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Measurements of accurate specific heats of metallic glasses by differential scanning calorimetry (DSC).
Part 1. Analysis of theoretical principles and accuracies of suggested measurement procedures

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Abstract

Two techniques for DSC specific heat measurements have been tested. They are, (1) the continual heating two run technique by means of a Perkin-Elmer DSC7 device and the scanning (differential) method, and (2) the programmed stepwise heating two-run technique by means of a Setaram DSC111 device and the integral (enthalpic) method. The correctness of the theoretical principles and the accuracies of obtained experimental data on metallic ribbons from 300 to 1054 K are analyzed. The measurements on $Fe_{73}Co_{12}B_{15}$ and $Co_{67}Cr_7Fe_4Si_8B_{14}$ metallic glasses are given as an example. The sensitivity is better than 0.05 J g^{-1} at^{-1} K^{-1}, the maximal dispersion of data is $\pm 1.2\%$. The main sources of irreproducibilities in measured $c_p(T)$ dependencies are the internal thermodynamic properties of the samples.

INTRODUCTION

The DSC technique is now widely used to investigate real solids. Using DSC one is capable of determining the specific heat capacity (specific heat) of a sample c_p directly from a single run presuming a knowledge of the heat capacity of the reference substance and a calibration of the symmetry by an all-empty-pans DSC run.

A substantial amount of c_p data has been generated since the commercialization of DSC by the Perkin-Elmer Company.

Several measuring methods have been developed and experimental specific heats for medium temperatures of real solid samples have been measured. Thus, for example, Vucelić et al. [1] have measured zeolite and Mraw [2] has measured pyrite samples by the use of three-run scanning (differential) method as well as of the enthalpic (integral) method. By either method the accuracies of their c_p measurements were from 1% to 2%. The simplified two run methods are being used as standard procedure

[3,4] and accuracies from 1% to 5% in the temperature region 300–700 K are reported. Heat conduction according to Newton's law and negligible temperature gradients within samples are always assumed.

The present study is devoted to the correct specific heat measurements of metallic glasses. Two techniques for DSC specific heat measurements are tested: the continual heating two run technique using a Perkin-Elmer DSC7 device and the scanning method or the programmed stepwise heating two-run technique using a Setaram DSC111 device and the integral method. Data accuracies obtained are comparable to those of traditional calorimetry.

PRINCIPLES OF SPECIFIC HEAT MEASUREMENTS BY DSC TECHNIQUE

It is well known that there are two kinds of differential scanning calorimeters: power-compensated differential scanning calorimeters (Perkin-Elmer DSC) and heat-flux differential scanning calorimeters or a quantitative differential thermal analyzer (e.g. Setaram DSC, Du Pont DSC, Netzsch DSC).

The technique of power-compensated DSC is as follows. There are two holders which are simultaneously two separate heaters in a DSC device, the measured sample X holder and a reference sample R holder. Both of them sit in an isolated compartment. The instrument measures the difference in electrical power $\Delta J_{(\mathrm{X}-\mathrm{R})} = J_\mathrm{X} - J_\mathrm{R}$, required to keep the two holders at the same temperature $T_\mathrm{X} = T_\mathrm{R}$.

In the case of the heat-flux instrument there is one metal block serving as a heater and simultaneously as a holder common for both fixed samples X and R. The differential scanning calorimeter measures the differences in heat flux transferred between the samples and their surroundings which are proportional to their actual temperatures (T_X, T_R, T_E) and to thermal contact resistances between heater-holder and a sample (R_X, R_R)

$$\Delta T_{(\mathrm{X}-\mathrm{R})}/R = T_\mathrm{X}/R_\mathrm{X} - T_\mathrm{R}/R_\mathrm{R}$$

The Perkin-Elmer instrument uses Al sample pans coverable with a lid to separate samples from holders and to ensure reproducible thermally equivalent positions, for example, of thermal contacts and heat losses between the samples and their surroundings $R_\mathrm{X}(T) \approx R_\mathrm{R}(T) \approx R(T)$. The Setaram instrument uses $\mathrm{Al_2O_3}$ pans with lids.

The holders are heated or cooled at a specific rate $w = \mathrm{d}T_\mathrm{E}/\mathrm{d}t$ driven by the differential scanning calorimeter programmer to be constant.

Assuming a simple model, the fundamental differential or integral calorimetric equations are written as

$$\frac{\mathrm{d}H_i(t)}{\mathrm{d}t} + C_{pi}\frac{\mathrm{d}T_\mathrm{E}}{\mathrm{d}t} = \frac{1}{K_i(t)}\left[Y_i + \tau_i\frac{\mathrm{d}Y_i}{\mathrm{d}t}\right] - J_i' \tag{1}$$

$$\int_{t_1}^{t_2}\frac{\mathrm{d}H_i(t)}{\mathrm{d}t}\mathrm{d}t+\frac{\mathrm{d}T_\mathrm{E}}{\mathrm{d}t}\int_{t_1}^{t_2}C_{pi}\,\mathrm{d}t=\int_{t_1}^{t_2}\frac{Y_i}{K_i(t)}\mathrm{d}t+\int_{t_1}^{t_2}\frac{\tau_i}{K_i(t)}\frac{\mathrm{d}Y_i}{\mathrm{d}t}\mathrm{d}t-\int_{t_1}^{t_2}J_i'\,\mathrm{d}t \tag{2}$$

where i refers respectively to the measured sample $i=\mathrm{X}$ and the reference sample $i=\mathrm{R}$, $\mathrm{d}H_i/\mathrm{d}t$ is the heat generation rate due to the eventual heat generation inside X, C_{pi} is the heat capacity of the sample pan together with the sample placed inside it, $(C_{p\mathrm{PX}}+C_{p\mathrm{X}})$ or $(C_{p\mathrm{PR}}+C_{p\mathrm{R}})$; $1/K_i\approx 1/R_i$ and Y_i are the sensitivity and signal registered by one of the two sensors of the differential scanning calorimeter detecting heads, respectively, τ_i is the time constant of a pan (with a sample) and J_i' is the heat flux to the surroundings (i.e. loss of heat not absorbed by the pan).

