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# ESTIMATION OF SPECIFIC HEATS OF METALLIC FOILS BY THE PULSE METHOD

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The applicability of the heat pulse method for measurement of the specific heat $c$(T) and thermal diffusivity $a$(T) of metallic foils was studied. A sample holder for the temperature range 280–1100 K is described. The reproducibility of the measurements was tested on crystalline Ni and glassy $Fe_{85}B_{15}$ foils.

A new technological process for the production of thin metallic foils in the glassy state by rapid cooling was recently developed. Simultaneously, the problem of the measurement of technical parameters of metallic foils arose.

The pulse method for the measurement of thermophysical quantities allows the fast determination of specific heat $c$, thermal diffusivity $a$ and thermal conductivity $\lambda$ with sufficient accuracy. The method is based on measurement of the parameters of the temperature response to a thermal pulse generated at a suitable site on the sample [1].

The purpose of this paper is to investigate the applicability of the pulse method for measurements of $c$ and $a$ of metallic crystalline Ni and glassy $Fe_{85}B_{15}$ foils.

## Experimental

### *Sample holder*

For the measurement of thin foils, it was necessary to construct a suitable holder. A scheme of the holder is presented in Fig. 1. A platinum wire (∅ 0.1 mm) was used as linear heat source. The heat source, together with mica (to ensure electrical insulation between the source and the foil), and the sample were mounted between quartz plates for thermal insulation. To decrease the temperature gradient along the foil, the whole system was mounted on a silver plate (0.2 mm thick). The other end of the foil was fixed between ceramic plates to ensure thermal contact between the silver plate and the foil. Niobium wire (∅ 0.1 mm) was used as an electrical contact to the heat source, to minimize heat losses from the heat source.

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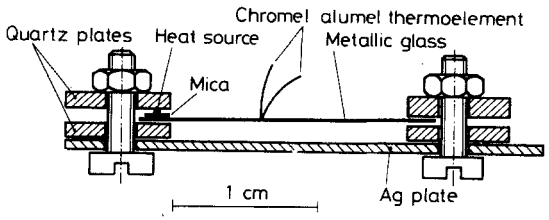


**Fig. 1** Scheme of sample holder for metallic foils

The construction parameters of the holder are the same for all measurements, and thus it can be calibrated by using known materials (e.g. crystalline Fe or Ni foils).

*Electronic apparatus and data processing*

An automatic measuring apparatus was built [2]. This apparatus ensures the following functions: (i) experiment control and measurement of the parameters necessary for calculation of the thermophysical quantities; (ii) local data processing in the time of sample temperature stabilization; (iii) data acquisition and reduction for storage in a data-base.

*Samples and measuring regimes*

The applicability of the pulse method for the investigation of metallic foils was tested on crystalline Ni foil with a thickness of $\sim 25$ μm (cold-rolled from 99.6% Ni from by Kovohutě Rokycany), and on foils of glassy $Fe_{85}B_{15}$ with a thickness of $\sim 35$ μm (produced by the melt spinning technique). The measurements were made in vacuum at room temperature and in a non-isothermal regime at a heating rate of $\sim 0.5$ deg $min^{-1}$. Several runs from 280 to 1100 K were performed to obtain stable crystalline phases of the Fe–B system.

The apparatus baseline was obtained from the $C(T)$ of the crystalline Ni foil. Absolute values were estimated with respect to the tabulated values and the values obtained by the DSC technique. A heating rate of 20 deg $min^{-1}$ was used for the $T_c$ determination.

## Results

### *Crystalline Ni foil*

The reproducibility of the measurements was tested with respect to the following factors: different type of holder construction; reproducibility and stability of the sample mounting into the holder; reproducibility and stability of the material properties; various measuring parameters; and stability of the sample-holder configuration after heat treatment. The averaged values from the data obtained are given in Table 1.

