

**STRUCTURAL RELAXATION, CRYSTALLIZATION KINETICS
AND DIFFUSION STUDY OF METALLIC GLASSES**

By

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AND DIFFUSION STUDY OF METALLIC GLASSES**

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ABSTRACT

This study is on the thermodynamics, electrical and diffusion properties of five bulk metal glasses, new materials of great importance in technology, and on a long-standing problem of the residual entropy of the glassy state. It describes (i) an investigation of spontaneous structural relaxation, (ii) discovery of memory effect, and (iii) an investigation of crystallization kinetics both isothermally and on rate heating of bulk metallic glasses by measurements of their enthalpy change with time, temperature, and annealing conditions. Furthermore, it provides a real-time electrical resistivity study of structural relaxation effects, and an electron microscopy study of the interdiffusion kinetics of atoms across a junction interface, i.e., the so-called Kirkendall effect.

It is shown that structural relaxation occurs according to a stretched exponential kinetics and distribution of relaxation times leads to memory effect for a glass sample of complex thermal history. This mechanism is confirmed by real time electrical resistivity measurements at different temperatures and explained in terms of the Ziman model. Crystallization of ultraviscous melts occurs in several steps but the first and major step follows the Kolmogorov-Johnson-Mehl-Avrami kinetics based upon the Poisson distribution of nucleation sites. Several other processes also occur including a possible spinodal decomposition with one phase remaining in the rigid glassy state. Thermally activated interdiffusion of atoms across a junction interface is inconsistent with the

vacancy diffusion model. Finally, it is shown that contrary to the recent arguments based upon the Boltzmann equation, a glass has residual entropy.

Seven papers based upon this study have been published in Journal of Non-Crystalline Solids, Journal of Chemical Physics, Journal of Physical Chemistry, Thermochemica Acta, and Philosophical Magazine.

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CHAPTER 1

INTRODUCTION

1.1 The Development of Metallic Glasses

Glassy state of metals was first made by Klement et al (1960) by hyperquenching of $\text{Au}_{80}\text{Si}_{20}$ melt in minute size droplets. Chen and Turnbull (1969) then made amorphous spheres of a series of ternary Pd-Si-X alloys, with X being Ag, Cu, or Au. Although x-ray diffraction showed all these alloys to be amorphous, the characteristic thermodynamic feature of transformation from glass to ultraviscous liquid on heating was demonstrated only for splat-quenched metallic glass, $\text{Au}_{77}\text{Ge}_{14}\text{Si}_9$, by Chen and Turnbull (1967), because this glass was the most stable formed by them. They found that the specific heat C_p of the glass was slightly higher than that of its crystallized state of mixed crystals up to a temperature of 295 K, and on heating C_p rose sharply by approximately $21 \text{ J mol}^{-1}\text{K}^{-1}$ and leveled off at a temperature of about 300 K to a value that smoothly extrapolated to the C_p of the molten liquid alloy. They showed that the endothermic C_p feature, which is characteristic of the glass to liquid transition, could be found when the melt was cooled and then reheated. A new metallic glass of composition $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ was made in 0.5 mm diameter size and its glass to ultraviscous liquid transition was also demonstrated by measuring its C_p . They found that for certain ternary Pd-Cu-Si and Pd-Ag-Si alloys, the supercooled liquid region on heating (the temperature range between the glass transition and the first crystallization temperature) for some glasses extended to 40 K, and this

enabled the researchers to perform the detailed studies of crystallization kinetics of metallic glasses. Chen (1974) also did investigations on Pd-X-P alloys, with X being Ni, Co, and Fe, and obtained a critical casting thickness on these glasses of the order of 1 mm. Since then there have been numerous attempts to obtain samples of metal alloy glasses with larger thickness as rods or other sheets, or else make them by relatively slow cooling of the melt in order that they could be produced commercially for an increasingly wider application in technology.

In the early 1980s, Turnbull and coworkers reinvestigated the formation of glassy Pd-Ni-P alloys. They were able to produce glassy rods of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ with a diameter of 5 mm by performing surface etching of the specimens followed by heating and cooling cycles. With this method, the heterogeneous nucleation was minimized. By processing the Pd-Ni-P melt in a boron oxide flux, they were able to improve the casting thickness to 1 cm (Kui et al 1984). Thus, Pd-Ni-P may be considered as the first bulk metallic glass to be developed.

In the late 1980s, the Inoue group in Sendai, Japan investigated the formation of glassy La-Al-Ni and La-Al-Cu alloys. By casting in Cu molds, they were able to produce glassy $\text{La}_{55}\text{Al}_{25}\text{Ni}_{20}$ as rods with a diameter of 5 mm or sheets with similar thickness (Inoue et al 1989). They were also able to produce glassy $\text{La}_{55}\text{Al}_{25}\text{Ni}_{10}\text{Cu}_{10}$ with casting thickness of up to 9 mm. In the early 1990s, the same group developed glassy Mg-Cu-Y, Mg-Ni-Y, and Zr-Al-Ni-Cu alloys. They found the largest glass forming ability obtained for $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ alloy for Mg-Cu-Y and Mg-Ni-Y alloys (Inoue et al 1991). Glassy Zr-Al-Ni-Cu produced had high thermal stability with the casting thickness of up to 15 mm

and the supercooled liquid region of 127 K for $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ glass (Zhang et al 1991).

Because of the growing commercial applications, in the early 1990s a group at the California Institute of Technology, led by Johnson began to search for compositions that could be cooled relatively slow to form bulk glassy metals. Peker and Johnson (1993) developed the pentary glassy $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$, commonly referred to as Vitreloy 1 (Vit1). With critical casting thickness of up to 10 cm, this glass was the first commercial bulk metallic glass. Variants include $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ (Vit4). Inoue and coworkers (Inoue et al 1997) reinvestigated the $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ alloy glass and replaced its 30% Ni by Cu. As a result, they were able to produce glassy $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ with a critical casting thickness of 72 mm. The Pd-Cu-Ni-P alloys are the metallic systems with the highest glass-forming ability known to date.

Since the first metallic glass made by Klement et al (1960) and others, the critical casting thickness increased by more than three orders of magnitude in the last 50 years. The growth of critical casting thickness of these “conventional” glassy metals, to which numerous groups have contributed, is plotted against the year in Fig. 1.1. The fit of the critical casting thickness data in Fig 1.1 shows that the critical casting thickness increased by one order of magnitude approximately every 12 years. It has been suggested that if such a trend continued, bulk metallic glass compositions that, like the oxide glasses, are difficult to crystallize may be found in the next 10 or 20 years (Loffler et al 2003).

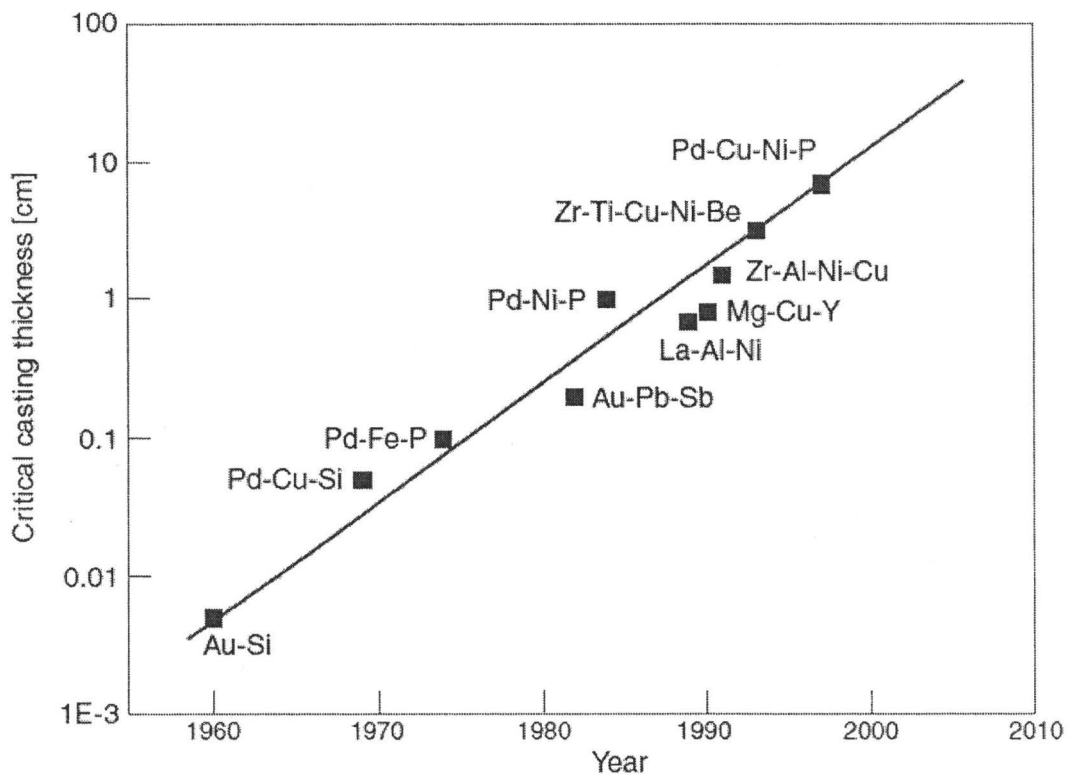


Fig. 1.1. Critical casting thickness for glass formation as a function of the year in which the corresponding alloy was discovered (Telford 2004).

1.2 Purpose of Research

Glassy state is generally metastable with respect to its crystal state and unstable with respect to its own equilibrium, disordered state. The first causes it to ultimately crystallize and the second to structurally change spontaneously with time. Both are related to atomic diffusion in the solid and ultraviscous states, and both occurrences change its physical properties. These cause time-, and temperature-dependent deteriorating effects on the use of metallic glasses as a device for electrical, magnetic and mechanical purpose, and on their use as a material for broader applications in the form of sheets produced by rolling and of varied shapes produced by casting and finishing

processes. The purpose of this research is to investigate these phenomena by thermodynamic and electrical measurements for bulk metallic glasses of five compositions: (i) $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, (ii) $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, (iii) $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, (iv) $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, and (v) $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$.

As research progressed it seemed academically and commercially important to determine the consequences of atomic diffusion across a junction interface with another metal, and hence to determine if the so-called Kirkendall effect can be observed for metallic glasses. Some of the research required developing automated new equipment for the purpose, that would be used in future studies.

During the course of this study, a number of papers appeared that argued that a glass has no configurational entropy and therefore has no residual entropy. Since it bears upon this study and also on thermodynamics of the glassy state in general, it became a purpose of our study to determine if the arguments given in these papers could be verified by experiments.

Details on the purpose of this research are given in the Introduction of subsequent chapters. Part of this study has been published in the form of seven papers.