Two programs can be used to calculate c_p of the measured sample from the DSC thermograms. The primary one is called the scanning (differential or continual mode) method and it is based on differential eqn. (1). The second one is called the integral (enthalpic or stepwise) method and is based on integral eqn. (2).

In the case of power-compensated DSC experiments

$$\frac{\mathrm{d}H_\mathrm{X}(t)}{\mathrm{d}t}+\left(C_{p\mathrm{PX}}+C_{p\mathrm{X}}-C_{p\mathrm{PR}}-C_{p\mathrm{R}}\right)\frac{\mathrm{d}T_\mathrm{E}}{\mathrm{d}t}$$
$$=\Delta J_{(\mathrm{X}-\mathrm{R})}+\tau\frac{\mathrm{d}\left[\Delta J_{(\mathrm{X}-R)}\right]}{\mathrm{d}t}-\Delta J'_{(\mathrm{X}-\mathrm{R})} \tag{3}$$

$$\int_{T_1}^{T_2}\mathrm{d}H_\mathrm{X}(T)+\int_{T_1}^{T_2}\left(C_{p\mathrm{PX}}+C_{p\mathrm{X}}-C_{p\mathrm{PR}}-C_{p\mathrm{R}}\right)\mathrm{d}T$$
$$=\frac{1}{w}\int_{T_1}^{T_2}\Delta J_{(\mathrm{X}-\mathrm{R})}\,\mathrm{d}T+\tau\int_1^2\mathrm{d}\left[\Delta J_{(\mathrm{X}-\mathrm{R})}\right]-\frac{1}{w}\int_{T_1}^{T_2}\Delta J'_{(\mathrm{X}-\mathrm{R})}\,\mathrm{d}T \tag{4}$$

where $T_1=T_\mathrm{E}(t_1)$ and $T_2=T_\mathrm{E}(t_2)$.

In the case of heat-flux DSC experiments

$$\frac{\mathrm{d}H_\mathrm{X}(t)}{\mathrm{d}t}+\left(C_{p\mathrm{PX}}+C_{p\mathrm{X}}-C_{p\mathrm{PR}}-C_{p\mathrm{R}}\right)\frac{\mathrm{d}T}{\mathrm{d}t}$$
$$=\frac{\Delta T_{(\mathrm{X}-\mathrm{R})}}{K(t)}+\frac{\tau}{K(t)}\frac{\mathrm{d}\left[\Delta T_{(\mathrm{X}-\mathrm{R})}\right]}{\mathrm{d}t}-\Delta J'_{(\mathrm{X}-\mathrm{R})} \tag{5}$$

$$\int_{T_1}^{T_2}\mathrm{d}H_\mathrm{X}(T)+\int_{T_1}^{T_2}\left(C_{p\mathrm{PX}}+C_{p\mathrm{X}}-C_{p\mathrm{PR}}-C_{p\mathrm{R}}\right)\mathrm{d}T$$
$$=\frac{1}{w}\int_{T_1}^{T_2}\frac{\Delta T_{(\mathrm{X}-\mathrm{R})}\,\mathrm{d}T}{K(T)}+\tau\int_1^2\mathrm{d}\left[\frac{\Delta T_{(\mathrm{X}-\mathrm{R})}}{K(T)}\right]-\frac{1}{w}\int_{T1}^{T_2}\Delta J'_{(\mathrm{X}-\mathrm{R})}\,\mathrm{d}T \tag{6}$$

In order to obtain the specific heat $c_{p\mathrm{M}}(T)$ of an unknown sample M two measuring cycles, one with the unknown sample $\mathrm{X}=\mathrm{M}$, and the second one with a standard sample $X = S$ having a known $c_{pS}(T)$ against always the same reference R are needed.

The instrument is not an adiabatic calorimeter, but the term $\Delta J'_{(X-R)}$ is controlled to become rather small due to the thermally equivalent positions of the pans. If (in the case of a non-reactive and non-encapsulated type of experiment) always the same measured sample and reference sample pans and lids as well as the setting of samples and pans, sample masses and the measuring parameters (w, T_1, T_2, etc) are used, then $C_{pPM} = C_{pPS}$ and $C_{pR} = \text{const.}$, ($\tau_X = \tau_R = \tau$ and $K_X(t) = K_R(t) = K(t)$) and the term $\Delta J'_{(X-R)}$ is almost the same for all measurements. Then the correction due to the heat losses is possible by subtraction (because it appears as a shift of the baseline which is the DSC signal).

