Original Research Paper

Volume - 16 | Issue - 01 | January - 2026 | PRINT ISSN No. 2249 - 555X | DOI : 10.36106/ijar

Physics

DIFFERENTIAL SCANNING CALORIMETERY: A SUMMARY OF THIS TECHNIQUE FOR GLASSY ALLOYS

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ABSTRACT The Differential Scanning Calorimeter (DSC) is a thermal study tool that procedures the temperature and heat flow related to material transitions as a function of time or temperature. To quantitatively evaluate experimental data from differential scanning calorimetry (DSC), Thermal parameters including symmetry melting temperature change of heat capacity and latent heat may be accurately determined with this approach, which can be complete routinely without the need for DSC worker. Specific heat (Cp), heat flow, enthalpy, glass transition temperature (Tg), crystallization temperature (Tc) and melting temperature (Tm) may all be easily calculated with DSC software.

KEYWORDS : Glass Transition Temperature, Crystallization Temperature, Specific Heat, Differential Scanning Calorimetry and Enthalpy

INTRODUCTION

DSC is a widely used thermosometric technique for characterizing the thermal uniqueness of materials, including as fluctuation in enthalpy and transition temperature (T_t) [1]. For more than a century, the thermal characteristics of solids have been studied using calorimetry. Heat flux and power compensating are two examples of the several DSC techniques. The power compensating DSC is based on the theory of physical phase transitions like endothermic or exothermic changes occur in the sample, a compensating power must be formed or taken up with respect to the reference. To maintain the same temperature for the reference and sample, the furnace must be taken or absorb at a constant rate. The distinct heat capacities of the sample and reference, which show up as an endothermic or exothermic peak that DSC trace, cause the shift in heat flow [2]. However, the International Confederation for Thermal Analysis and Calorimetry (ICTAC) established an improved classification of research methods in 1999. These days, thermal analysis (TA) should be considered a methodology that evaluates how a material's characteristics change with temperature and time, whereas calorimetry is a way to measure heat. A widely used approach for measuring the kinetics of non-isothermal transition is DSC. This technique is mostly utilized for the glass and crystallization kinetics investigation of glassy compounds because it is more sensitive, has a fast rate, takes relatively few glass samples to get parameters related to crystallization [3].

A mechanism called nucleation and growth may account for the commonly recognized amorphous to crystalline (a–c) phase transitions. The (a–c) phase transition, which is characterized by an activation energy ΔEn and an Avrami exponent n in accordance with the Johnson-Mehl-Avrami Kinetic Law [4–6], has been studied using a variety of techniques. The non-isothermal DSC approach, which also enables simultaneous analysis of the conversion across a wider temperature range, may determine these parameters in a comparatively quick and accurate manner. Multiple DSC curves provide the result $n\Delta E_c$ when the several scan method is employed for the study. However, exact knowledge of n and, consequently, the crystallization mechanism is necessary to determine the actual amount of ΔE_c. A single scan method that provides $\Delta E_c/n$ and ΔE_c independently can be used to determine each of these values individually. It is widely acknowledged that adding a third element to binary glasses increase thermal stability of these glasses [7].

These DSC measurements are referred to as non-isothermal mode. The second category consists of calorimeters (adiabatic, relaxation, and ac calorimetric) that measure the sample's temperature when a tiny quantity of heat is applied. The calorimeter's temperature is maintained during the measurement in these kinds of DSC devices. The term "isothermal mode" refers to this kind of DSC measurement. The modified differential scanning calorimeters have recently been adopted by researchers for case analysis [8]. In this review article I have discussed the DSC technique for glassy alloys.

Experimental Technique

Differential scanning calorimeter (PerkinElmer-Pyris diamond) with two 1 g furnaces was utilized for studies of all type of materials. In this technique nitrogen (N_2) (99.99% purity) gas was used to clean the DSC at a particular rate of 50 mL min^{-1}. Heat flow and temperature were calibrated under the same environments as the samples to be measured using indium (In) (a highly pure metal) supplied by PerkinElmer with surely known enthalpy of fusion and melting point are $\Delta H_{fusion} = 28.47$ J g^{-1} or 6.80 cal g^{-1} and $T_{m0} = 156.4$ °C respectively. A microbalance was used to weigh the items in an aluminum sample pan, using the same empty pan as a reference.

