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# THE USE OF "BOERSMA" TYPE DIFFERENTIAL SCANNING CALORIMETERS IN THE MEASUREMENT OF EXOTHERMIC TRANSITIONS

S. DALLEK and L. KABACOFF
*Naval Surface Weapons Center, White Oak, Silver Spring, MD 20910 (U.S.A.)*

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## ABSTRACT

Questions have been raised about the suitability of the "Boersma" type differential scanning calorimeter for the measurement of exothermic transitions such as the crystallization of a metallic glass. However, it is demonstrated that provided the mass of the sample is kept lower than a certain value, which depends on the transition being studied (typically about 10–15 mg at a heating rate of 20 K $\text{min}^{-1}$ for a metallic glass), errors due to differences between actual sample temperature and that recorded by the instrument are negligible.

## INTRODUCTION

A recent review by Greer [1] has extensively discussed the use of the "Boersma" [2] type differential scanning calorimeter (DSC) such as the Dupont 910 [3] in the measurement of Curie temperatures of metallic glasses. No mention is made, however, of the suitability of the DuPont system for the measurement of exothermic transitions such as the crystallization of amorphous materials. It has been argued in the literature that only "servo" type DSCs such as the Perkin-Elmer DSC-2 [4] can give good quantitative data under these circumstances [5]. Nevertheless, the DuPont system is being used to make measurements on crystallization phenomena in our laboratory and elsewhere [6]. A discussion of the quality of the data so obtained is clearly in order.

In the absence of an exothermic (or endothermic) transition, the actual temperature of the sample will lag behind that of the thermocouple which monitors this temperature by an amount [1]

$$\Delta T_L = HC_S R_S \tag{1}$$

where $H$ is the programed heating rate, $C_S$ is the specific heat of the sample, and $R_S$ is the thermal resistance between the sample platform and sample. This expression is not valid during a transition in which a significant amount of energy is evolved, for two reasons: firstly, no dynamic equilibrium exists

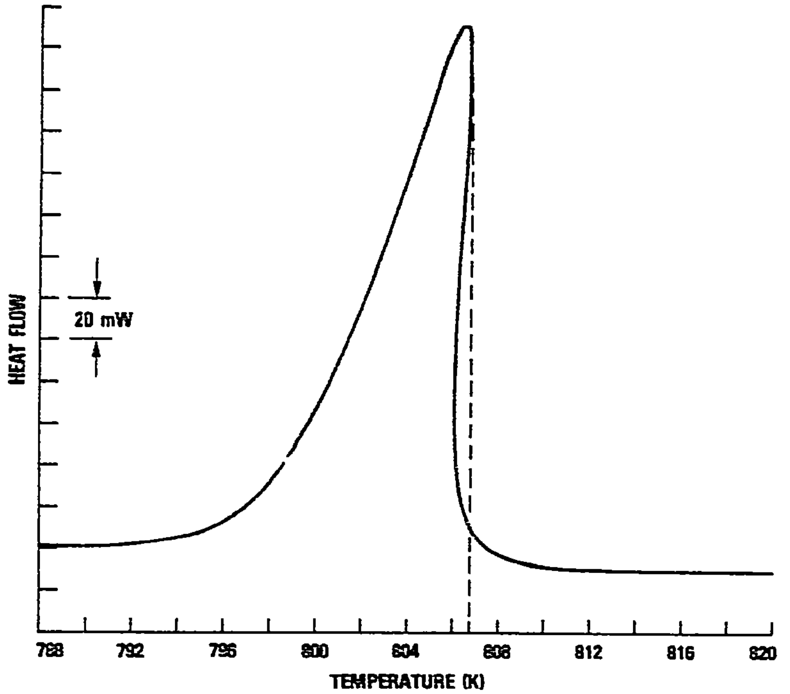

Fig. 1. Typical DSC curve for an exothermic reaction in which the heat evolved is large enough to raise the sample and sample platform temperature higher than the surrounding oven. Under these conditions, the platform temperature lags behind that of the sample.

within the DSC cell, as assumed by this expression; secondly, the increase in sample temperature does not occur solely as the result of heat conduction from the sample platform. In fact, if enough heat is generated in the sample, both the sample and sample platform will be hotter than the surrounding oven. This may be seen in Fig. 1, which shows a DSC curve for a very large metallic sample during crystallization. Following crystallization, the sample temperature decreases until dynamic equilibrium is re-established with the oven. One must be concerned about differences between the true sample temperature and that reported by the DSC, and about whether the area under the DSC curve accurately reflects the heat evolved during the transition. It should be noted that errors due to changes in $C_S$ and $R_S$ are negligible compared to these other effects.