1.3 Thesis Organization

This thesis is organized as follows. Chapter 2 presents the study of structural relaxation of four bulk metallic glasses. In this chapter, the structural relaxation is discussed extensively by using thermodynamic concept based upon the measured calorimetric data. The modeling of the structural relaxation is also presented. Chapter 3

presents the study of memory effect of four bulk metallic glasses. The concept of memory effect in this chapter is closely correlated with the concept of structural relaxation in Chapter 2. As in Chapter 2, the memory effect is discussed extensively based upon the measured calorimetric data and the modeling is also presented. In Chapter 4, the study of crystallization kinetics of three bulk metallic glasses is presented. The discussion of the crystallization in this chapter was based upon the isothermal and non-isothermal data measured by using calorimetry. The study of electrical resistivity of two bulk metallic glasses is presented in Chapter 5. The characteristics of structural relaxation and electrical properties of these glasses are discussed based upon the electrical resistivity data. Chapter 6 presents the study of diffusion between a bulk metallic glass and a crystalline metal. This chapter describes the results of the diffusion couple experiments. Chapter 7 presents the investigation of the existence of residual entropy in glasses. In this chapter, the investigation was based upon the measured data of two bulk metallic glasses and the data of other glasses provided in the literature. Finally a summary of this research is given in Chapter 8.

CHAPTER 2

STRUCTURAL RELAXATION PROCESS AND ITS MODELING

2.1 Introduction

In general, properties of a glass change with time at a rate that increases with higher temperatures. Therefore, its physical properties depend upon its thermal history and change during its use as a device or as a design-material. By studying the structural relaxation of a glass, one can predict the changes in properties of a glass with time. To elaborate when a glass is heated toward its glass-softening temperature or when a glass is cooled, all its physical properties change not only with temperature but also with time. Moreover, when a glass is kept at a certain temperature, its properties change with time. Change in properties during structural relaxation of glasses in general has been generally studied by measuring the enthalpy, volume and viscosity (Scholze and Kreidel 1986), mechanical modulus (Cavaille et al 1986, Muzeau et al 1992), refractive index (Macedo and Napolitano 1967), magnetic behavior (Guo et al 1986), electrical and thermal resistivities (Balanzat 1980, Balanzat et al 1985), dielectric polarization (Johari 1982, Pathmanathan et al 1986), and localized motions (Johari and Goldstein 1970, 1971).

Structural relaxation in metallic glasses has been extensively studied by Chen (1978a, 1981a), Scott et al (1980a, 1980b, 1980c), Berry and Pritchett (1973, 1981), Egami et al (1976, 1978a, 1978b, 1982), Taub et al (1980, 1981), Shim and Johari (1999),

Johari and Shim (2000). Based on the study of structural relaxation in multicomponent metallic glasses, Egami (1977, 1986) and Elliot (1983) concluded that there is a distinction between the topological short range order (TSRO) and the chemical short range order (CSRO). They have discussed the change of TSRO and CSRO of metallic glasses due to annealing or ageing. X-ray and electron diffraction measurements have been used to test the validity of this concept but little is known about the atomic diffusion processes occurring either during the isothermal annealing or during heating toward T_g . Buekel and Radelaar (1983) have described structural relaxation is associated with two separate TSRO and CSRO processes. Based on their study of structural relaxation in several Pd- and (Fe, Ni)- based metal-metalloid glasses and Zr-(Cu,Fe,Ni) binary and ternary metallic glasses, Inoue et al (1984, 1985) have concluded that at low temperatures structural relaxation occurs by local and medium range rearrangement of the atoms with weak bonding. In contrast, at high temperatures it occurs by the long range cooperative regrouping of metal and metalloid atoms.

Johari and coworker (1999, 2000) studied several Ni-based metallic glasses and organic and inorganic glasses. They found that there is no difference between structural relaxation in metallic glasses and other types of glasses when the distribution of self-diffusion times is considered. They showed that structural relaxation of metallic glasses can be simulated by the same stretched-exponential relaxation function of diffusion times and non-linearity of relaxation behavior as used for polymeric and inorganic glasses. This similarity led to the conclusion that structural relaxation of metallic glasses instead involves changes in both TSRO and CSRO. They concluded that the origin of the

relaxation is seen in the time- and temperature-dependent achievement of the equilibrium state. Those local groups of atoms, whose diffusion is fast enough to allow loss of enthalpy and entropy on their approach to an equilibrium configurational state of low energy on annealing, absorb heat to reach their new equilibrium configuration state of higher energy at a higher temperature on heating at a certain rate. Hence each mode of atomic diffusion in the structure has its own ‘mini glass-transition temperature’, and reversible relaxation is a reflection of a broad distribution of times arising from temporal and spatial variations in the atoms’ environment.

The study described here is intended to further examine the various conclusions reached in earlier studies with both technological and academic viewpoint. Three papers based upon part of this study have been published (Johari and Aji 2008, 2010, Aji and Johari 2010).

2.2 Experimental Methods

2.2.1 Materials: Bulk Metallic Glasses

Bulk metallic glasses (abbreviated in the literature as BMGs) of ternary, quaternary, and pentary compositions (i) $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, (ii) $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, (iii) $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and (iv) $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ were prepared by the group at Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing, China. These were given to us by Dr. Ping Wen who spent seven months in our research group learning theoretical aspects of glass science and performing studies on polymers. The Beijing group had prepared these glasses by arc-melting of an

accurately weighed mixture of pure elements under a titanium-gettered argon atmosphere and transferring the melt to a water-cooled copper crucible. To homogenize the melt, the glassy solid was melted two to four times and re-cooled and they prepared samples as 1 - 3 mm thick, 5 - 10 mm wide, and 50 - 100 mm long plate or as 3 - 5 mm diameter 50 - 100 mm long rod, the latter by suction casting in a copper mold. Their glassy nature was already characterized by diffraction methods (Wang et al 2000a, 2006, Xi et al 2005a) and calorimetry (Wang et al 2001, 2006, Xi et al 2005a) and their mechanical properties (Wang et al 2003, 2006, Xi et al 2005b) have been published. The samples given to us were broken pieces of their as-cast plates and cylinders, that had been in storage for a period of at least 4 months at ambient temperature.

2.2.2 Differential Scanning Calorimetry and Measurements

A Pyris Diamond Perkin Elmer differential scanning calorimetry (DSC) was used for heat measurement. Briefly, the reference holder and sample holder in this instrument are each provided with individual heaters and thermometers as illustrated in Fig. 2.1A and the core of the sample and reference holders is illustrated in Fig. 2.1B. The DSC uses a ‘null-balance’ principle. During heating, cooling or isothermal holding, the temperature of the reference and sample is measured. If there is an endothermic or exothermic process in the sample, a temperature difference between the reference and sample will be detected, therefore the feedback built into the instrument by adding or subtracting power to the reference or sample to remove this temperature difference. As the output, the DSC records the heat flow, dH/dt , which is proportional to the difference between the heat input to the reference and to the sample.

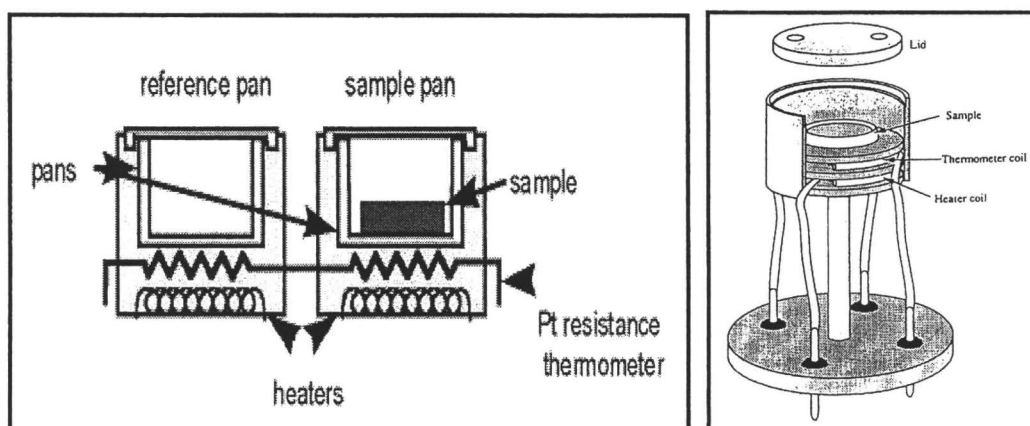


Fig. 2.1. Schematic diagram of the DSC sample holders (left, source: Ref. a) and the heater and sensor connections (right, source: Ref. b).

The sample is held in a sealed metal pan to avoid contamination of the sample holder. The sample pan and reference pans are made from aluminum, stainless steel, platinum or carbon. The aluminum pans used had a 5 mm diameter, 2 mm height, 0.1 mm thickness and a nominal mass of 20 mg. An empty aluminum pan, as a reference pan, is placed in the reference compartment to balance the thermal mass with that of the sample compartment in which the sample pan is placed. The samples used had typical sample masses between 3.5 to 13 mg with an accuracy of 0.01 mg. The thermal lag between the samples and the heaters is minimized by using small sample masses and crimp-sealed pan. A continuous flow of 99.9 % pure argon purges at approximately 25 psi through the cell, and this maintains an inert environment for the sample. The temperature range over which the samples are studied is from 373 K to 723 K.

The recorded heat flow, $(dH/dt)_q$, is proportional to the specific heat, C_p , of the sample. Therefore, a change in C_p of the sample due to any thermal event manifests itself

as a change in $(dH/dt)_q$, where the heating or cooling rates q are fixed. By using different mass of the sample, it was ensured that the $(dH/dt)_q$ divided by the sample's mass differed by less than 0.2 %. Thus the effect of the samples' mass on the measured values were negligible. A baseline $(dH/dt)_q$ signal was recorded with the empty pans placed in the reference and sample compartments and was subtracted from the measured $(dH/dt)_q$ signal in real time measurement. This minimized the errors of the data arising from the difference in the sample pan weight and thermal lag. In addition to reduce the thermal drift, the DSC was stabilized in the temperature range of interest for at least one hour. The correction for the thermal lag of the instrument was 0.5 K for a heating rate of 20 K/min. The DSC was calibrated periodically. Pure indium and zinc metals were used as the accurate calibrating standards. Their $\Delta H_{\text{(fusion)}}$ s are 28.57 J/g and 111.98 J/g for zinc and indium, respectively, and melting points are 429.75 K and 692.68 K for indium and zinc, respectively (Lide 2000). The latent heat and melting temperatures for both standards measured by the DSC deviated by less than 0.15 J/g and 0.05 K. The sensitivity of heat flow signal of the DSC is 0.01 mJ/s.

Before cutting the as-cast pieces of the specimens by using diamond cutting saw with oil cooling to keep the specimens at ambient temperature, surfaces of the specimens were ground using a sand paper to remove any impurity and oxides. The shape of the cut sample was made such that its surface made a good thermal contact with the pans. Repeat measurements showed that the metallic glass sample or its components did not chemically react or form an alloy with the aluminum pan over the temperature range of the study.