**Table 1** Room temperature data of specific heat $c$ and thermal diffusivity $a$ and Curie point $T_c$ of crystalline Ni and glassy $Fe_{85}B_{15}$ foils

| Quantity | Unit | Absolute values | | | Imprecision | Uncertainty |
|---|---|---|---|---|---|---|
| | | tabulated | DSC | pulse method | | |
| | | | Nickel | | | |
| $c$ (300 K) | $J\,kg^{-1}\,deg^{-1}$ | 442 [3] | 418 | 607 | ±2.2% | ±14.2% |
| $a$ (300 K) | $m^2\,s^{-1}$ | $1.72 \cdot 10^{-5}$ [3] | — | $1.158 \cdot 10^{-5}$ | ±0.7% | ±23.8% |
| $T_c$ | K | 627 [4] | 622 | 624 | ±0.2% | ± 2.2% |
| | | | $Fe_{85}B_{15}$ | | | |
| $c$ (300 K) | $J\,kg^{-1}\,deg^{-1}$ | — | 1779 | 1487 | ±3.8% | ±13.4% |
| $a$ (300 K) | $m^2\,s^{-1}$ | — | — | $3.245 \cdot 10^{-6}$ | ±4.8% | ± 8.0% |
| $T_c$ | K | — | 548 | 550 | | ± 1.8% |

+ Cement chemistry notation used: $C$ – CaO, A – $Al_2O_3$, F – $Fe_2O_3$, $\bar{S}$ – $SO_3$ and H – $H_2O$.

The averaged values of the tabulated data of specific heat $c$, thermal diffusivity $a$ and Curie point $T_c$ for Ni (bulk material) have an uncertainty of ±0.3%. The data are influenced by the chemical purity, by the method of measurement and by the thermodynamic state given by the material production and sample preparation. The mean absolute value of $c$ for the investigated foil within the range 328–353 K was estimated on a DSC-2 (Perkin–Elmer) with an imprecision of ±0.2%.

The effective absolute value of $c$ measured with the heat pulse method was 145.2% and 137.3% of the DSC absolute value and the tabulated value, respectively.

There is uncertainty in the maximum estimated inaccuracy of the measurement. In the measurement of $c$, the uncertainty is practically caused by the long-term instability of the parameters of the sample-holder configuration. In the case of $a$, this contribution is only ±3.7%. The major uncertainty in $a$ is caused by the poor

reproducibility of the thermal contacts. The value of $T_c$ found through the $a(T)$ anomaly is always lower ($\sim 1.5$ deg) than that defined by the $c(T)$ anomaly. The major part of the uncertainty in $T_c$ is caused by relaxational changes in the heat-treated samples.

The temperature-dependences of $c(T)$ and $a(T)$ were studied in several runs shown in Fig. 2. The curves are qualitatively the same in all runs. However, via the relaxation, the heat treatment influenced the thermodynamic state of the cold-rolled foils, as well as the quality of all thermal contacts in the measuring system. For this reason the following runs generally give different $c(T)$ and $a(T)$ values and transformation temperatures from those of the first run of the as-prepared sample and measuring system. The uncertainty in the measured curves of $c(T)$ of well-relaxed samples is $\pm 4.4\%$. The difference between the relaxed curve $c_2(T)$ and the extrapolated tabulated curve $c_2(T)$ represents the apparatus baseline for Ni foils.

The dependence $a(T)$ relaxed towards lower absolute values in the whole temperature region. An anomalous effect at the beginning of every run at room temperature has not yet been clarified. The apparatus baseline $a(T)$ was not constructed.

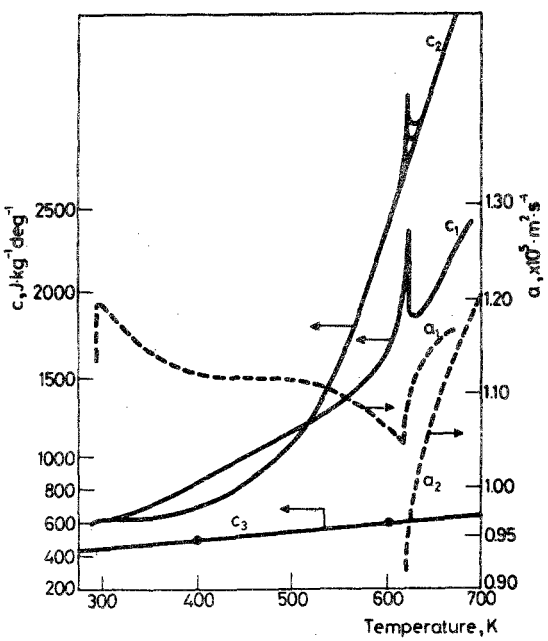


**Fig. 2** Reproducibility of specific heat $c$(T) and thermal diffusivity $a$(T) of crystalline Ni foil with thickness of $\sim 25$ μm. $c_1$, $a_1$ — the 1st run of as-prepared sample and measuring system, $c_2$, $a_2$ — the following runs, $c_3$ — an extrapolated tabulated dependence