If the power-compensated DSC and the scanning method are used, the two thermograms $\Delta J_{(M-R)}(T)$ and $\Delta J_{(S-R)}(T)$ are measured and subtracted, then the specific heat $c_{pM}(T)$ calculated at any operator-selected temperature T is

$$c_{pM}(T) = \frac{\Delta J_{(M-R)}(T) - \Delta J_{(S-R)}(T)}{w m_M} + \frac{\tau}{w m_M}\left\{\frac{\mathrm{d}[\Delta J_{(M-R)}(\mathrm{d}T)]}{\mathrm{d}t} - \frac{\mathrm{d}[\Delta J_{(S-R)}(T)]}{\mathrm{d}t}\right\} + \frac{m_S}{m_M} c_{pS}(T) \tag{7}$$

assuming $\mathrm{d}H_M(T)/\mathrm{d}t = 0$, m_M and m_S being the masses of M and S.

If M and S are metals, as in our case, then their $c_p(T)$ slopes at elevated temperatures are approximately equal and the second term on the right side of eqn. (7) can be neglected. Thus the simplified eqn. (7) is the basis of the standard specific heat software for the 7 Series thermal analysis system of Perkin-Elmer.

If the heat-flux DSC and the integral method are used, the two thermograms $\Delta T_{(M-R)}$ and $\Delta T_{(S-R)}$ are measured; then after numerical integration through any operator-selected temperature (or time) interval T_1–T_2 (or t_1–t_2) (which is small enough for the mean value approximation for specific heats $\overline{c_{pi}(T_1, T_2)}$ and sensitivity coefficient $\overline{K(T_1, T_2)}$) the mean specific heat for temperatures from T_1 to T_2 is

$$\overline{c_{pM}(T_1, T_2)} = \left\{\frac{1}{w}\left[\int_{T_1}^{T_2}\Delta T_{(M-R)}\,\mathrm{d}T - \int_{T_1}^{T_2}\Delta T_{(S-R)}\,\mathrm{d}T\right] + \tau\left\{\int_1^2 \mathrm{d}[\Delta T_{(M-R)}] - \int_1^2 \mathrm{d}[\Delta T_{(S-R)}]\right\}\right\} \times \left\{m_M \cdot (T_2 - T_1) \cdot \overline{K(T_1, T_2)}\right\}^{-1} + \frac{m_S}{m_M}\overline{c_{pS}(T_1, T_2)} \tag{8}$$

assuming that

$$\int_{T_1}^{T_2} \mathrm{d}H_{\mathrm{M}}(T) = 0.$$

The instrument sensitivity coefficient $K(T)$ can be calibrated by either the Joule effect electrical method [5] which is based on measurement of thermal response of the known standard sample to the known value of heat $\int_{T_1}^{T_2} \mathrm{d}H_{\mathrm{X}}$ generated in the sample electrically or by the above described two measuring cycles experiment on some known M and standard S samples. Then

$$\overline{K(T_1, T_2)} = \left\{ \frac{1}{w} \left[\int_{T_1}^{T_2} \Delta T_{(\mathrm{M-R})} \mathrm{d}T - \int_{T_1}^{T_2} \Delta T_{(\mathrm{S-R})} \mathrm{d}T \right] \right.$$
$$\left. + \tau \left\{ \int_1^2 \mathrm{d}\left[\Delta T_{(\mathrm{M-R})}\right] - \int_1^2 \mathrm{d}\left[\Delta T_{(\mathrm{S-R})}\right] \right\} \right\}$$
$$\times \left\{ (T_2 - T_1) \cdot \left[w_{\mathrm{M}} \overline{c_{p\mathrm{M}}(T_1, T_2)} - m_{\mathrm{S}} \overline{c_{p\mathrm{S}}(T_1, T_2)} \right] \right\}^{-1} \tag{9}$$

The architecture of an automatic measuring and data acquisition program based on correct eqns. (8) and (9) is described, for example, in ref. 5 and ±1% reproducibility of $c_p(T)$ is reported.

Often a simplified and approximate case is solved. Instead of the reference sample R the blank B, e.g. the empty reference pan, is measured ($C_{p\mathrm{R}} = 0$); minor differential terms $\mathrm{d}[\Delta Y_i]$ are neglected and the calorimetric eqns. (3) or (4) corresponding to X = M and X = S are divided. Then the specific heat is

$$c_{p\mathrm{M}}(T) = \frac{\Delta Y_{(\mathrm{M-R})}(T)}{\Delta Y_{(\mathrm{S-R})}(T)} \cdot \frac{m_{\mathrm{S}}}{m_{\mathrm{M}}} \cdot c_{p\mathrm{S}}(T) \tag{10}$$

$$\overline{c_{p\mathrm{M}}(T_1, T_2)} = \frac{\int_{T_1}^{T_2} \Delta Y_{(\mathrm{M-R})}(T) \mathrm{d}T}{\Delta Y_{(\mathrm{S-R})}(T) \mathrm{d}T} \cdot \frac{m_{\mathrm{S}}}{m_{\mathrm{M}}} \cdot \overline{c_{p\mathrm{S}}(T_1, T_2)} \tag{11}$$

Measuring procedures based on simplified eqns. (10) or (11) were commercialized in the standard specific heat software, for example, for the Perkin-Elmer DSC1 and were used by, for example Vucelić et al. [1] and Wunderlich [6] or Neumann [7], respectively, and the accuracies 1–3% for various solids were reported.