2.2.3 Calorimetric Procedure for Structural Relaxation Study

It was necessary to determine first the glass-softening temperature T_g and the onset of crystallization temperature of the metallic glass so that the temperature range for our study could be determined. To note again, T_g is defined as the temperature at which the structural relaxation time of a glass on heating at 20 K/min rate reaches 100 s and it appears as the onset temperature for the endothermic rise in a DSC scan or in C_p measurement. It was also necessary to remove the effect of inadvertent annealing of the as-cast sample during storage and/or its handling prior to the experiments. As an example of this procedure, we describe a typical study for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass: The sample was first heated at a rate, q , of 20 K/min in the DSC from 333 K to 573 K. This led to its crystallization, as shown by the sharp exothermic minimum in the DSC scan shown in Fig. 2.2 at $T > 450$ K. There is also a broad exotherm at high temperature indicating further crystallization of the sample. From this scan, we obtain the onset crystallization temperature, T_x , as 473 K, and the temperature range of the supercooled ultraviscous liquid of about 433 – 473 K. Its low temperature region enlargement in Fig. 2.3 shows a broad exotherm over the 25 K range which is due to the structural relaxation on first heating of the as-cast sample and a glass-liquid transition endotherm in the 400 – 450 K range.

After this, a new as-cast sample was repeatedly heated at 20 K/min and cooled at 20 K/min three times from 333 K to 443 K. Fig. 2.4 shows the heating scans after cooling the sample. 1st heating is for the first time heating after its preparation, which shows an exotherm corresponding to the irreversible relaxation as is also seen in Figs. 2.2 and 2.3.

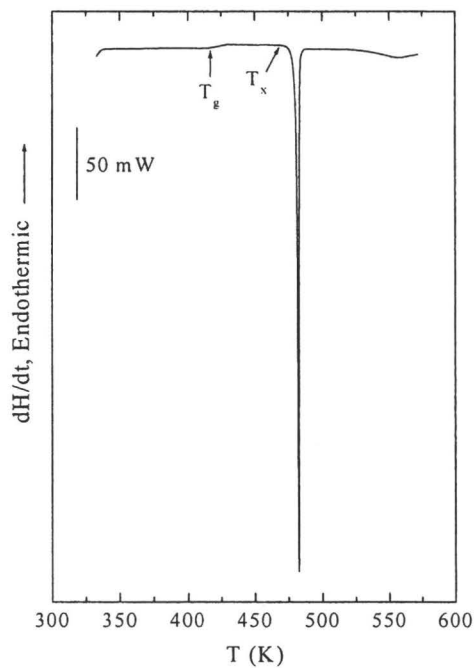


Fig. 2.2. The DSC scan of an as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate from 333 K to 573 K.

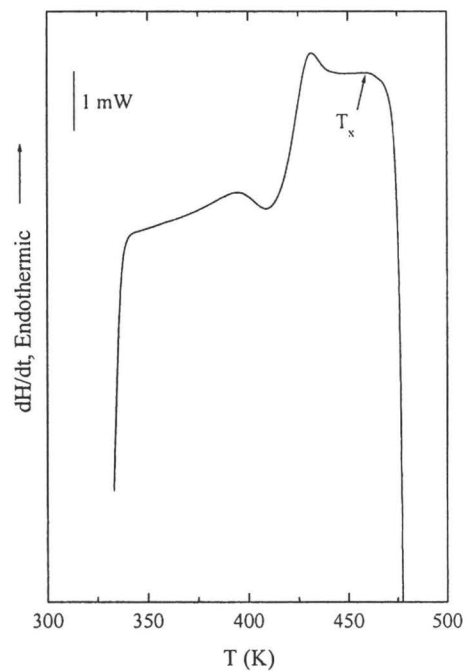


Fig. 2.3. Rescaling of the DSC scan for 300 to 500 K range in Fig. 2.2.

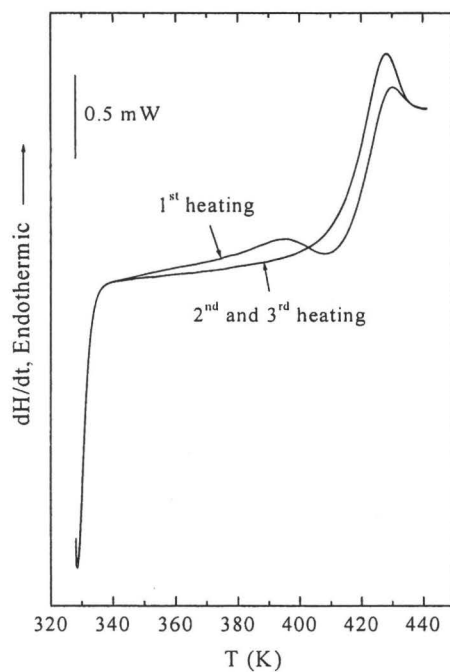


Fig. 2.4. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate from 333 K to 443 K repeated 3 times. 1st heating is after as-cast condition, 2nd and 3rd heatings are after cooling rate 20 K/min from 443 K to 333 K.

The 2nd and 3rd heatings show no exotherm corresponding to the irreversible relaxation seen in the first curve. These two scans show also the reversibility of the sample's state and its properties on heating and cooling several times. From these scans, we obtained the T_g of 415 K for the heating rate of 20 K/min and ΔC_p as 13.3 J/mol K.

For isothermal structural relaxation studies by annealing experiments, two sets of experiments were done, (i) for a fixed annealing time and different annealing temperatures and (ii) for a fixed annealing temperature and different annealing times. The temperature-time diagram for experiments (i), i.e., at a fixed annealing time and varied annealing temperatures is shown in Fig. 2.5A. The temperature-time diagram for experiments (ii), i.e., at a annealing temperature and varied annealing time is shown in

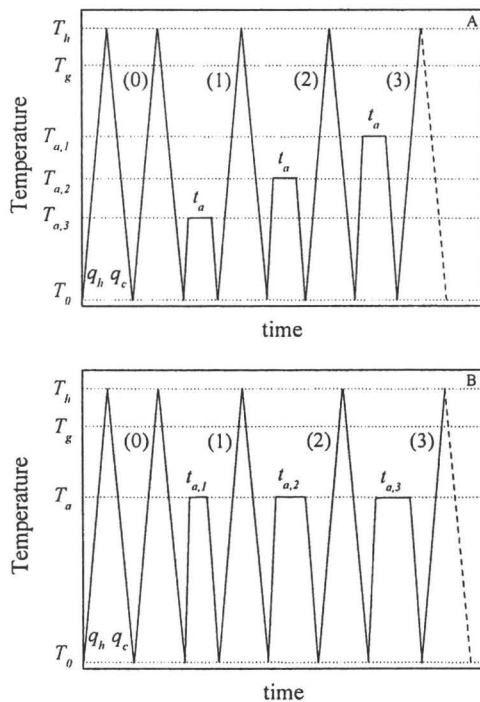


Fig. 2.5 The temperature – time diagram of thermal cycling used for isothermal annealing experiments for, (A) a fixed annealing time and different annealing temperatures, (B) a fixed annealing temperature and different annealing times.

Fig. 2.5B. Here T_0 is the temperature to which the sample was cooled, T_h is the highest temperature, T_a is the annealing temperature, t_a is the annealing time, and T_g is the glass-liquid transition temperature. The heating rate, q_h , and cooling rate, q_c , used for range $T_0 - T_h$ are 20 K/min.

Briefly, an (equilibrium) ultraviscous melt at a temperature, T_{eq} , is cooled at a (chosen) high rate, q_c , to a temperature, T_0 , which is 75% to 80% of the calorimetric T_g . It is then heated at a chosen rate, q_h , from T_0 to T_{eq} . The DSC scan obtained on heating in this case is for the unannealed sample, or for $t_a = 0$. The sample is then cooled from T_{eq} at the same rate, q_c , to T_0 and then heated at the fastest rate to the chosen annealing temperature, T_a , kept at T_a for a period of t_a min, cooled at the fastest rate to T_0 , and then immediately heated to T_{eq} at rate q_h and its DSC scan obtained. This scan is for the sample annealed for t_a min at T_a . The procedure is repeated for different annealing periods, t_a (1), t_a (2), etc., for the same T_a . It is also then repeated but at different T_a s. The sample is cooled back from T_{eq} to T_0 and then immediately heated at the fastest rate to a new T_a , say T_a (1), kept at T_a (1) for the same t_a as at the previous T_a . It is cooled back at the fast rate to T_0 and then finally heated to T_{eq} to obtain a new DSC scan. The procedure is repeated for a fixed t_a but for different T_a . The overall procedure is also then repeated but by changing t_a .

Finally, we use $Mg_{65}Cu_{25}Tb_{10}$ as an example to describe a typical annealing experiment for structural relaxation studies. In case (i) for isothermal annealing for a fixed t_a , the t_a s were 3, 5, and 7 min and the T_a s for each annealing time were 363 K, 368 K, 373 K, 378 K, 383 K, 388 K, 393 K, 403 K, 408 K, and 413 K. In case (ii) for

annealing at a fixed T_a , the T_a s were 363 K, 373 K, 383 K, 393 K, 403 K and 413 K, and for each temperature, the t_a s were 5, 10, 20, 60 and 120 min. These are summarized in Table 2.1.

Table 2.1. The conditions and values of T_a , t_a , T_0 , and T_h used for isothermal annealing for structural relaxation of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass.

T_g (K)	T_a (K)	t_a (min)	T_0 (K)	T_h (K)
415	363	5, 10, 20, 60, 120	333	443
	373		333	443
	383		333	443
	393		333	443
	403		333	443
	413		333	443
	363, 368, 373, 378,	3	333	443
	383, 388, 393, 398,	5	333	443
	403, 408	7	333	443

In the procedure I used, a new as-cast sample was heated from 333 K (initial temperature, T_0) to 443 K (upper temperature limit, T_h) at 20 K/min and cooled from 443 K to 333 K at 20 K/min, i.e., the heating rate (q_h) and cooling rate (q_c) used for range T_0 and T_h are 20 K/min. After this, the sample was heated and cooled again over the same temperature range and the same heating and cooling rate as for the first scan. The second heating scan was obtained for the unannealed sample. After the second cooling, the sample was heated at heating rate of 80 K/min to T_a of 363 K, held for 3 min at 363 K, and then cooled at 80 K/min to 333 K. The sample then heated at a heating rate of 20

K/min to 443 K and cooled at 20 K/min to 333 K. The heating scan obtained was the heating scan after annealing at T_a of 363 K for 3 min. The DSC scanning was repeated for the T_a s of 368 K, 373 K, 378 K, 383 K, 388 K, 398 K, 403 K, and 413 K for t_a of 3 min for each T_a , so the heating scans were obtained for T_a of 368 K, 373 K, 378 K, 383 K, 388 K, 398 K, 403 K, and 413 K for t_a of 3 min. Experiments were done also for t_a s of 5 and 7 min with other new as-cast samples for the same T_a s as given above.

The annealing experiments for the other glasses were performed in the same manner as on $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, but at different T_a , T_0 , and T_h . The details of the procedure for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ are summarized in Table 2.2, for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ in Table 2.3 and for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ in Table 2.4.

Table 2.2. The conditions and values of T_a , t_a , T_0 , and T_h used for isothermal annealing for structural relaxation of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass.

T_g (K)	T_a (K)	t_a (min)	T_0 (K)	T_h (K)
423	373	5, 10, 20, 60, 120	343	458
	383		343	458
	393		343	458
	403		343	458
	413		343	458
	383, 393, 403, 408, 413	3	343	458
		5	343	458
		7	343	458

Table 2.3. The conditions and values of T_a , t_a , T_0 , and T_h used for isothermal annealing for structural relaxation of of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass.

