2.1 Introduction

Thermal Analysis is a branch of material science where the properties of materials are studied as they change with temperature or it is a group of techniques in which a physical property of a substance and/or its reaction products are measured as a function of temperature when the substance is subjected to a controlled temperature programme [2.1]. The structure of the material is affected by its thermodynamic state which further causes the change in its properties. So, variations in the thermodynamic state of a material thus lead to variations in its properties. For the study of the kinetics of chemical reaction and crystallization of glass, thermal analysis has been used extensively. Several methods are commonly used which are distinguished from one another by the property which it measures. The output signal measured in the thermal analysis can include heat flows, mass, temperature changes, evolved gases, length changes, elastic modulus, conductivity, luminescence and many other properties that characterize the material or reaction of interest. The thermal analysis techniques can be classified according to the type of temperature programme that the sample is subjected to and the measured output signal. Isothermal and non-isothermal (heating at constant rate) are the most commonly used temperature profiles to study the sample.

The heat into or out of a sample is measured by calorimeter. A differential calorimeter, measures the heat of sample relative to a reference. Differential Scanning Calorimetry (DSC) is a technique in which difference in heat flow to a sample and to reference pan is monitored against time or temperature. The

temperature of sample and reference are made identical by varying the power input to the two surfaces and heats the sample with a linear temperature ramp [2.2]. The energy required to do this is the enthalpy or heat capacity changes in the sample relative to reference. In the endothermic reactions, heat flows into the sample whereas in exothermic reactions heat flows out of the sample. DSC is a method of thermal analysis that is widely used to study thermal transitions, i.e., solid-solid transitions as well as solid-liquid and various other transitions and reactions. By using thermal analysis it is possible to understand what is happening in a material even if there is no visual evidence that a change has occurred. In a controlled atmosphere DSC measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature. It also provides quantitative and qualitative data on endothermic (heat absorption) and exothermic (heat evolution) processes of materials during physical transitions that are caused by phase changes, melting, glass transitions, crystallization, oxidation, and other heat related changes [2.3]. This information helps the scientist or engineer identify processing and end-use performance. The DSC instrument works in conjunction with a controller and associated software to allow for data acquisition and analysis. Using DSC, one can better understand phase transitions and reactions in materials, and how they contribute to the properties and characteristics of the material. DSC is an efficient and powerful tool for quick determination of the specific heat and enthalpy of change accompanying the primary or secondary phase transition of substance [2.4].

In addition to materials research applications, thermal Analysis (DSC and TGA) have found uses in a large number of industries, such as tools manufacturing, semiconductor technology, battery safety, food technology, explosives manufacturing, metallurgy, cosmetics, textiles, energy companies – petroleum and coal.

2.2 Instrumentation basics

Types of DSC

There are mainly two types of DSC: 1) Power compensated and 2) Heat flux. The information obtained from both DSC is same but their instrumentation is different [2.5]

1) In power–compensation DSC using separate, identical furnaces the temperatures of the sample and reference are controlled independently. By varying the power input to the two furnaces the temperatures of the sample and reference are made identical and the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

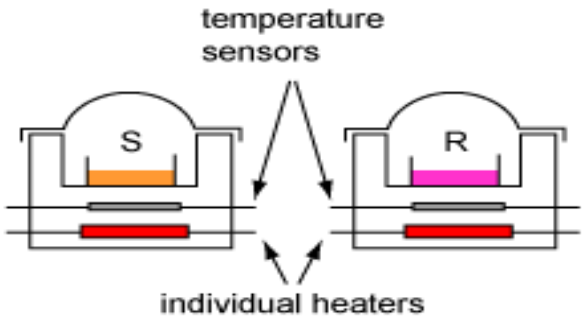

Fig 2.1 Schematic diagram of power compensated DSC
(Source: http://www.mtarr.co.uk)

2) In heat–flux DSC, the sample and reference are connected by a low–resistance heat–flow path using metal disc. The sample and reference are enclosed in the same furnace. The change in enthalpy or heat capacity of the sample causes a difference in its temperature relative to the reference, although the resulting heat flow is small because sample and reference are in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments. This system is a modification of differential thermal analysis (DTA), differing only by the fact that the sample and reference crucibles are linked by good heat–flow path. The fact that the temperature difference is small is important to ensure that both containers are exposed to essentially the same temperature programme.

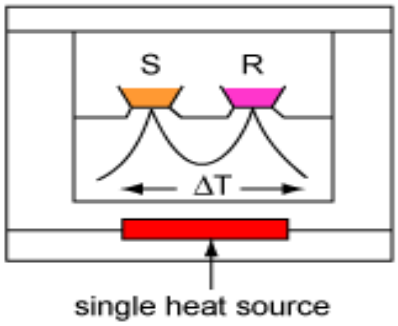

Fig 2.2 Schematic diagram of heat flux DSC
(Source: http://www.mtarr.co.uk)

The DSC cell is enclosed in a cylindrical, silver heating black, which dissipates heat to the specimens via a constantan disc which is attached to the silver block. The disc has two raised platforms on which the sample and reference pans are placed. The differential temperature between the two pans is determined by chromel-constantan thermocouple. A separate thermocouple

embedded in the silver block serves a temperature controller for the programmed heating cycle. An inert gas can be passed through the cell at a constant flow rate or the experiment can be carried out in air atmosphere. The thermal resistances of the system vary with temperature. Under such situation instruments can be operated in the 'calibrated' mode, during which the amplification is automatically varied with temperature to give a nearly constant calorimetric sensitivity [2.6].