SAMPLES

Three types of samples were used, namely a massive synthetic sapphire as a calibration normal for determination of sensitivity $K(T)$ of the Setaram DSC apparatus, a massive pure crystalline cobalt as a normal for the absolute $c_p(T)$ recalibration for the Perkin-Elmer DSC apparatus and the $Fe_{73}Co_{12}B_{15}$ (35 μm × 10 mm × several meters) and $Co_{67}Cr_7Fe_4Si_8B_{14}$ (25 μm × 30 mm × several meters) glassy ribbons investigated which were prepared by the melt spinning technique with a cooling rate of about 10^6 K s^{-1}. They were stored in air at room temperature for about 2 years.

To prepare the glassy samples for the Perkin-Elmer measurements the ribbons were cut into small pieces of about 2 mm × 2 mm. The Al pan was filled with about 50 mg mass and closed by the Al lid. To prepare the samples for the Setaram measurements the glassy ribbons were cut into pieces of about 3 mm × 8 mm and they were packed into an Al_2O_3 pan to a mass of 360 mg.

EXPERIMENTAL APPARATUSES AND MEASURING REGIMES

The specific heat $c_p(T)$ of massive sapphire and cobalt and metallic glassy ribbons at temperatures from 300 to 1054 K was measured on the heat-flux Setaram DSC111 with a Comodore Data Station and the integral method based on precise eqns. (8) and (9) and at temperatures from 305 to 470 K on the power-compensated Perkin-Elmer DSC7 with the PE 3700 Data Station and the scanning method based on eqn. (7) with neglected right side second term.

Samples were prepared and placed by the reproducible manner always into the same sample pans ($C_{pPM} = C_{pPS}$). The reference pans were always empty ($C_{pR} = 0$).

All first measured cycles on unknown samples M were related to the one common measured cycle on an equivalent but empty sample S pan, e.g. $Y_S(T)$ = blank, and $C_{pS}(T) = 0$.

In the case of Setaram DSC programmed discontinuous (stepwise) heating, measuring and data acquisition procedure [5] was used. The linear heating periods with the heating rate of $w = 5$ K min^{-1} for 200 s were followed by isothermal stabilization periods for 400 s, when a quasistatic thermodynamically steady state of measured assembly can be reached. During this period the thermal response of the sample was measured, the program specified the signals T_1, T_2, $\Delta T_{(M-R)}(T_1)$, $\Delta T_{(M-R)}(T_2)$, derived $d[\Delta T_{(M-R)}(T_1)]$ and $d[\Delta T_{(M-R)}(T_2)]$ for the measured sample M, took out from its memory the equivalent data for the standard sample S, numerically integrated corresponding measured curves (eqn. (8)) and calculated the mean specific heat $\overline{c_p}$. The resulting quasilinear heating rate was $\overline{w} \doteq 1.6$ K min^{-1}, the temperature interval for the integration of measured data was $T_2 - T_1 \doteq 16$ K.

In the case of Perkin-Elmer DSC the continual heating regime with the heating rate of $w = 5$ K min^{-1} was used. Before and after these scans the 2 min and 5 min isotherms at the starting T_{start} and final T_{final} temperatures, respectively, were measured to reach the equilibrium baselines. The PE

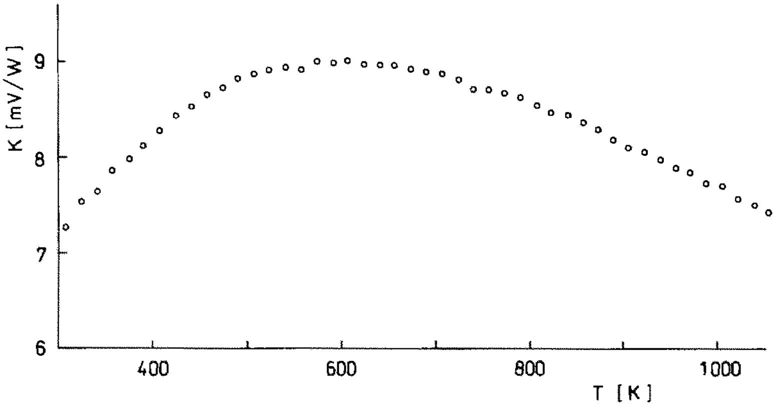

Fig. 1. Temperature dependence of the sensitivity coefficient of the Setaram DSC111 instrument.

DSC7 specific heat software (No. N 519-0708, PETAN-9) program then made a linear interpolation of those isotherms to determine the hypothetical baselines. All DSC measured values $\Delta J_{(i-\mathrm{R})}$ were normalized by subtracting them from their appropriate interpolated baseline values and the specific heat c_p at each point during the run was calculated (eqn. (7)).

The instruments were calibrated in their continuous heating regimes ($w = 5$ K min^{-1}) to the temperatures and heats of melting of indium, zinc, lead, tin and eventually aluminium. The standardization factor of the Setaram DSC, e.g., its sensitivity coefficient $K(T)$, was calibrated by the procedure described by eqn. (9). We have used the commonly proposed synthetic sapphire as a calorimetric standard for specific heat measurements. The measured $c_{p(\mathrm{Setaram,Al_2O_3})}(T)$ data were related to the known tabulated $c_{p(\mathrm{tab,Al_2O_3})}(T)$ data [8]. Within the temperature region of these experiments (300–1054 K) the derived $K(T)$ dependence (Fig. 1) was fitted by a polynomial to be

$$K(T) = 6.5753 - 9.8992 \times 10^{-3}T + 6.7013 \times 10^{-5}T^2 - 9.7607 \times 10^{-8}T^3 + 4.1520 \times 10^{-11}T^4 \quad (12)$$

with a maximal error $\chi_{\max} = -2.0\%$.