T_g (K)	T_a (K)	t_a (min)	T_0 (K)	T_h (K)
569	523	5, 10, 20, 60, 120	483	600
	533		483	600
	543		483	600
	553		483	600
	563		483	600
	513, 523, 533, 543, 553, 563, 573, 578	3	483	600
		5	483	600
		7	483	600

Table 2.4. The conditions and values of T_a , t_a , T_0 , and T_h used for isothermal annealing for structural relaxation of of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass.

T_g (K)	T_a (K)	t_a (min)	T_0 (K)	T_h (K)
622	563	5, 10, 20, 60, 120	513	663
	573		513	663
	583		513	663
	593		513	663
	603		513	663
	563, 573, 583, 593, 603, 608, 613, 618	3	513	663
		5	513	663
		7	513	663

2.3 Results and Data Analysis

Some of the irreversible relaxation of a typical metallic glass is seen in Fig. 2.4, where the first curve is the heating scan of a sample after its preparation and storage at

room temperature for about six months. It shows a shallow exothermic minimum in the 393 to 418 K range. This spontaneous process occurs in all metallic glasses heated for the first time after their preparation. This is due to spontaneous relaxation to a lower enthalpy state and it is called irreversible relaxation because the change of state of the glass due to relaxation cannot be reversed unless its preparation procedure is repeated after heating to the molten state. Fig. 2.6 shows the heating curves from experiments in which the as-cast sample was heated at 20 K/min from 333 K to 383 K (curve 1) and cooled at 20 K/min to 333 K. Then the sample was heated at 20 K/min to 388 K (curve 2) and cooled at 20 K/min to 333 K. The heating was repeated to temperatures 393 K (curve 3), 398 K (curve 4), 408 (curve 5), 418 (curve 6), and 443 K done three times (curves 7, 8, and 9).

In all annealing experiments to study structural relaxation, a great amount of time and effort was spent on ensuring that no crystallization occurred. Crystallization was evident when $(dH/dt)_q$ in its ultraviscous melt state was lesser than before. When that was found the data were rejected and new samples studied. Thus the criteria used was that a sample's original state is recovered when its $(dH/dt)_q$ value in the ultraviscous melt did not change. As an example of a case in which crystallization was evident, we show the DSC scans for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ in Fig. 2.7. These show that at 383 K, which shows the effect of annealing up to 120 min, the sample began to show signs of crystallization after annealing even after 5 min.

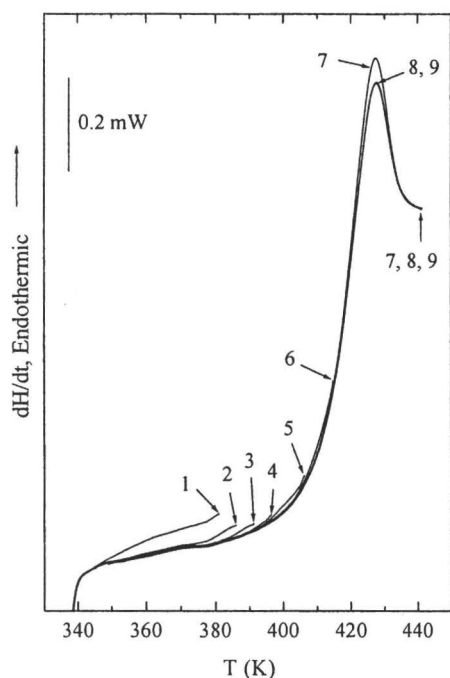


Fig. 2.6. The DSC scans of as-cast $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ during heating at 20 K/min rate from 333 K to 383 K (labeled 1), 388 K (labeled 2), 393 K (labeled 3), 398 K (labeled 4), 408 K (labeled 5), 418 K (labeled 6), and to 443 K (labeled 7, 8, 9) after cooling at 20 K/min rate before each heating except for the first heating (labeled 1) of the as-cast sample.

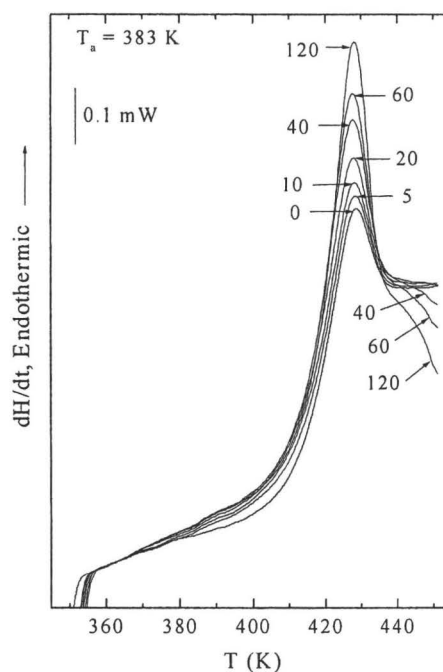


Fig. 2.7. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 383 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes. The figure shows that for annealing time of 40, 60, and 120 min partial crystallization occurs which interferes the observation of structural relaxation.

An isothermally annealed or structurally relaxed glass generally shows an endothermic feature or an ‘overshoot’ in the DSC scan (Moynihan et al 1976a, Chen 1981a, Inoue et al 1984, 1985, Scherer 1986, Gutzow and Schmelzer 1995, Hohne et al 2003). The DSC scans of the annealed and unannealed samples of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass obtained during heating at 20 K/min after annealing for a fixed annealing time at different annealing temperatures are shown in Figs. 2.8 – 2.10. (For convenience of reading and to save page space, several figures are put on one page. These can be enlarged to obtain the actual data. The relevant data have been given also in the tables to follow in the next

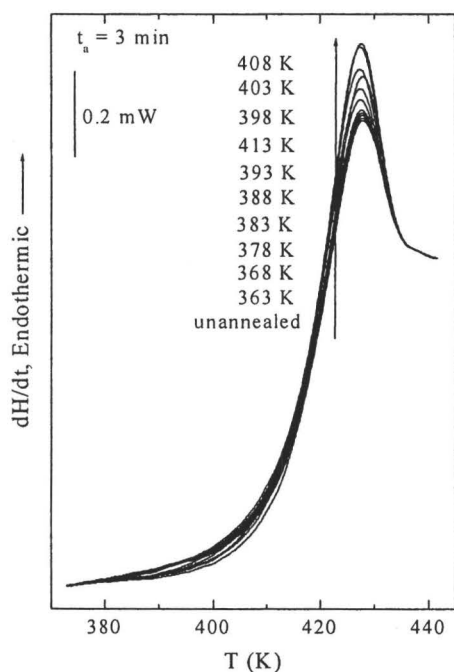


Fig. 2.8. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing for the annealing time of 3 min and the annealing temperatures at 368, 373, 378, 383, 388, 393, 403, 408, and 413 K.

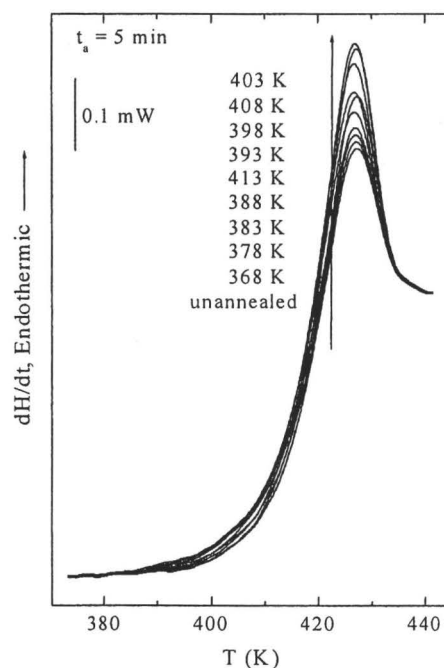


Fig. 2.9. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing for the annealing time of 5 min and the annealing temperatures at 368, 373, 378, 383, 388, 393, 403, 408, and 413 K.

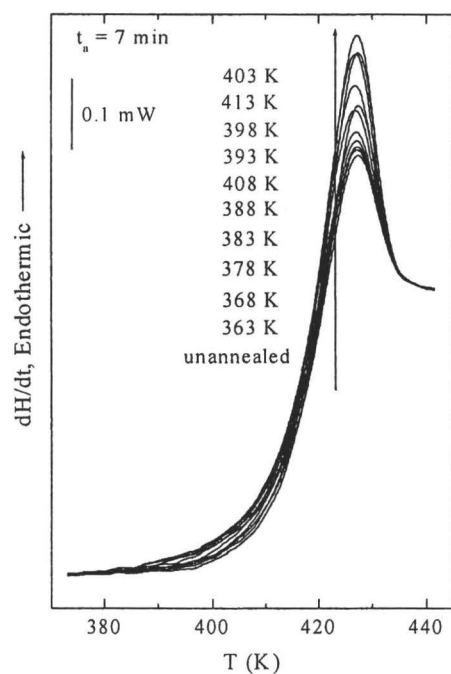


Fig. 2.10. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing for the annealing time of 7 min and the annealing temperatures at 363, 368, 373, 378, 383, 388, 393, 403, 408, and 413 K.

section.) The $(dH/dt)_q$ plot for annealed sample shows an excess endothermic heat flow or an overshoot. The $(dH/dt)_q$ measured in the scan was multiplied by molecular weight and divided by the mass of the sample and by the heating rate, q_h , and thus converted to (dH/dT) in units of J/mol K. The plots of (dH/dT) for t_a s of 3, 5, and 7 min are shown in Figs. 2.11A – 2.13A. The numbers shown refer to the annealing temperatures ordered according to the maximum of the curves. The difference between the annealed DSC scan and unannealed DSC scan, i.e., $[(dH/dT)_{annealed} - (dH/dT)_{unannealed}]$ is plotted against T in Figs. 2.11B, 2.12B, and 2.13B for t_a s of 3, 5, and 7 min, respectively. The DSC scans of the annealed and unannealed samples of $Mg_{65}Cu_{25}Tb_{10}$ obtained during heating at 20 K/min after annealing at a fixed T_a for different t_a s are shown in Figs. 2.14 – 2.19. The plots of (dH/dT) for T_a s of 363 K, 373 K, 383 K, 393 K, 403 K and 413 K are shown in Figs. 2.20A – 2.25A. The numbers labeled to the curves refer to the annealing time in minutes. The difference between the annealed DSC scan and unannealed DSC scan, i.e., $[(dH/dT)_{annealed} - (dH/dT)_{unannealed}]$ is plotted against T in Figs. 2.20B – 2.25B for T_a s of 363 K, 373 K, 383 K, 393 K, 403 K, and 413 K, respectively.

Similar experiments performed on structural relaxation of $Pr_{60}Cu_{20}Ni_{10}Al_{10}$, $Pd_{40}Ni_{10}Cu_{30}P_{20}$, and $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ glasses showed qualitatively similar plots to the $Mg_{65}Cu_{25}Tb_{10}$ glass. For the sake of brevity, their corresponding figures are not included. The conditions for their annealing experiment have already been given in Section 2.2.3, and the results obtained from the analysis of their data are tabulated along with the resulting figures in Section 2.4.