2.3 Measurement of Enthalpy difference in DSC

In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. An empty aluminum pan or alumina is used as the reference. At a constant rate, the temperature of both the sample and reference are increased. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes [2.7]:

$$\left(\frac{dq}{dt}\right)_p = \frac{dH}{dt} \tag{1}$$

The heat flow difference between the sample and the reference is:

$$\Delta\frac{dH}{dt} = \left(\frac{dH}{dt}\right)_{Sample} - \left(\frac{dH}{dt}\right)_{reference} \tag{2}$$

and can be either positive or negative. *ΔdH/dt* is positive if the process endothermic and in most phase transitions, heat will be absorbed, therefore heat flow to the sample will be higher than that to the reference. While in exothermic process, such as crystallization, the opposite is true and *ΔdH/dt* is negative.

2.4 Experimental

In DSC the temperature difference between sample and reference would result due to some thermal event, which may occur, in the sample. The ordinate signal, the rate of energy absorption by the sample (e.g., in mW) is proportional to the specific heat of the sample since the specific heat at any temperature determines the amount of thermal energy necessary to change the sample temperature by a given amount. Any transition accompanied by a change in specific heat produces a discontinuity in the power signal, the exothermic enthalpy changes give peaks whose area are proportional to the total enthalpy change.

In the present investigation heat flux DSC (DSC-50, Shimadzu, Japan) is utilized. The DSC scans were recorded by a thermal analyzer (TA-50 WSI, Shimadzu, Japan) interfaced to a computer. The set up is shown in Fig 2.3. The detection sensitivity of the instrument is ~10 μW. The heat transformations and other essential physical quantities were obtained from the thermograms with the help of software, provided with the equipment. In DSC-50, the exothermic events are displayed by the upside shift of the baseline.

Ingots of alloys of nominal composition $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$ were obtained using arc melting technique. The amorphous ribbons of $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$ composition were prepared by a single roller melt-spinning technique in an argon atmosphere at Bhabha Atomic Research Centre (BARC), Mumbai (India). The as-quenched samples of $Zr_{52}Cu_{18}Ni_{14}Al_{10}Ti_6$ ribbons were cut into small pieces (~5mg) and crimped in aluminum pans and loaded in the DSC cell with the

reference material α- alumina. Energy Dispersive Analysis of X-rays (EDAX) was done to confirm its elemental composition of the present metallic glass. Thermal analysis of sample was carried out in a DSC-50 Shimadzu, Japan, at four different heating rates 5, 10, 15, and 20^0C/min. Aluminum pans were used as sample holders. The sample was heated in air atmosphere up to 560^0C at different heating rates.

Fig.2.3 A picture of DSC (Shimadzu, Model DSC-50)

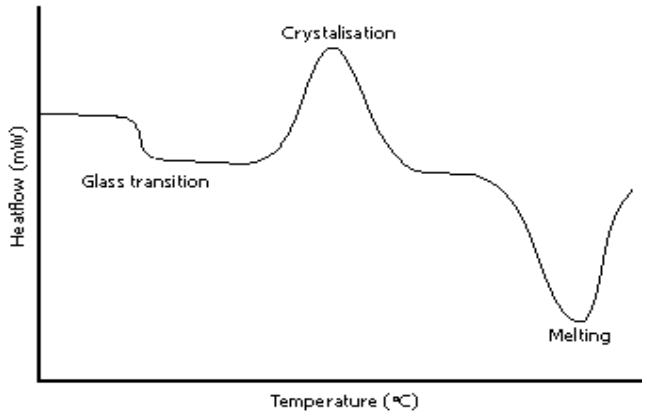

Fig 2.4 A schematic DSC curve demonstrating the appearance of several common features
(Source: http://www.thefullwiki.org)

In this experiment several different types of phase transitions will be observed for the metallic glass system. When a metallic glass sample is heated at a constant heating rate, as the temperature increases the material undergo various phase transitions. Firstly, it will undergo a glass transition where its heat capacity is increased, but no latent heat is present. Then material will crystallize and release energy showing an exothermic peak in the thermogram.

The enthalpy of crystallization can be calculated by formula:

$$\Delta H = \frac{\text{Area under peak}}{(\text{Heating rate})^* (\text{Mass of sample})}$$

The material can undergo solid-solid phase transitions by re-crystallizing into different arrangements this is known as polymorphism. Finally material melts indicating an endothermic event. Also additional phase changes in the liquid phase may take place. Inherently crystalline materials thus may only undergo

solid to solid transitions and then melt. As stated earlier, depending on the thermodynamic state of the material it may undergo a solid to gas transition in a process known as sublimation, and the latent heat of sublimation may be measured.

DSC can measure glass transitions, melting and boiling points, crystallization time and temperature, percent crystallinity, heats of fusion and reactions, specific heat capacity, oxidative/thermal stability, rate and degree of cure, reaction kinetics and purity

References

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