After the measuring cycle, measuring heads with samples were reproducibly cooled to the load temperature. The cooling rate in Setaram experiments was $5 < |w| < 15$ K min^{-1} and in Perkin-Elmer experiments $w = -200$ K min^{-1}.

All measurements were done in an inert atmosphere.

RESULTS

Specific heat of pure cobalt

In order to measure the specific heats of metallic glassy ribbons more correctly, it was necessary to first solve two problems. The first one was to

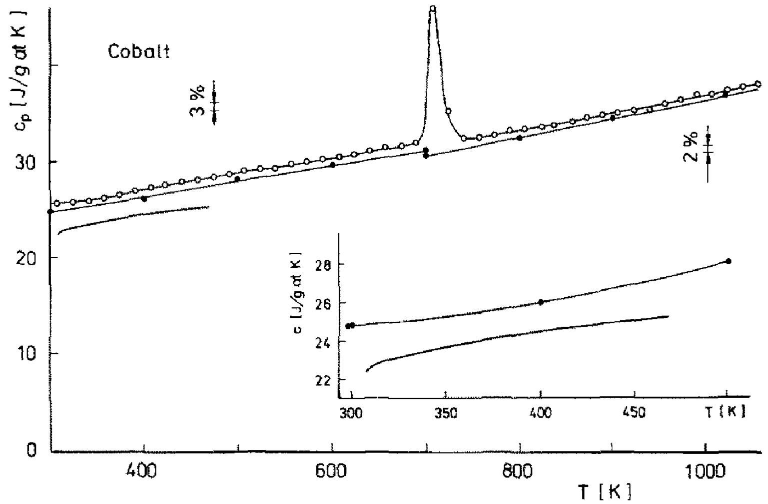

Fig. 2. Temperature dependence of specific heat of pure cobalt ○, measured by Setaram DSC111 and integral method ($\bar{w} = 1.6$ K min^{-1}); ———, measured by Perkin-Elmer DSC7 and scanning method ($w = 5$ K min^{-1}); and ●, tabulated data [8]. In detail the enlarged $c_{p(\text{Perkin-Elmer,cobalt})}(T)$ and $c_{p(\text{tab,cobalt})}(T)$ are ——— and ●.

recalibrate the instruments for measurement on metals in order to keep up our assumption of equivalency of heat transfer conditions of measured and calibration samples (C_{pi}, $\mathrm{d}[\Delta Y_{i-\mathrm{R}}]/\mathrm{d}T$, $K_i(T)$, τ_i). The other was the problem of the format of samples being cut from a thin deformable ribbon and thus having problematic thermal contacts with pans.

We have measured at first the specific heat $c_p(T)$ of an equilibrium pure cobalt. The Setaram differential scanning calorimeter and the integral method as well as the Perkin-Elmer differential scanning calorimeter and the scanning method were used. The measured data of $c_p(T)$ were related to the tabulated values [8] and they are shown in Fig. 2. It can be seen that the experimental Perkin-Elmer DSC $c_p(T)$ data deviate systematically from the tabulated values by about -7%. Assuming that this was due to the incorrect calibration of the instrument to the enthalpies of melting of temperature calibration normals instead of to their specific heats, all the following measured Perkin-Elmer specific heats will be corrected according to the recalibration factor

$$F(T) = c_{p(\text{tab.,cobalt})}(T) - c_{p(\text{PE,cobalt})}(T) \tag{13}$$

The problem of the form of samples was not solved because we have not found the appropriate stable normalization material.

Specific heat of $Fe_{73}Co_{12}B_{15}$ metallic glass

$Fe_{73}Co_{12}B_{15}$ metallic glassy ribbons were investigated in three limiting states: (1) the so-called as-quenched glassy state, e.g. initial non-equi-

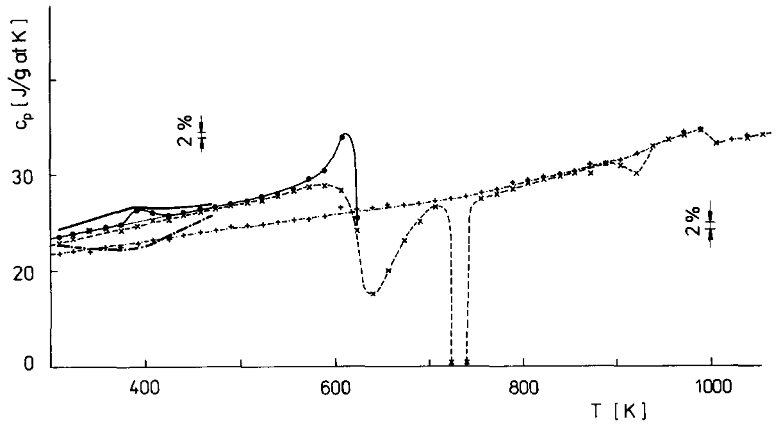

Fig. 3. Temperature dependence of specific heat of $Fe_{73}Co_{12}B_{15}$ metallic glass: ●, as-quenched; ×, relaxed; +, crystalline measured by Setaram DSC111 and integral method ($\bar{w} = 1.6$ K min^{-1}). ———, as quenched; ·—·—·, crystalline measured by Perkin-Elmer DSC7 and scanning method ($w = 5$ K min^{-1}).

librium state of a glassy material prepared by rapid quenching from its melt without any other thermal treatment (excluding the ageing at room temperatures), (2) the so-called relaxed glassy state, e.g. the quasi-equilibrium state of a glassy material not changeable (in real time) by any other heat treatment, (3) the crystalline state, e.g. the equilibrium state of the material after the multistep crystallization and recrystallization of the complicated heterogeneous glassy metallic alloy. To do this three successive heating runs under the equivalent measuring conditions were necessary.