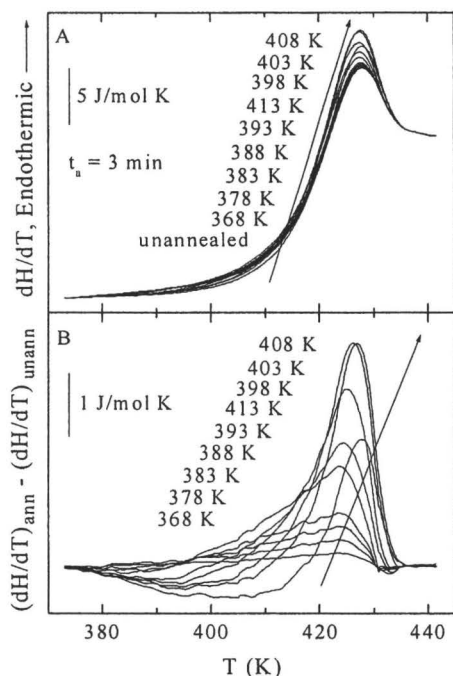


Fig. 2.11. A. The dH/dT plots for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass against the temperature after isothermal annealing for 3 min at different annealing temperatures. B. The difference curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass obtained by subtracting the DSC scan of the unannealed sample from the DSC scan of the annealed samples.

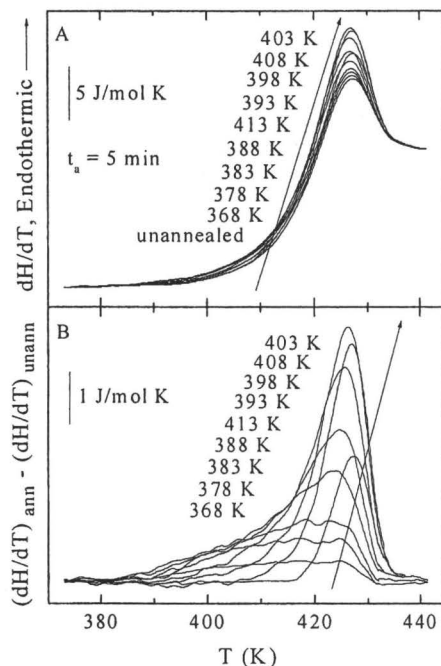


Fig. 2.12. A. The dH/dT plots for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass against the temperature after isothermal annealing for 5 min at different annealing temperatures. B. The difference curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass obtained by subtracting the DSC scan of the unannealed sample from the DSC scan of the annealed samples.

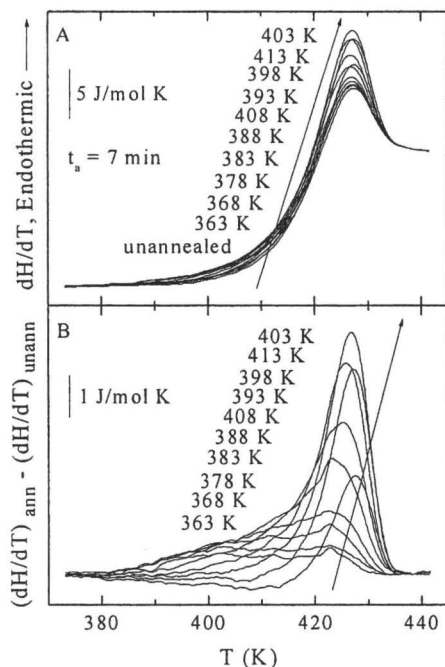


Fig. 2.13. A. The dH/dT plots for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass against the temperature after isothermal annealing for 7 min at different annealing temperatures. B. The difference curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass obtained by subtracting the DSC scan of the unannealed sample from the DSC scan of the annealed samples.

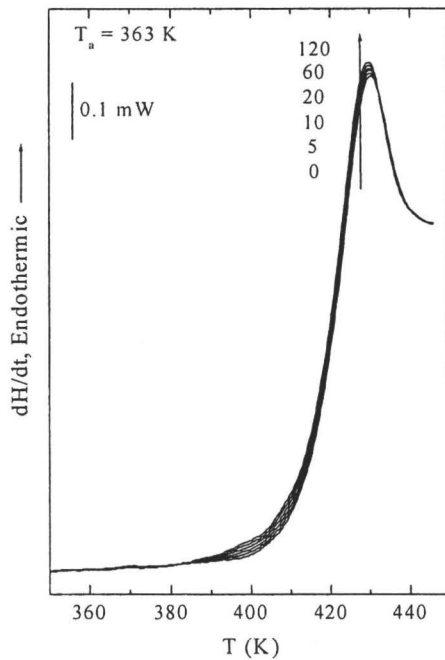


Fig. 2.14. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature at 363 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

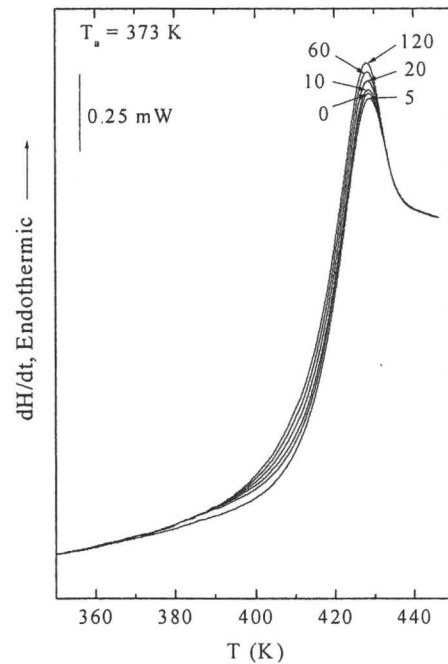


Fig. 2.15. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 373 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

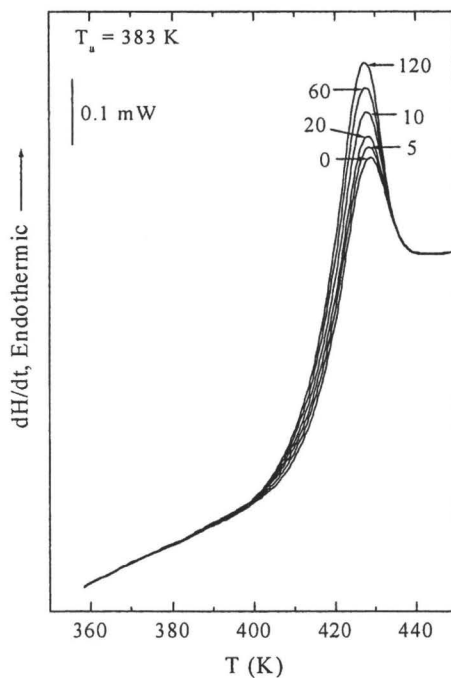


Fig. 2.16. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 383 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

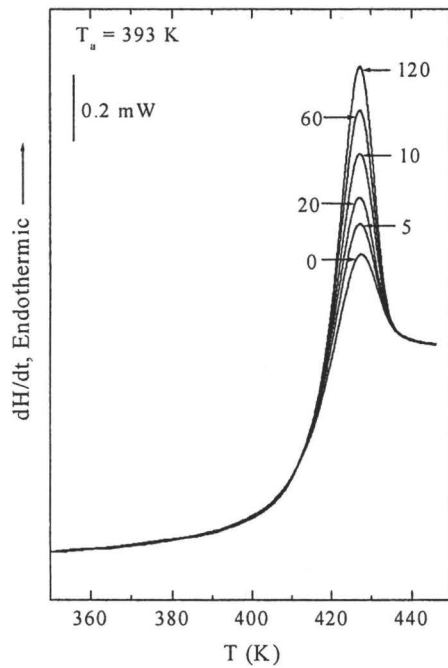


Fig. 2.17. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 393 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

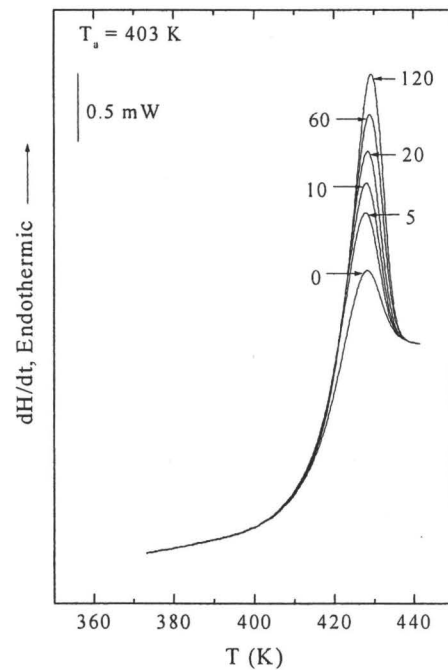


Fig. 2.18. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 403 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

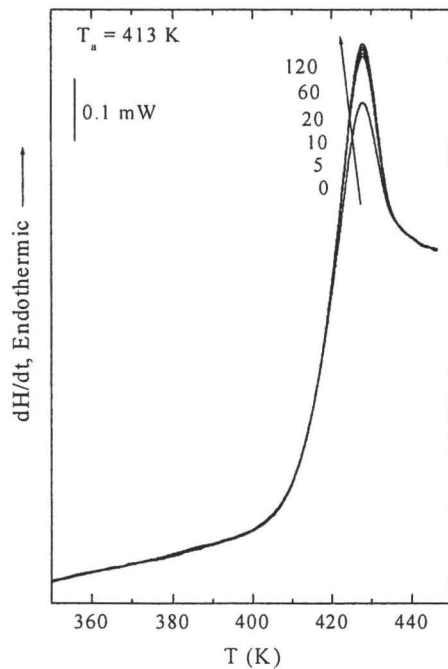


Fig. 2.19. The DSC scans of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at 20 K/min rate after isothermal annealing at annealing temperature of 413 K for different annealing times. The numbers labeled to the curves refer to the annealing time in minutes.