The situation is not as bad as it might seem. This may be seen as follows. In the limit of very small sample mass, the heat generated in the sample during the exothermic transition is insufficient to raise the temperature of the sample at the programed heating rate. Thus, heat flows from the sample platform to the sample, and the temperature lag between the sample platform and sample is even smaller than that predicted by eqn. (1), which is itself very small because $C_S$ scales with sample mass. As sample mass is increased, the temperature lag between the sample and thermocouple decreases, then changes sign and increases. Thus, there is a range of sample mass over which the difference between the true sample temperature and that reported by the DSC is negligible. Likewise, departures of the sample heating rate from the programed heating rate will be small. Finally, the heat flow into the sample is proportional to the temperature difference generated between the sample and reference. Under the conditions discussed here, this parameter will also be accurately measured.

It is now necessary to determine the range of sample mass over which the DSC will give accurate results. A theoretical evaluation of heat flow within the DSC cell involves a number of empirically determined parameters, such as various thermal resistances, specific heats, widths of DSC peaks, etc. It is much simpler to examine the response of the machine using various sample masses and heating rates. This has been done using the crystallization of the metallic glass $Fe_{80}B_{15}Si_{5-x}Ge_x$. For contrast, we have also examined the melting of pure indium which, being endothermic, can be considered a "worst case" situation.

## EXPERIMENT AND RESULTS

Samples of amorphous $Fe_{80}B_{15}Si_{5-x}Ge_x$ ($x = 0, 1, 2, 3$ and 5) were prepared in ribbon form by meltspinning onto the surface of a rotating copper

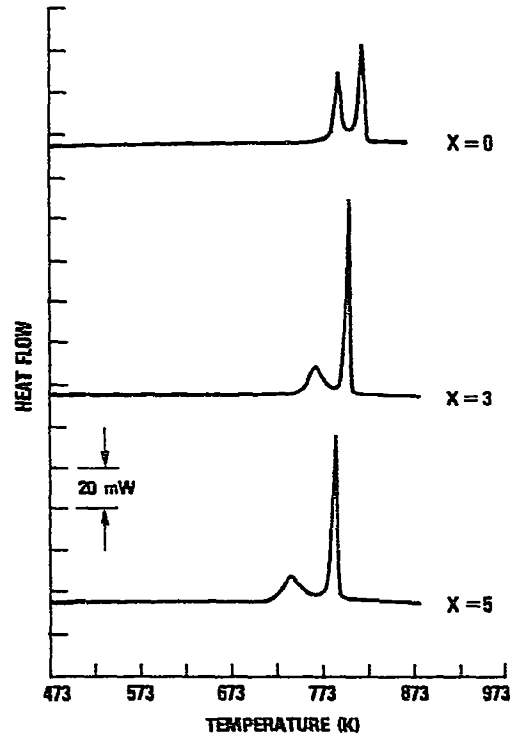

Fig. 2. DSC curves for $Fe_{80}B_{15}Si_{5-x}Ge_x$ ($x = 0, 3$ and 5). Heating rate: 20 K $min^{-1}$. Data is not normalized for sample mass.