Specific heat $c_p(T)$ was measured by Setaram DSC111 and integral method at temperatures from 300 K to 1054 K and by the Perkin-Elmer

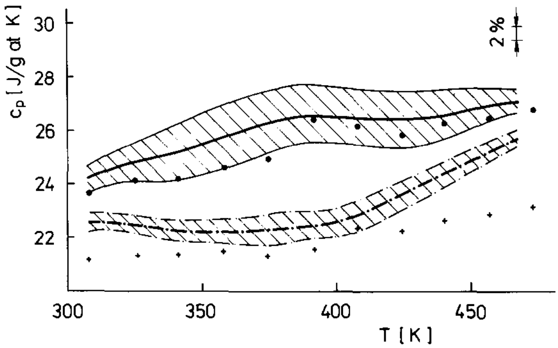

Fig. 4. Comparison between the corrected mean values of Perkin-Elmer DSC7 specific heat of $Fe_{73}Co_{12}B_{15}$ metallic glass and the relevant data measured by Setaram DSC111. ———, as-quenched and ·—·—·, crystalline measured by Perkin-Elmer differential scanning calorimeter ($w = 5$ K min^{-1}); ●, as-quenched and +, crystalline measured by Setaram instrument ($\bar{w} = 1.6$ K min^{-1}). The scattering of Perkin-Elmer data is shaded.

TABLE 1

Statistical errors of measured specific heats of metallic ribbons using the Setaram DSC111 instrument by the integral method and the Perkin-Elmer DSC7 instrument by the scanning method

	Setaram DSC111		Perkin-Elmer DSC7	
	300 K	1054 K	300 K	468 K
Inaccuracy in T (K)	±1.	±1.	±0.5	±0.5
Inaccuracy in $c_{p(\mathrm{Co})}$ (J g^{-1} at^{-1} K^{-1})	±0.7	±0.5	−1.9	−2.2
Sensitivity of T (K)	±8.	±8.	±0.01	±0.01
Sensitivity of $c_{p(\mathrm{FeCoB})}$ (J g^{-1} at^{-1} K^{-1})	±0.01	±0.01	±0.05	±0.05
Max. noise of $c_{p(\mathrm{Co})}$ (J g^{-1} at^{-1} K^{-1})	±0.2	±0.4	±0.05	±0.05
Max. dispersion of $c_{p(\mathrm{FeCoB})}$ (J g^{-1} at^{-1} K^{-1})	±0.2	±0.4	±0.24	±0.24
Reproducibility of $c_{p(\mathrm{Co})}$ (J g^{-1} at^{-1} K^{-1})			±0.08	±0.04
Reprod. of $c_{p(\mathrm{FeCoB,as\text{-}q})}$ (J g^{-1} at^{-1} K^{-1})	±0.6		±0.48	±0.61
Reprod. of $c_{p(\mathrm{FeCoB,cryst.})}$ (J g^{-1} at^{-1} K^{-1})	±0.4	±0.4	±0.38	±0.41
Reprod. of $c_{p(\mathrm{CoCrFeSiB,cryst.})}$ (J g^{-1} at^{-1} K^{-1})			±0.05	±0.02

DSC7 and scanning method from 305 K to 470 K. An example of both measured sets of $c_p(T)$ dependencies is seen in Fig. 3. Figure 4 shows the relation between the corrected mean values of $c_p(T)$ of glassy and crystalline $\mathrm{Fe}_{73}\mathrm{Co}_{12}\mathrm{B}_{15}$ samples measured by both techniques. The absolute values correlate well within experimental error. Some differences in the slopes of the $c_{p(\mathrm{Perkin\text{-}Elmer})}(T)$ dependencies probably represent systematic errors due to the cut ribbon form of samples.

DISCUSSION

Estimation of errors

To discuss critically the measuring methods and the specific heats of measured ribbons the determined imprecision of the individual points (standard deviation from the mean value curve) and the possible systematic errors should be analyzed. These are summarized in Table 1.

The inaccuracy in T measurement was estimated by calibration of the measuring sensors (thermocouples) at the melting temperatures of indium, zinc and similar substances.

The inaccuracy in c_p measurement was estimated by measurement of a pure cobalt sample having known $c_p(T)$ properties. Because a systematic error of about -7.6% of $c_{p(\text{Perkin-Elmer})}$ data caused by the incorrect calibration procedure was found, it was shifted to be zero by correction of all the following measured data using the recalibration factor $F(T)$.