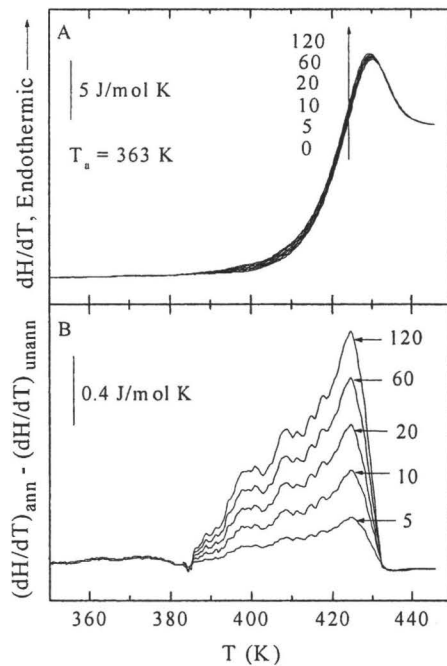


Fig. 2.20. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature after isothermal annealing at 363 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

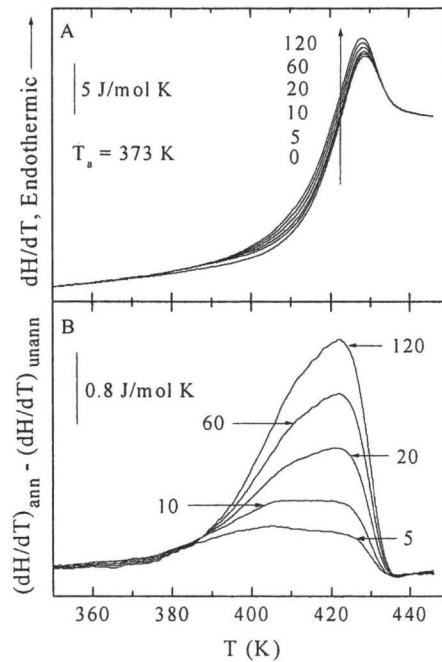


Fig. 2.21. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature after isothermal annealing at 373 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

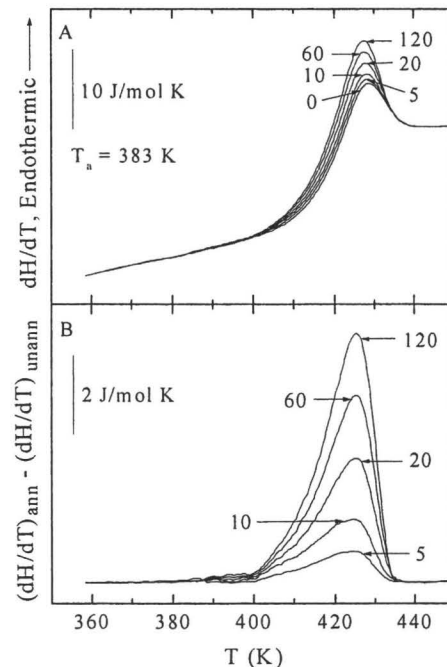


Fig. 2.22. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature after isothermal annealing at 383 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

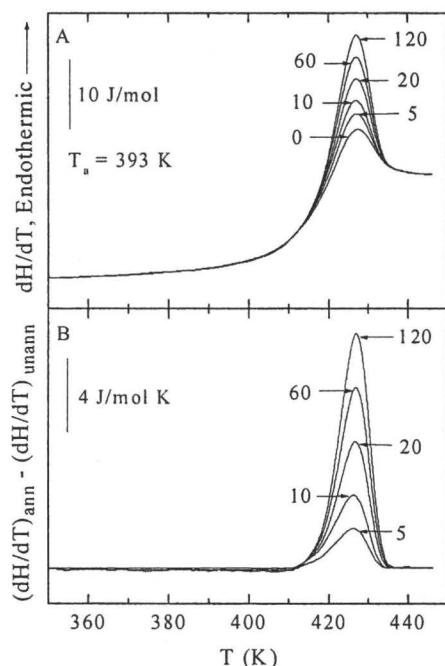


Fig. 2.23. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature after isothermal annealing at 393 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

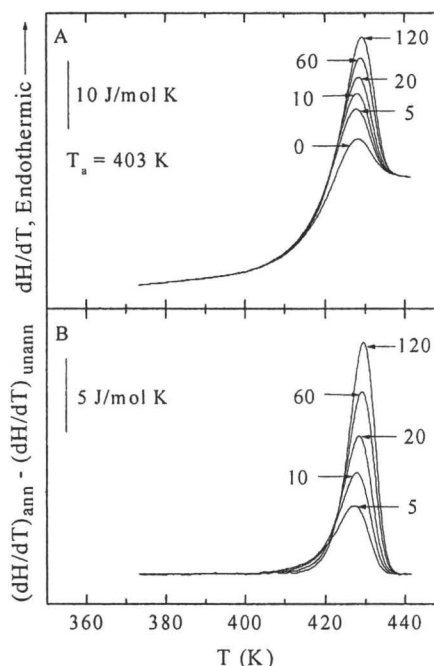


Fig. 2.24. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained after isothermal annealing at 403 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

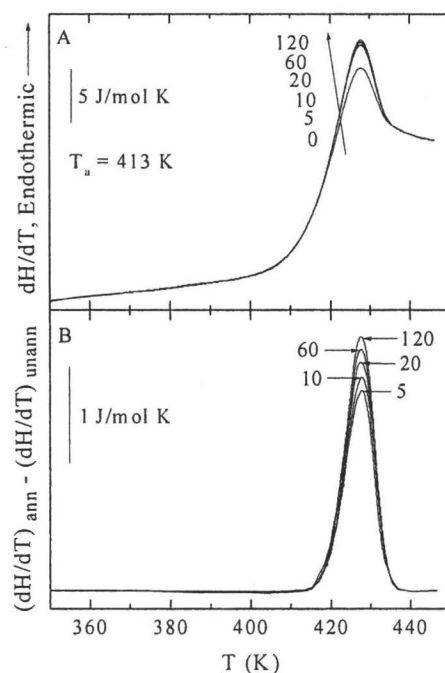


Fig. 2.25. A. The dH/dT plots for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained after isothermal annealing at 413 K for different annealing times. B. The difference curves for $Mg_{65}Cu_{25}Tb_{10}$ glass against the temperature obtained by subtracting the DSC scan of the unannealed sample (curve 0) from the DSC scan of the annealed samples.

2.4 Discussion

2.4.1 General Feature of Structural Relaxation

In general when a glass has been stored for a long period at a temperature not far below its T_g , its structure relaxes significantly and rapidly, and large changes in properties due to further structural relaxation are observed on heating it. This is also evident in Fig. 2.3 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass that had been stored at ambient temperature. Thermodynamically, its state during heating approaches a structure of lower energy and entropy. Moreover, in the production methods of a metallic glass by cooling inside a mold, some parts of the sample in the bulk cool more slowly than other parts. The resulting thermal gradients cause internal strains in the specimen across its thickness. When such a sample is heated, the elastic energy associated with internal strains is released and this also appears as an exothermic feature in the DSC scan. This feature is referred to as irreversible relaxation. Thus the feature observed at 393 – 418 K in the first heating scan in Fig. 2.4 is due to a combination of the loss of enthalpy and entropy as well as loss of (mechanical) internal strain in the sample. The amount of heat released from the latter is usually much less.

After the first heating of the as-cast sample from its glass to its supercooled liquid, any further relaxation that occurs on thermal cycling is referred to as reversible relaxation. In this reversible relaxation, the physical properties are recovered after subjecting the glass to a variety of thermal histories. Chen (1981a), Inoue et al (1985), and Haruyama and Asahi (1991) have shown this reversibility feature by first heating the glass to supercooled liquid state then performing the thermal cycling.

Figs. 2.8 – 2.25 show exothermic and endothermic features of the DSC scans on structural relaxation. Johari and Shim (2000) suggests that the decrease in enthalpy and entropy is as a result of: (i) localized atomic diffusion in the disordered structured, and (ii) changes in the phonon frequencies and the corresponding density of states.

2.4.2 Isothermal Structural Relaxation of Enthalpy and Entropy

On isothermal structural relaxation, H and S decrease with time, and density, frequency of vibrational modes, refractive index, and elastic modulus increase. The phenomenon studied at temperature not far below T_g is widely known as physical ageing in the polymer discipline and as annealing in the glass-making discipline. It is distinguished from another type of ageing that occurs at T far below T_g , such as the ageing of commercial silicate glasses at ambient temperature, whose density and refractive index also increase but by an almost imperceptible amount over a period of decades when a glass is kept at T of nearly half of its T_g , or lower. Such ageing was first reported by James Prescott Joule who had observed that the zero temperature point of a gas thermometer made from a silicate glass shifted with time over a period of 38.5 years (Joule 1884). Nemilov and Johari (2003, 2004) have discussed in details showing this ageing has a different mechanism than structural relaxation on physical ageing or on annealing.

For analyzing the t -, and T -dependence of H and S , we first use a general expression for the *irreversible* change and later use a phenomenological model used for molecular liquids (Moynihan et al 1976b), polymers (Hodge 1994) and inorganic melts (Pacheto et al 1994). The change in H is the sum of all the changes that occur during the

cooling of a liquid, during the time of annealing, and during the heating of a glass and is written as,

$$\begin{aligned}
 d\Delta H_a = & \left(\frac{\partial \Delta H_a}{\partial t_a} \right)_{T_a, q_h, q_c} dt_a + \left(\frac{\partial \Delta H_a}{\partial T_a} \right)_{t_a, q_h, q_c} dT_a \\
 & + \left(\frac{\partial \Delta H_a}{\partial q_c} \right)_{T_a, t_a, q_h} dq_c + \left(\frac{\partial \Delta H_a}{\partial q_h} \right)_{T_a, t_a, q_c} dq_h
 \end{aligned} \quad (2.1)$$

where $d\Delta H_a$ is the difference between the enthalpy of the glass before and after the annealing, q_h is the heating rate, q_c is the cooling rate, and other notations are as defined before. The derivatives imply change only in one direction, as is done in analyzing chemical kinetics equations and not in the usual thermodynamic equations. The corresponding change in S is given by,

$$\begin{aligned}
 d\Delta S_a = & \left(\frac{\partial \Delta S_a}{\partial t_a} \right)_{T_a, q_h, q_c} dt_a + \left(\frac{\partial \Delta S_a}{\partial T_a} \right)_{t_a, q_h, q_c} dT_a \\
 & + \left(\frac{\partial \Delta S_a}{\partial q_c} \right)_{T_a, t_a, q_h} dq_c + \left(\frac{\partial \Delta S_a}{\partial q_h} \right)_{T_a, t_a, q_c} dq_h
 \end{aligned} \quad (2.2)$$

where the terms have the same meaning as in Eq. (2.1). The prefix Δ is used to maintain that the H and S measured are with respect to the $H(0 \text{ K})$ and $S(0 \text{ K})$, respectively, and not the absolute values of H and S , where $H(0 \text{ K})$ and $S(0 \text{ K})$ are the enthalpy and entropy of the glass at 0 K. $H(0 \text{ K})$ decreases on annealing as the structure densifies, as does $S(0 \text{ K})$ because the randomness of the zero-point energy changes (Johari and Perez 1994). Thus Eqs. (2.1) and (2.2) include the effect of structural relaxation on the zero Kelvin

values of the enthalpy and entropy. All four terms in Eqs. (2.1) and (2.2) are of practical significance because they describe the changes in the state of a glass when T fluctuates during its storage, and its rate varies.

The first term on the right hand side of Eq. (2.1) represents the enthalpy loss with respect to the annealing time for fixed T_a , q_h , and q_c . The second term represents the enthalpy loss with respect to the annealing temperature for fixed t_a , q_h , and q_c . The third term represents the enthalpy loss with respect to the cooling rate for fixed t_a , T_a , and q_h and the fourth term represents the enthalpy loss with respect to the heating rate, for fixed t_a , T_a , and q_c . The magnitudes of the third and fourth terms are zero because q_h and q_c for the experiments are kept fixed. The first term was determined here from the plots in Figs. 2.20B – 2.25B, and the second term from the plots in Figs. 2.11B – 2.13B.