The furnace in the DSC setup had identical metal covers covering the sample and reference pans. At the fixed heating rate, denoted as β ($\beta = dT/dt$), heating and cooling scans were performed. A prearranged cooling cycle preceded a second heating cycle following the completion of the first isothermal/heating scan. The sample geometry effect may also be reduced by the preheating and cooling scans, providing the measurement a more uniform, flat layer that makes excellent contact with the pan's bottom. Each sample must go through at least two more observations under the same conditions since the fusion can change the heat transfer between the sample and reference pan, which can impact the predicted peak onset temperature.

Set-up Description

The amount of energy required to create a virtually zero temperature differential between a substance and an inert reference material may be determined using the DSC method. In a controlled heating or cooling environment, the two specimens are shown in Fig. 1 under similar temperature regimes. This kind of DSC uses a low-resistance heat flow route to connect the sample and reference. The entire unit is enclosed by a single furnace.

Working Principle Of DSC

The sample and reference pans in heat flux DSC are kept in the same furnace. The heat change in the sample is caused by additional energy conduction between the sample and reference through the attached metallic disk, which results from the difference in energy needed to keep them at almost the same temperature. The system's thermal resistances change with temperature because the heat transfer between the inert reference and sample pans determines the temperature gap that develops between them. This change was captured in calibrated mode, which provides a virtually constant calorimetric sensitivity by automatically varying the amplification with temperature. The block diagram in Fig. 2. illustrates the conclusions drawn from taking into account the system's heat flow sources.

The following definitions apply to the terms used:

T_{SP} , T_{RP} = sample and reference system temperatures, respectively. TSP is often plotted as a DSC curve's abscissa.

T_F= The heating block's silver temperature.

R_{D0}= Thermal resistance (units Cmin J^{-1}) between the sample or reference platforms and the furnace wall.

R_{S1}, R_{R1}= Thermal resistance between the sample and the reference platform.

C_{S0}, C_{R0}= The sample's and reference's respective containers' heat capacities.

H = Induced heating rate.
ΔT_{R0} = The reference platform's temperature lag in relation to the furnace.
ΔT_{S0} = Sample platform's temperature lag with respect to the furnace
ΔT_{L0} = sample's temperature lag in association with the sample thermocouple.

$$\Delta T_{R0} = HR_{D0}C_{0R} \quad (1)$$
$$\Delta T_{S0} = HR_{D0}C_{S0} \quad (2)$$
$$\Delta T_{0} = HR_{D0}(C_{S0} - C_{R0}) \quad (3)$$
$$\Delta T_{L0} = HR_{S1}C_{S0} \quad (4)$$
$$\Delta T_{S0} = \Delta T_{R0} + \Delta T_{0} \quad (5)$$

$$\Delta T_{L0} = \frac{R_{s1}}{R_{D0}\Delta T_{S0}} \quad (6)$$

Measurements Using DSC

DSC technique, the glass transition kinetics have been thoroughly investigated in the literature using the non-isothermal [9,10]. This technique is mainly important due to its easy to apply, needs tiny sample, is very delicate, and is mostly free of sample shape. A typical DSC scan of $Se_{75}Te_5Cd_{10}In_{10}$ glassy alloy at a heating rate of 25 K/min is present in Figure 3.

From figure 3 there is distinct endothermic peaks at the glass region and melting region and a single exothermic peak at the crystallization region. Figure 3 displays the $T_{g(onset)}$, $T_{g(peak)}$, and $T_{g\ (endset)}$ for glassy region are onset, peak and endset glass transition temperature respectively. Exothermic peak has T_c onset, T_c peak, and T_c endset crystallization temperatures are shown in Figure 3, respectively.

Glass transition kinetics has been investigated using (T_g) and activation energy (E_g). The concept of structural relaxation, which was developed by Moynihan and associates [9], is widely used in the literature to assess (E_g) from the heating rate dependency of T_g.

$$\frac{d(\ln\alpha)}{d\left(\frac{1}{T_g}\right)} = -\frac{E_g}{R} \quad ---(7)$$

The plot between ln α against $1/T_g$ gives straight line from equation (9), the slope of this plot may be used to calculate the E_g associated with the molecular rearrangements and movements around (T_g).

Kissinger's relations [10] are also used to assess the values of (Eg):

$$\ln\left(\frac{\alpha}{T_g^2}\right) = -\frac{E_g}{RT_g} + \text{constant} \quad (8)$$

As said, there are activation energies for nucleation, growth, and the entire crystallization process. Additionally, it has been shown in several studies [11–13] that the activation for growth can be taken to be equal to the activation energy of all crystallization (E_c) if it is confirmed by thermal study of the sample.

The crystallization activation energy (E_c) has been calculated by using the Kissinger model based on the variation of the (T_p) with the heating rates (α).