Sensitivities of T and c_p data eventually should represent the last digits of the measured data. In the case of the Perkin-Elmer DSC instrument the proportionality of insensitivity to the term $55 \times 10^{-5}/(mw)$ was found. Because of the integral method used in the Setaram DSC the temperatures as well as the specific heats measured represent the mean values corresponding to the interval being integrated. $\overline{T}$ is insensitive to ± 8 K; on the other side $\overline{c_p}$ is sensitive to ± 0.01 J g^{-1} at^{-1} K^{-1}. The sensitivities do not depend on temperature.

The maximal deviation of measured data from the smoothed curve was named dispersion; in the case of measurement of the recalibration standard cobalt it represents the noise of $c_p(T)$ data. In contrast to the sensitivity, dispersion as well as noise of $c_p(T)$ data measured by Setaram DSC are strongly temperature dependent.

The main source of error at high temperatures is apparently attributed to the radiation heat losses. As was estimated by other authors [9], these rise strongly from $\pm 0.2\%$ at 700 K to $\pm 1.0\%$ at 1100 K.

The reproducibility of measured specific heats was calculated from at least 3 independent measurements. The short-time reproducibility of a room temperature measurement on one crystalline metallic ribbon sample with constantly defined thermal contacts represents $\pm 0.6\%$ but it rises strongly to $\pm 2.1\%$ when the position and the sample were changed. The $\pm 1.2\%$ error contribution to this is related to a new different sample.

Analysis of the conditions of specific heat measurements with the Perkin-Elmer differential scanning calorimeter by the scanning method

In order to obtain accurate specific heat data of metallic ribbons, conditions of the measurements should be carefully optimized. Among many items to be considered these relations have been found:

Effect of the mass m_M

With decreasing mass of measured sample the principal character of the $c_p(T)$ curve remains preserved, possible anomalies are less pronounced, the sensitivity decreases but measured c_p magnitudes are systematically shifted to higher absolute values (Fig. 5).

Effect of dimensions of the cut pieces of a sample

Dimensions of the ribbon sample influence the curvature of measured $c_p(T)$ dependence. Elements which are too large (probably due to the

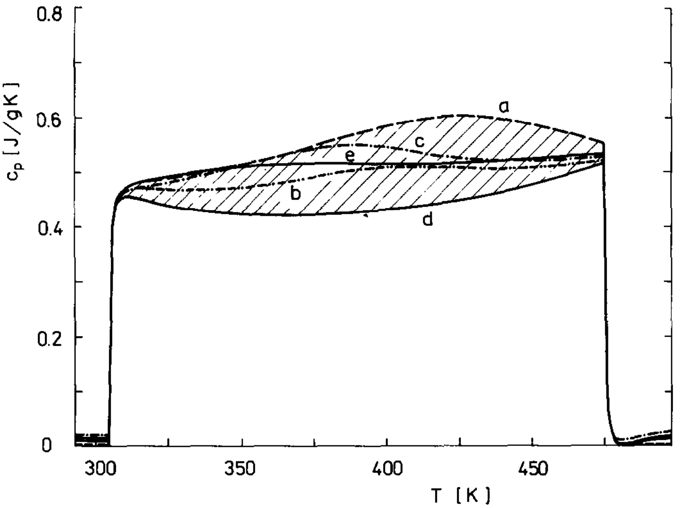

Fig. 5. Reproducibility of specific heat of as-quenched glassy $Fe_{73}Co_{12}B_{15}$ ribbon measured by Perkin-Elmer DSC7 ($w = 5$ K min^{-1}): a, b, different samples; c, small sample mass m_M; d, big sample pieces; e, bad reference pan.

critically bad (minimal) thermal contacts) systematically decrease the measured absolute values of c_p (Fig. 5). The minimal correct sample dimensions previously referred to are about 20 μm [10].

Effect of heating rate w

The heating rate is related to the program controlled sensitivity of the measuring DSC instrument.

Role of the width of the temperature interval $T_{start} - T_{final}$

Some systematic curvature deviation of measured $c_p(T)$ dependence (an extreme example was seen on the crystalline ribbon sample in Fig. 4) is proportional to the width of the temperature interval used. The first 2 min of data after T_{start} should be omitted because they represent the transient region of the runs before the instrument reaches scanning equilibrium. In order to measure the wider $c_p(T)$ dependence several successive steps of the measurement in the overlapping temperature intervals could be selected [11].

Effect of the empty standard sample pan measuring cycle

The long term reproducibility of the empty pan $\Delta J_{(S-R)}(T)$ data is ±0.3%. The systematic error due to the false standard sample pan is ±1.2%.

Effect of the metallic glassy sample

Comparing the reproducibilities of measured specific heats of investigated $Fe_{73}Co_{12}B_{15}$ ribbons with other rapidly quenched $Co_{67}Cr_7Fe_4Si_8B_{14}$