2.4.3 Glass-liquid Irreversible Path and Entropy

The spontaneity of structural relaxation makes the segment of the C_p path in the glass-softening range of its plot against T is irreversible in the sense that cooling and heating at the same rate do not yield the same values of C_p . Because of that, one may object to determining $d\Delta S_a$ from Eq. (2.2) here. Therefore, we first examine whether our analysis of the data to obtain $d\Delta S_a$ is valid, as follows, we use the criteria that if C_p path is irreversible, the T_f determined from the $C_p d\ln T$ integral would be very different from the T_f determined from the $C_p dT$ integral. Therefore, if we analyze the same set of DSC data in two ways, and determine T_f^S from the $C_p d\ln T$ integral and T_f^H from the $C_p dT$ integral and find the two to be the same, our use of $C_p d\ln T$ integral would be justified.

To do so, we determine the enthalpy change from the area between the curves, i.e., the $C_p dT$ integral from the plots in Fig. 2.4, as described by Moynihan et al (1976a),

$$\int_{T^*}^{T_f'} (C_p^{liq} - C_p^{glass}) dT = \int_{T^*}^{T_f'} (C_p - C_p^{glass}) dT \quad (2.3)$$

where T^* is any temperature above the transition region, C_p^{liq} is C_p of the liquid, C_p^{glass} is C_p of the glass, T is the temperature well below the glass transition region, and T_f' is the fictive temperature, which is noted here as T_f^H . Errors arising from this approximation are higher the longer is the extrapolation. Moynihan et al (1976a) had used DSC scans for q_h of 10 K/min, irrespective of q_c . Here, q_h of 20 K/min is used, because it is assumed that this rate yields $T_g (= T_f^H)$ at which the structural relaxation time of the liquid is 100 s. Pacheto et al (1994) and Johari and Aji (2008) had described its exceptions based on the width of the distribution. Also, these quantities are determined by using the DSC scans on the premise that the ratio of the heat flow (in J s⁻¹) to q_h , $[(dH/dt)/q_h]$, is proportional to C_p of the glass, including the thermal effects of structural relaxation on C_p . From area matching according to Eq. (2.3) we determine T_f^H of 411.3 K from scans 1 and 2 in Fig. 2.4. Similarly, we determine T_f^H of 403.2 K for the sample that had been annealed for 120 min at 403 K from the plot in Fig. 2.24A by area matching shown graphically in Fig. 2.26A. Note that both T_f^H values differ from the T_g of 415 K, that was obtained by the usual intersection method for scans 2 and 3 shown in Fig. 2.4.

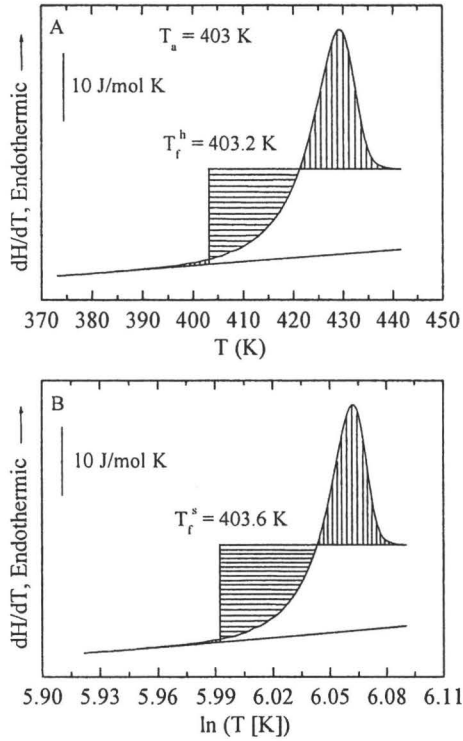


Fig. 2.26. A. The plots of C_p against T for determining T_f^H by matching the area shown by vertical lines with the area shown by horizontal lines. The sample was cooled at 20 K/min from 433 K to 333 K, annealed for 120 min at 403 K and reheated at 20 K/min. B. The same plots of C_p but against $\ln T$ for determining T_f^S by matching the area shown by vertical lines with the area shown by horizontal lines. Note that the $C_p dT$ integral yields the same T_f as the $C_p d\ln T$ integral.

To estimate T_f^S , we replace dT in Eq. (2.3) by $d\ln T$ to match the area for the entropy change,

$$\int_{T^*}^{T_f^S} (C_p^{liq} - C_p^{glass}) d\ln T = \int_{T^*}^{T_f^S} (C_p - C_p^{glass}) d\ln T \quad (2.4)$$

Similar area matching in C_p against $\ln T$ curves based on Eq. (2.4) yields T_f^S as 403.6 K as is shown in Fig. 2.26B for the sample annealed for 120 min at 403 K. It is evident that T_f^S and T_f^H are the same within the experimental and analytical errors, and therefore we may use Eq. (2.2) for determining the net entropy change.

2.4.4 Dependence of Structural Relaxation on the Annealing Temperature at a Fixed Annealing Time

To investigate the effects of the T_a for a fixed annealing time, we first determine the second term on the right hand side of Eqs. (2.1), and (2.2), i.e., the enthalpy and entropy loss when a glass is annealed at a selected T_a s for a fixed period. The magnitude of $d\Delta H_a$ of Eq. (2.1) was determined from the area of the difference between the annealed DSC scan and unannealed DSC scan, i.e., $[(dH/dT)_{annealed} - (dH/dT)_{unannealed}]$ plotted on a linear temperature scale using Eq. (2.5) shown in Figs. 2.11B – 2.13B for $Mg_{65}Cu_{25}Tb_{10}$, and $d\Delta S_a$ was determined from the area of the difference curve plotted on a logarithmic temperature scale using Eq. (2.6).

$$d\Delta H_a = \int_{T_1}^{T_2} \left[\left(\frac{dH}{dT} \right)_{annealed} - \left(\frac{dH}{dT} \right)_{unannealed} \right] dT \quad (2.5)$$

$$d\Delta S_a = \int_{T_1}^{T_2} \left[\left(\frac{dH}{dT} \right)_{annealed} - \left(\frac{dH}{dT} \right)_{unannealed} \right] d \ln T \quad (2.6)$$

The area under the peaks in the difference curves in Figs. 2.11B – 2.13B was integrated against T with a baseline at $dH/dT = 0$ and this gave the value of the enthalpy recovered on heating the annealed sample, which should be the same as the enthalpy lost on structural relaxation during isothermal annealing at a chosen T_a and t_a , plus any other enthalpy lost on heating when the sample does not crystallize or chemically react during cooling, annealing, or heating. To determine the entropy decrease on structural relaxation, the difference $[(dH/dT)_{annealed} - (dH/dT)_{unannealed}]$ was plotted against $\ln(T)$ instead of against T . The peak area in the difference curve of such a plot yielded the

entropy recovered on heating, which should be the same as the entropy decrease on structural relaxation at a chosen T_a and t_a . The enthalpy and entropy loss on annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ for a fixed t_a and different T_a s are summarized in Table 2.5.

Similar changes were observed on structural relaxation on annealing of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ samples for t_a s of 3, 5, and 7 min at different T_a s. These data are not tabulated. Instead, the decrease in ΔH and ΔS on annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ samples for t_a s of 3, 5, and 7 min at different T_a s is plotted against T_a in Figs. 2.27, 2.28, 2.29, and 2.30, respectively. In these figures, $d\Delta H_a$ and $d\Delta S_a$ reach a maximum value as T_a increases and then decrease, showing a broad peak. The decrease in enthalpy and entropy on structural relaxation is written as (Rudisser et al 1996),

$$\partial\Delta H_a(t_a, T_a) = \Delta H_a(T_a) \left[1 - \exp \left\{ - \left(\frac{t_a}{\tau} \right)^\beta \right\} \right] \quad (2.7)$$

$$\partial\Delta S_a(t_a, T_a) = \Delta S_a(T_a) \left[1 - \exp \left\{ - \left(\frac{t_a}{\tau} \right)^\beta \right\} \right] \quad (2.8)$$

where $\Delta H_a = [\Delta H(t_a = 0) - \Delta H(t_a \rightarrow \infty)]$, $\Delta S_a = [\Delta S(t_a = 0) - \Delta S(t_a \rightarrow \infty)]$ for a fixed t_a , β is the stretched exponential parameter ($0 < \beta < 1$), and τ is the characteristic structural relaxation time. The latter is written as, $\tau = \tau_0 \exp \left(\frac{E^*}{RT_a} \right)$, where τ_0 is the pre-exponential factor of the Arrhenius equation, E^* is the activation energy, and R is the gas

Table 2.5. The enthalpy and entropy loss during isothermal annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass for t_a s of 3, 5 and 7 min at different T_a s.

t_a (min)	T_a (K)	Enthalpy (J/mol)	Entropy (J/mol K)
3	363	6.39 ± 0.05	0.016 ± 0.005
	368	11.14 ± 0.05	0.028 ± 0.005
	373	16.91 ± 0.05	0.042 ± 0.005
	378	16.95 ± 0.05	0.041 ± 0.005
	383	28.59 ± 0.05	0.069 ± 0.005
	388	26.48 ± 0.05	0.063 ± 0.005
	393	31.73 ± 0.05	0.075 ± 0.005
	398	33.43 ± 0.05	0.079 ± 0.005
	403	29.25 ± 0.05	0.068 ± 0.005
	413	4.73 ± 0.05	0.010 ± 0.005
5	368	17.86 ± 0.05	0.044 ± 0.005
	373	26.22 ± 0.05	0.064 ± 0.005
	378	35.00 ± 0.05	0.085 ± 0.005
	383	47.14 ± 0.05	0.114 ± 0.005
	388	53.41 ± 0.05	0.128 ± 0.005
	393	62.27 ± 0.05	0.148 ± 0.005
	398	60.22 ± 0.05	0.142 ± 0.005
	403	48.51 ± 0.05	0.114 ± 0.005
	413	16.15 ± 0.05	0.037 ± 0.005
7	363	17.73 ± 0.05	0.044 ± 0.005
	368	24.45 ± 0.05	0.059 ± 0.005
	373	31.59 ± 0.05	0.077 ± 0.005
	378	39.62 ± 0.05	0.096 ± 0.005
	383	54.31 ± 0.05	0.131 ± 0.005
	388	59.28 ± 0.05	0.141 ± 0.005
	393	63.75 ± 0.05	0.151 ± 0.005
	398	61.02 ± 0.05	0.144 ± 0.005

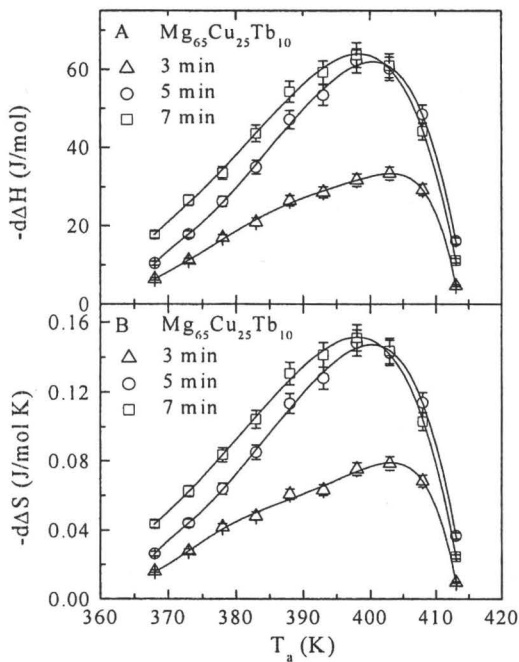


Fig. 2.27. The enthalpy and entropy loss are plotted against annealing temperature during isothermal annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass for the annealing time of 3, 5, and 7 min.