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_c}{RT_p} + \text{constant} \quad (9)$$

The value of E_c for the crystallization area may be calculate by using the plot of $\ln(\alpha/T_p^2)$ as a function of $1000/T_p$ equation (11), which yields straight lines. The Ozawa equation may also be used to determine the E_c based on the variation of onset crystalline temperature (T_c) with heating rate.

$$\ln\alpha = -E_c/RT_c + \text{constant}. \quad (10)$$

$$K_p = \left(\frac{\beta E_c}{RT_p^2}\right) \quad (11)$$

Rate constant (K_p) and Hruby number (K_{gl})

Rate constant K_p at peak crystallization temperature (T_p) with a fixed heating rate has been calculated by using the following formula given by Gao–Wang model [14] to get information on the growth morphology.

Hruby number [15] is the ratio of ($T_c - T_g$) to ($T_m - T_c$).

$$K_{gl} = \frac{(T_c - T_g)}{(T_m - T_c)} \quad ---(12)$$

The nucleation process is stuck by higher values of ($T_c - T_g$), whereas the growth process is delayed by lesser values of ($T_m - T_c$).

CONCLUSIONS

This book chapter discusses differential scanning calorimetry, a very sensitive and accurate thermos analytical method that is often employed because to its availability, speed, and simplicity. It is useful in a number of fields, including drug and chemical analysis, food science, liquid crystal research, and polymers. Different parameters, such as T_g, T_c, C_p, E_g, E_c, K_p, K_{gl}, and others, may be obtained accurately using DSC.

Acknowledgement

Dr. Sunil Kumar would like to express his gratitude to Prof. Kedar Singh SPS JNU New Delhi providing research facilities.

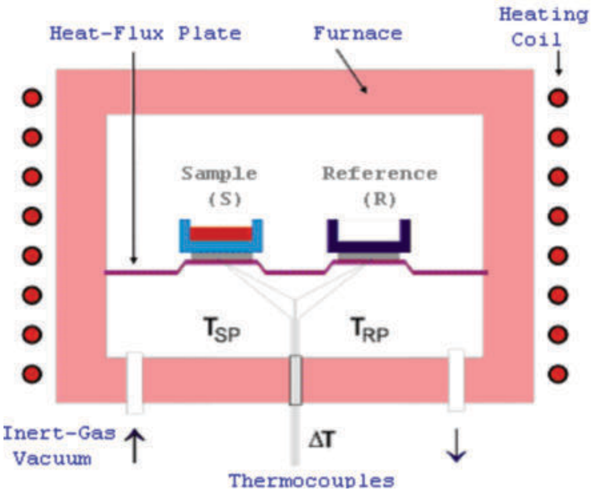

Fig. 1 *Heat flux DSC*

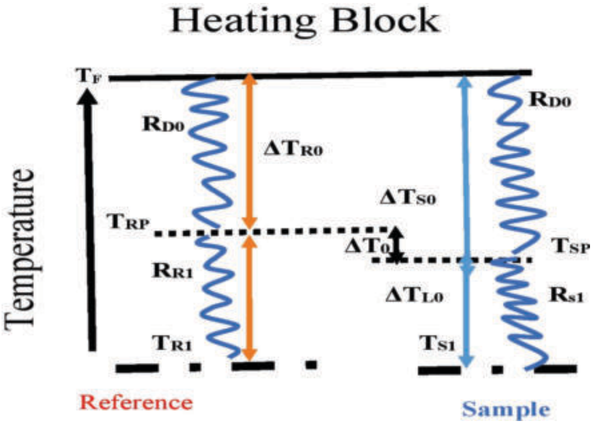

Fig.2. *Heating block of DSC*

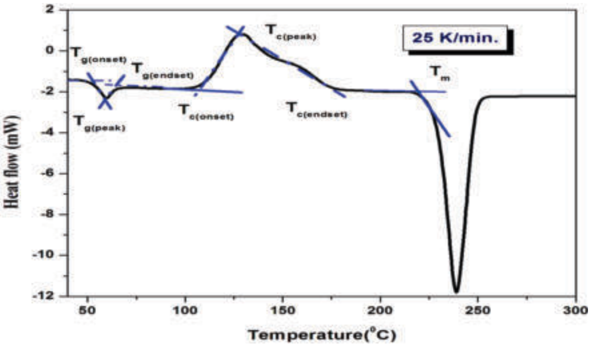

Figure 3. DSC thermogramme of $Se_{75}Te_5Cd_{10}In_{10}$ glassy alloy at fixed

heating rate 25 K/min.

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