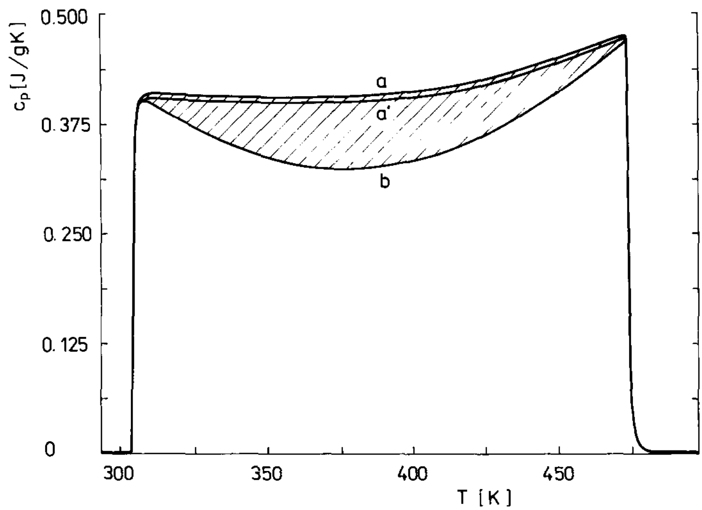

Fig. 6. Reproducibility of specific heat of crystalline $Fe_{73}Co_{12}B_{15}$ ribbon measured by Perkin-Elmer DSC7 ($w = 5$ K min^{-1}): a, a′, two successive runs without any change; b, after the change of thermal contacts.

ribbons and with equilibrium crystalline cobalt in Table 1 and Figs. 5–8 the role of thermodynamic state and mechanical properties of metallic glassy ribbons can be analyzed.

It was confirmed that the main contribution to the imprecision of experimental specific heats ($\pm 1.2\%$ from the total $\pm 2.1\%$) as well as the curvature of $c_p(T)$ dependence of $Fe_{73}Co_{12}B_{15}$ samples is due to irrepro-

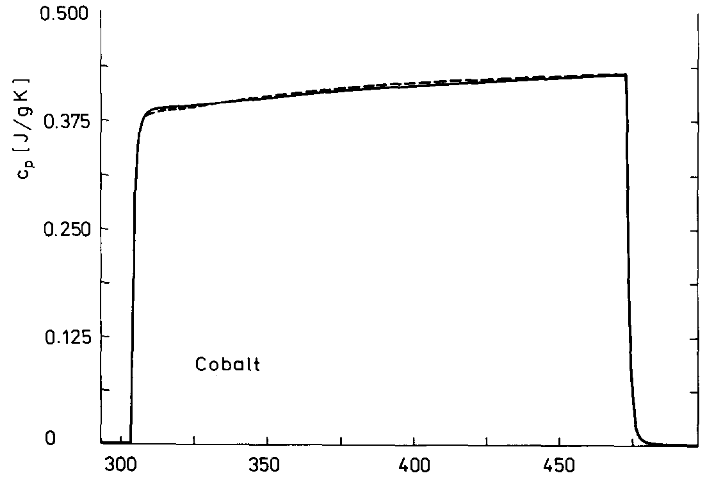

Fig. 7. Reproducibility of specific heat of pure cobalt measured by Perkin-Elmer DSC7 ($w = 5$ K min^{-1}).

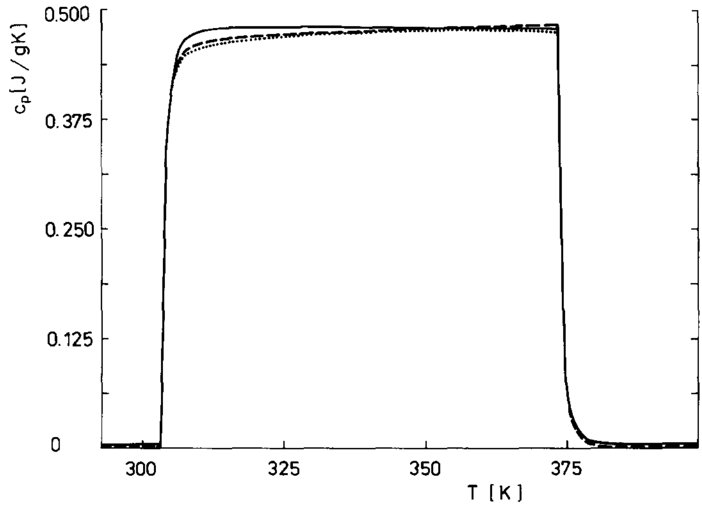

Fig. 8. Specific heat of $Co_{67}Cr_7Fe_4Si_8B_{14}$ ribbon measured by Perkin-Elmer DSC7 ($w = 5$ K min^{-1}): ———, as-quenched glassy; — — —, relaxed glassy; ······, crystalline.

ducibility of internal thermodynamic heterogeneities of various new samples. The thermodynamic properties of the technical glassy ribbons of $Co_{67}Cr_7Fe_4Si_8B_{14}$ are much more reproducible.

The first run $c_p(T)$ data of an as-quenched glassy sample are always very problematic because of the bad reproducibility of the internal thermodynamic heterogeneities in a sample, of a pronounced structural relaxation effect in the as-quenched sample and of relaxation of every thermal contact in the measuring system (Fig. 5).

All the complex analyses presented above (see Experimental section) allowed the optimal parameters for measuring $c_p(T)$ of glassy metallic ribbons to be determined by the DSC technique.

CONCLUSION

DSC can be conveniently used for accurate measurements of specific heats of a variety of metallic glassy samples, at least below 1100 K. The sensitivity is better than 0.05 J g^{-1} at^{-1} K^{-1} and the maximal dispersion is $\pm 1.2\%$.

The advantages of a DSC experiment are minimal restrictions on the sample, its quick and easy insertion into the measuring instrument, the relatively quick (thermodynamically steady-state) measuring regime ($w \approx$ 1–10 K min^{-1}), the simple but physically correct commercializable scanning and integral methods of data processing.

Our measurements on metallic glassy ribbons are given as examples.

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