TABLE 1

Typical values of $T_x$ and $T_p$ for various sample masses of $Fe_{80}B_{15}Si_4Ge_1$ at a heating rate of 20 K $min^{-1}$ (the subscripts refer to the first and second crystallization peaks)

| Sample mass (mg) | $T_{x1}$ (K) | $T_{p1}$ (K) | $T_{x2}$ (K) | $T_{p2}$ (K) |
|---|---|---|---|---|
| 1.926 | 769.9 | 780.5 | 802.2 | 809.0 |
| 5.182 | 770.5 | 780.7 | 802.2 | 809.7 |
| 12.730 | 770.5 | 780.9 | 802.5 | 810.7 |

wheel. The amorphous nature of the material was confirmed by X-ray diffraction using Mo$K\alpha$ radiation. Samples of various mass (ranging from 1 to 20 mg) were heated at rates of 1, 5, 20, 50 and 100 K $min^{-1}$. A DuPont 1090 thermal analysis system operating with a standard DuPont DSC cell was used throughout this work. Some typical DSC curves are shown in Fig. 2. Crystallization takes place in two stages. the first of which is the precipitation of $\alpha$-Fe; this is followed by the crystallization of the remaining material. Not visible in Fig. 2, due to scale, is the specific heat anomaly associated with the Curie transition. This will not be treated here except to note that the effect of heating rate and sample mass on the apparent Curie

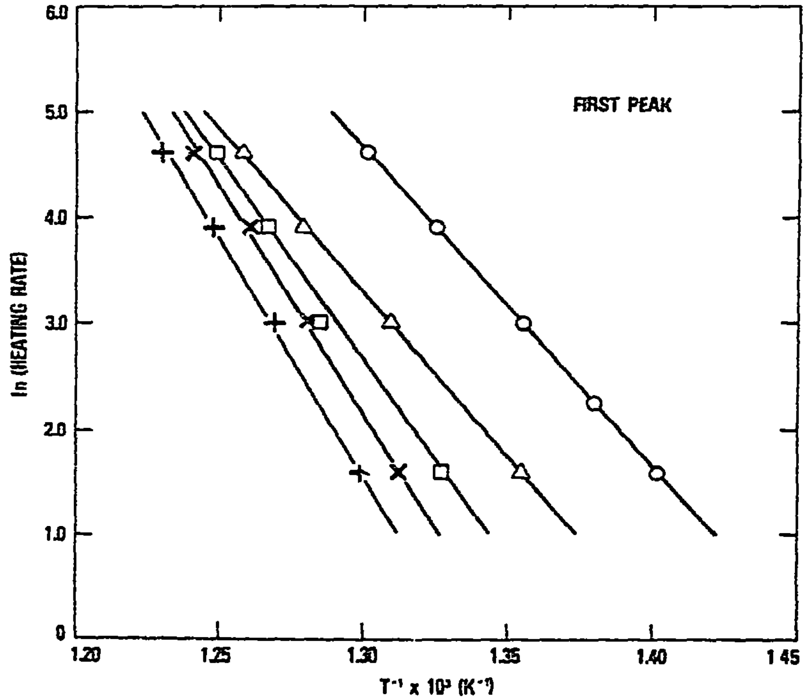

Fig. 3. Arrhenius plot for first crystallization peak in $Fe_{80}B_{15}Si_{5-x}Ge_x$. $x=0$ (+), 1 (×), 2 (□), 3 (△). and 5 (○).