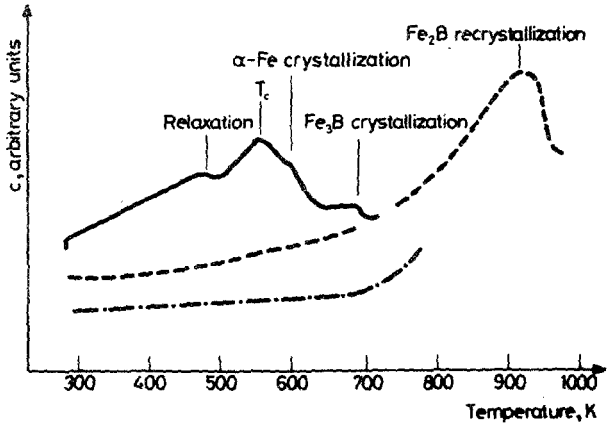


**Fig. 3** Specific heat of $Fe_{85}B_{15}$. Plotted curves belong to selected consecutive runs (300–1000 K). ——— — as quenched sample, — — — after α-Fe and $Fe_3B$ crystallizations, —·— completely crystallized sample

*Glassy $Fe_{85}B_{15}$ foil*

The metallic glass $Fe_{85}B_{15}$ exhibits the following types of structural changes in the temperature region from 300 to 1100 K (Fig. 3): (i) relaxation of the amorphous structure above 420 K, (ii) Curie point of the amorphous phase at ~550 K, (iii) partial crystallization of α-Fe from the amorphous phase above 590 K, (iv) crystallization of $Fe_3B$ from the remaining (amorphous phase above 685 K, (v) $Fe_2B$ recrystallization of $Fe_3B$ phase above 850 K, and (vi) Curie point of crystalline Fe at ~1050 K.

The measured data concerning the room-temperature thermophysical quantities are presented in Table 1. The low thermal diffusivity of the glass caused a radical increase of the imprecision. The effect of thermal contacts in this case is not decisive.

Through spontaneous structural relaxation, the glassy system changes towards a move "equilibrated" state. This process is represented by $\Delta c \sim -10.3\%$ and $\Delta a \sim -2.7\%$ changes in the room-temperature data, and $\Delta T_c \sim +5$ deg. The three-step crystallization is manifested by $\Delta c \sim -55\%$ and $\Delta a \sim +190\%$. The uncertainty in $c$ and $a$ is lowered to $\pm 3.3\%$ and $\pm 1.7\%$, respectively. The $c(T)$ dependence of the totally crystallized $Fe_{85}B_{15}$ sample (the last run of Fig. 3) represents the first approximation of the baseline for the $Fe_{85}B_{15}$ system.

## Discussion

The influence of the heat pulse energy $Q$ and of the width of the heat pulse $\Delta t$ on the specific heat $c(Q)$ and the thermal diffusivity $a(\Delta t)$ has been investigated elsewhere [1].

To construct the true apparatus baselines $c(T)$ and $a(T)$, the $c(Q)$ and $a(\Delta t)$ corrections and correction for the temperature-dependence of heat losses should be performed. The specific apparatus baselines $c(T)$ and $a(T)$ are necessary for every material.

* * *

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## References

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**Zusammenfassung** — Die Anwendbarkeit der Wärmepulsmethode zur Messung der spezifischen Wärmekapazität $c(T)$ und der Temperaturleitfähigkeit $a(T)$ metallischer Folien wird untersucht. Ein Probenhalter für den Temperaturbereich 280—1100 K wird beschrieben. Die Reproduzierbarkeit der Messungen wird mit Folien aus kristallinem Nickel und $Fe_{85}B_{15}$-Glas getestet.

**Резюме** — Изучена применимость метода теплового импульса для измерения удельной теплоты $c$(T) и теплового коэффициента диффузии $a$(T) металлической фольги. Описан держатель образца для температурного интервала 280—1100 K. Воспроизводимость измерений проверена на кристаллическом никеле и фольге стеклообразного $Fe_{85}B_{15}$.