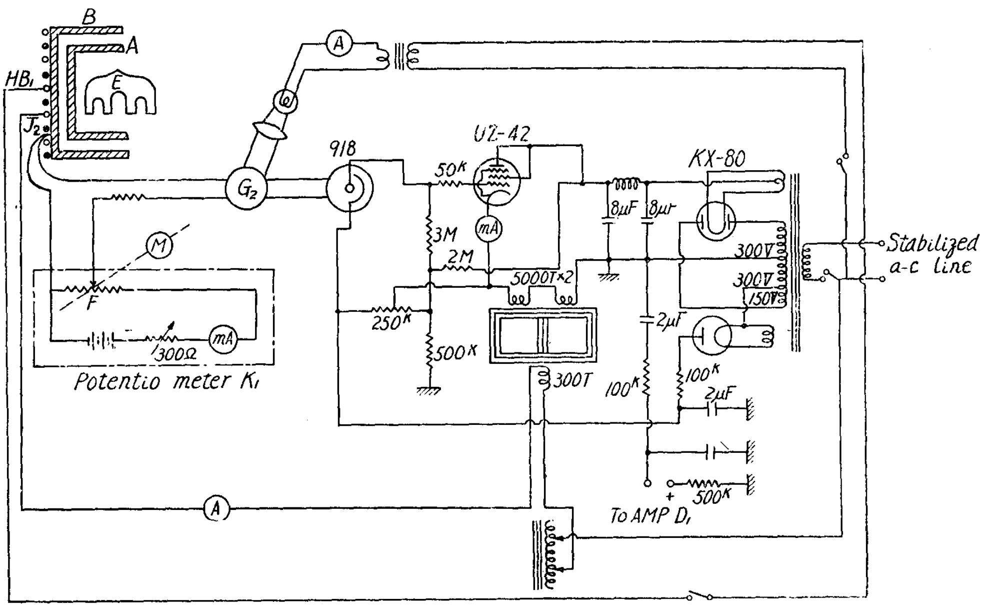

Fig. 4. Device of heating the cylinder A at constant rate.

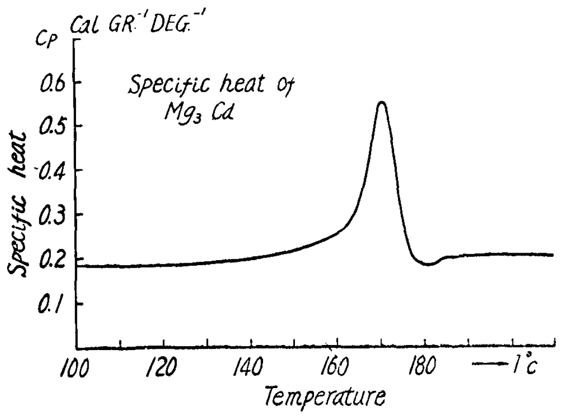

Fig. 5. Specific heat vs. temperature curve of Mg_3Cd obtained from the recorded chart.

the current strength which flows the potentiometer K_1.

IV. Examples and discussions

For the purpose of a confirmation of the functions of whole apparatus the specific heat of a binary alloy of Mg_3Cd in a temperature range of order-disorder transformation was measured and the curve of specific heat vs. temperature is shown in Fig. 5. This result agrees quite well with that of Nagasaki's[4] measurement by another method. For an example of the typical recorded chart for the specimen of semi-conductor a case of FeS is shown in Fig. 6. As mentioned above, the damped oscillation in the heater current was observed when the input voltage changes suddenly. As an example of such a case, a recorded chart of measurement on the α-transformation of FeS is shown in Fig. 7. Part A and B in the figure shows respectively a damped oscillation in the current due to an accidental change of several volts in a-c line voltage. Part C in the same figure shows a case when the line voltage fluctuates

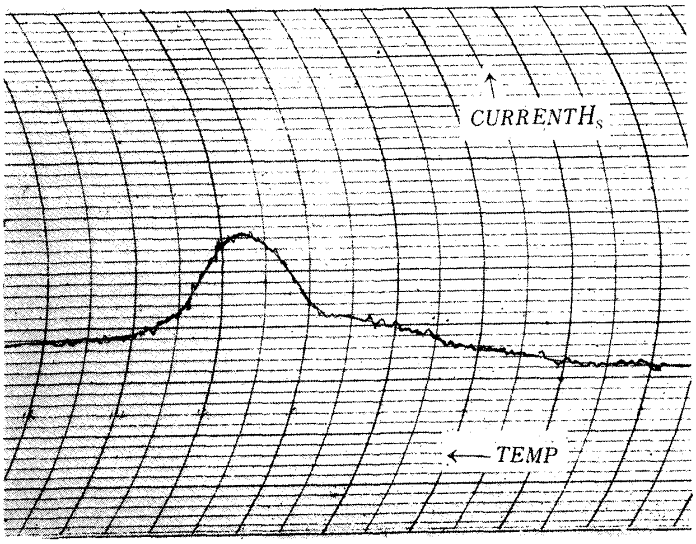

Fig. 6. Typical recorded chart of the semi-conductor ($FeS_{1.03}$)