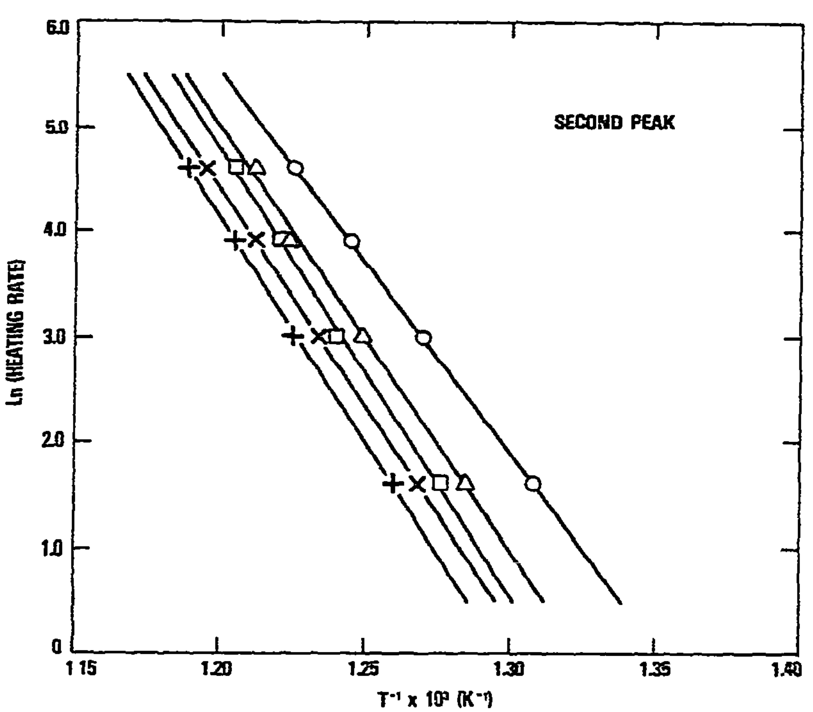

Fig. 4. Arrhenius plot for second crystallization peak in $Fe_{80}B_{15}Si_{5-x}Ge_x$. $x=0$ (+), 1(×), 2 (□), 3 (△), and 5 (○).

temperature agrees perfectly with the analysis of Greer [1] as summarized in eqn. (1).

It was found that, for a heating rate of 20 K $min^{-1}$, neither the onset crystallization temperature nor the crystallization peak temperature varied with mass, provided the sample mass was less than 15 mg (proportionately less for higher heating rates). The former is defined by the intersection of the steepest tangent with the baseline, while the latter is defined by the maximum in the DSC curve. Typical values of crystallization temperatures as a function of mass are given in Table 1. The various crystallization temperatures are expected to vary according to an Arrhenius relation

$$H = C\exp(E_a/kT), \tag{2}$$

where $H$ is the heating rate, $E_a$ is the activation energy of crystallization, $k$ is Boltzmann's constant, and $T$ is either $T_p$, the crystallization peak temperature, or $T_x$, the crystallization onset temperature [7,8]. Figures 3 and 4 show Arrhenius plots for each of the alloy compositions using values of $T_p$. Typical sample mass was 7–10 mg. As may be seen from the Figs., the plots are extremely linear, with a very small scatter in the data. Inaccuracies in the measurement of $T_p$ of a couple of degrees due to temperature lag between sample and thermocouple would give these curves noticeable curvature, as would significant departure of the true sample heating rate from the programmed heating rate. No such curvature is evident.

TABLE 2

Melting point and enthalpy of fusion of a 13.052 mass of indium as a function of heating rate

| Heating rate (K $\text{min}^{-1}$) | Melting point (K) | Enthalpy of fusion (J $g^{-1}$) |
|---|---|---|
| 5 | 428.4 | 30.9 |
| 10 | 428.5 | 31.5 |
| 20 | 428.7 | 31.2 |
| 50 | 430.3 | 31.6 |
| 100 | 431.5 | 31.6 |

Finally, a 13 mg sample of pure indium was heated through the melting point at several heating rates. The melting point and enthalpy of melting are shown as a function of heating rate in Table 2. Since this is an endothermic transition, the temperature lag will be even worse than that predicted by eqn. (1). Thus, this represents a very extreme form of "worst case" analysis. Nevertheless, the dependence of both the melting point and enthalpy of melting on heating rate is very modest. This gives an additional indication that crystallization data may be obtained with great accuracy.

## CONCLUSION

The results indicate that in the amorphous alloy system $Fe_{80}B_{15}Si_{5-x}Ge_x$, changes in crystallization temperature due to instrumental effects are too small to be detected provided that the sample mass is less than 15 mg at a heating rate of 20 K $\text{min}^{-1}$, proportionately less at higher heating rates. It should be noted that the sensitivity of the DSC also scales with the heating rate, so one would ordinarily use less sample when using the higher heating rates. Usually, a sample size of 3–5 mg is sufficient to obtain good DSC curves at 20 K $\text{min}^{-1}$. While the permissible sample size depends on the nature of the material, it is clear that, with minimal precautions, the "Boersma" type DSC cell will give excellent quantitative data on exothermic phenomena such as the crystallization of a metallic glass.

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