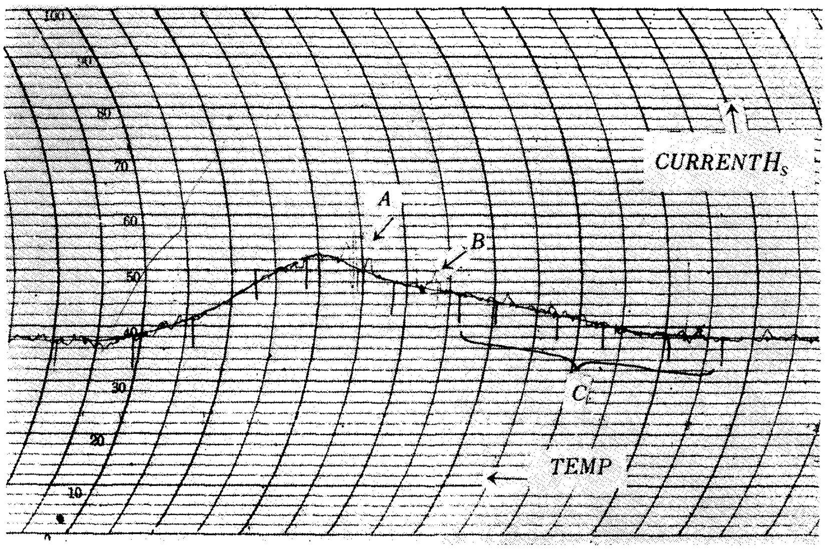

Fig. 7. Recorded chart of measurement of FeS in the case of voltage fluctuations were happen.

(4) S. Nagasaki, N. Hirabayashi and H. Nagasu, Nippon Kinzoku-Gakkai-Shi; **13** (1949), No. 6, p. 1.

continuously. In this case, the specimen was enclosed in an evacuated telex glass capsule E, hence several minutes were required for the thermal equilibrium due to the slow heat conduction from the heater H_s to the differential junction through the glass wall of capsule and the specimen itself. Therefore, the effect of the voltage change in a-c line could not be compensated instantly.

When the temperature controlling of the sample or vacuum in calorimeter was not guaranteed sufficiently, the correction for heat absorption or emission by the sample due to the thermal radiation or conduction is not negligibly small. In the present case this correction was performed approximately from the data of the change of equilibrium current in H_s, at same rate of temperature rising as the case of measurement, caused by definite value of temperature difference between the sample and cylinder A.

The maximum temperature deviation of the specimen from the cylinder A in the course of the measurement was several thousandths of a degree at a range corresponding to the flat part in the curve of specific heat vs. temperature and was less than 0.01°C for the steep part at the curve of specific heat. In the case of examples in Fig. 6, the amount of the anomalous absorption of heat was about 300 cal/mol and the maximum temperature deviation was of the order of 0.01°C at the range which corresponds to the maximum specific heat. In some cases of the large anomalous specific heat, the curve of the heater current became osillatory, if the heating rate was too fast. This tendency was more accentuated when the curve of the specific heat had sharp maximum because the maximum current of heater H_s was limited to 90 ma by the output tube of the present apparatus. Therefore, accurate measurement by the present apparatus cannot be done for the case of latent heat, such as the case of the transition of the first kind; whereas in the case of small anomalous specific heat, this method can be used with sufficient accuracy.

Some general precautions, for adiabatic methods of specific heat measurement, must be also suggested for this method. (1) Intimate contact must be kept between the specimen and the heater or junction in order to avoid the thermal retardation among them. Under such a condition the thermal loss due to radiation between the specimen and the cylinder A can be minimized by increasing the sensitivity of the controlling system without causing oscillations; although the correction of the radiation loss can be computed from the recorded chart. (2) For the sake of avoiding the fluctuation of the specimen temperature, the heat capacity of the cylinder B should be made possibly small. On the whole, by decreasing the thermal inertia the fluctuation in the heating rate diminishes by high sensitivity of the circuit. Lastly it was observed that the velocity fluctuation of the driving motor due to the frequency fluctuation of the a-c line was very small in the usual case.