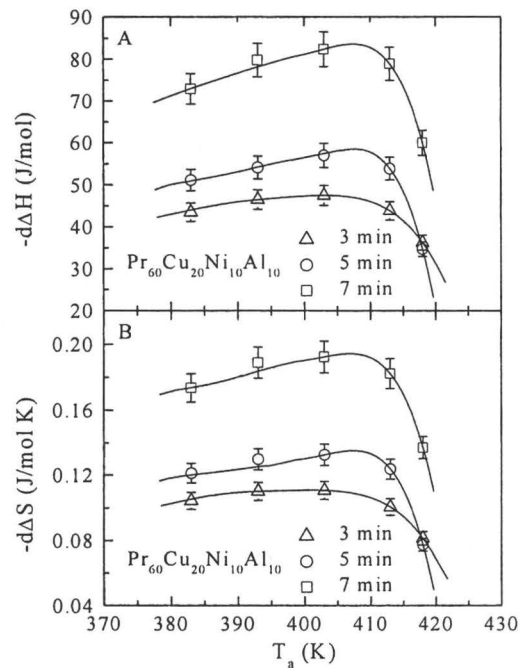


Fig. 2.28. The enthalpy and entropy loss are plotted against annealing temperature during isothermal annealing of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass for the annealing time of 3, 5, and 7 min.

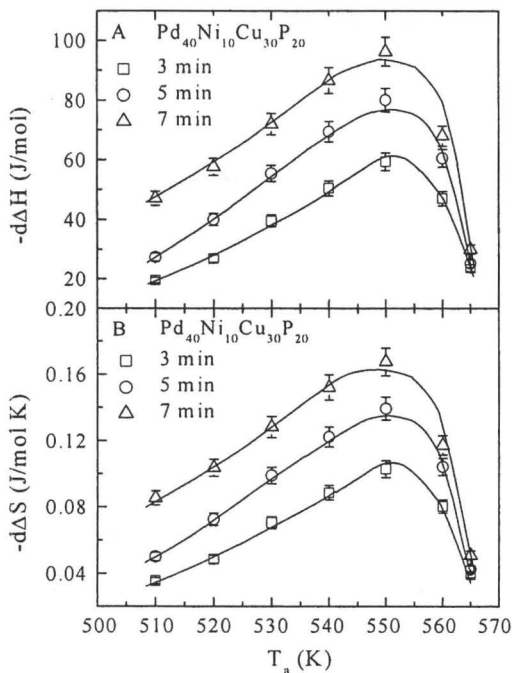


Fig. 2.29. The enthalpy and entropy loss are plotted against annealing temperature during isothermal annealing of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass for the annealing time of 3, 5, and 7 min.

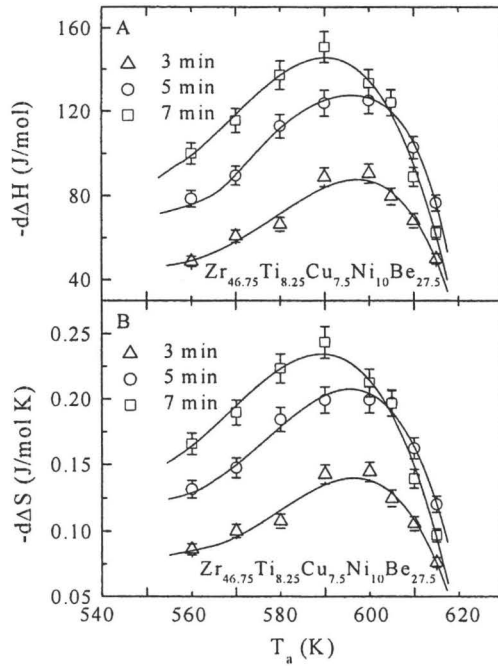


Fig. 2.30. The enthalpy and entropy loss are plotted against annealing temperature during isothermal annealing of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass for the annealing time of 3, 5, and 7 min.

constant. The shape of $d\Delta H$ and $d\Delta S$ plots against T_a as shown in Figs. 2.27 – 2.30 are determined by two processes. The first process is a kinetically limiting process that increases $d\Delta H$ and $d\Delta S$ as T_a is increased. This process is related to the relaxation time, τ . When T_a is increased, τ decreases rapidly so that at each T_a there is a progressive decrease in ΔH and ΔS . The second process is a thermodynamically limiting process that decreases the terms $\Delta H_a = [\Delta H(t_a = 0) - \Delta H(t_a \rightarrow \infty)]$ and $\Delta S_a = [\Delta S(t_a = 0) - \Delta S(t_a \rightarrow \infty)]$, as T_a is increased. The magnitudes of ΔH_a and ΔS_a decrease toward zero as T_g is approached on heating. For T_a s below the peaks, even though ΔH_a and ΔS_a are large, τ is exceedingly long, which makes the decreases in ΔH and ΔS are small, so the first process controls the relaxation. For T_a s above the peaks, even though τ is very short, ΔH_a and ΔS_a are small, which make the decreases in ΔH

and ΔS are small, so the second process controls the relaxation. Therefore, on structural relaxation for a fixed t_a and different T_a s, the conditions when a peak appears in $d\Delta H_a(t_a, T_a)$ and $d\Delta S_a(t_a, T_a)$ plots are,

$$-\frac{\partial \ln \Delta H_a(T_a)}{\partial T_a} = \frac{\beta t_a^\beta E^*}{\tau^\beta R T_{peak}^2} \quad (2.9)$$

$$-\frac{\partial \ln \Delta S_a(T_a)}{\partial T_a} = \frac{\beta t_a^\beta E^*}{\tau^\beta R T_{peak}^2} \quad (2.10)$$

where T_{peak} is the temperature of the peak. By rearranging Eqs. (2.9) and (2.10),

$$T_{peak} = \left(\frac{\beta t_a^\beta E^*}{-\tau^\beta R [\partial \ln \Delta H_a(T_a) / \partial T_a]} \right)^{1/2} \quad (2.11)$$

$$T_{peak} = \left(\frac{\beta t_a^\beta E^*}{-\tau^\beta R [\partial \ln \Delta S_a(T_a) / \partial T_a]} \right)^{1/2} \quad (2.12)$$

The behavior of metallic glasses on annealing for a fixed t_a and different T_a s here, as shown in Figs. 2.27 – 2.30, are also observed in polymers and other glasses (Chen 1981a, 1981b, Johari and Sartor 1997, Shim and Johari 1999, Johari and Shim 2000).

To illustrate the enthalpy and entropy loss, the plots of ΔH versus T at a fixed t_a for different T_a s for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ are shown in Figs. 2.31 – 2.33. These plots can be deduced by integrating the plots of (dH/dT) against T for determining the enthalpy, and the plots of (dH/dT) against $\ln(T)$ for determining the entropy from the plots shown in Figs. 2.11B – 2.13B. Since H and S of an equilibrium liquid at a temperature substantially above its T_g is independent of the path by which it is reached from the glassy state, we can determine the enthalpy and entropy at all temperatures between T_0

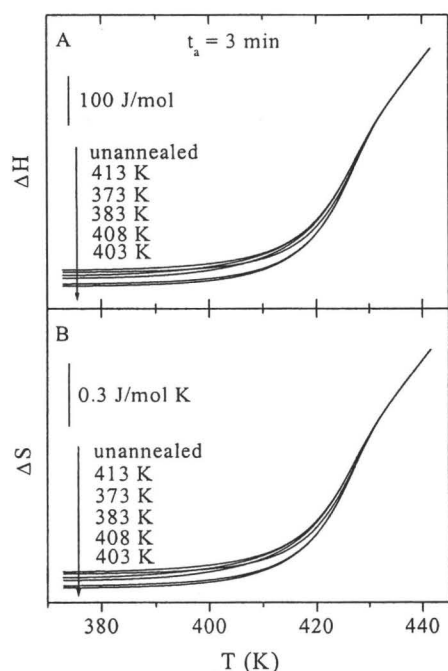


Fig. 2.31. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass are plotted against the temperature after isothermal annealing for 3 min at different annealing temperatures. The numbers shown refer to the annealing temperatures ordered according to the left edge of the curves.

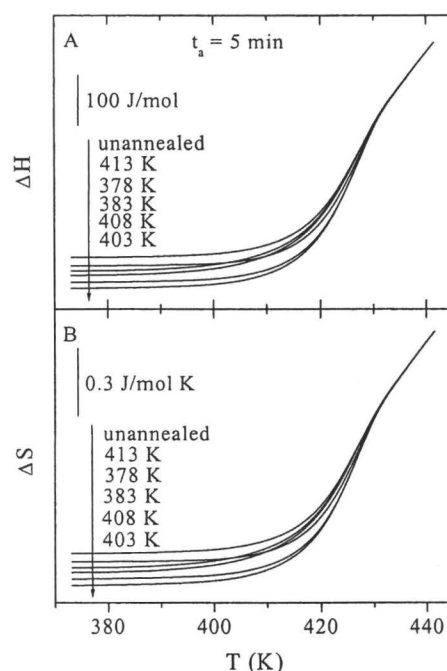


Fig. 2.32. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass are plotted against the temperature after isothermal annealing for 5 min at different annealing temperatures. The numbers shown refer to the annealing temperatures ordered according to the left edge of the curves.

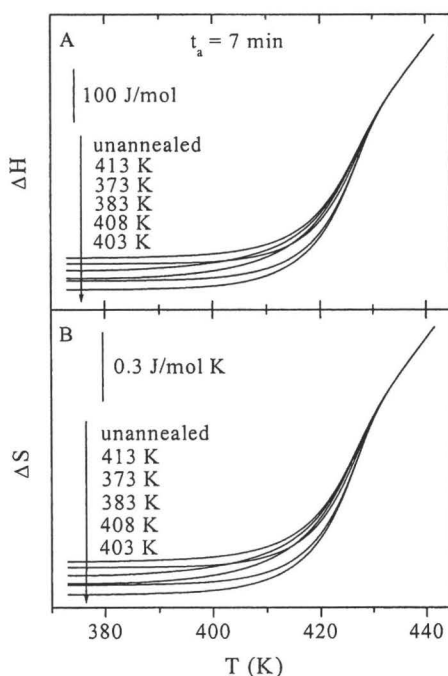


Fig. 2.33. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass are plotted against the temperature after isothermal annealing for 7 min at different annealing temperatures. The numbers shown refer to the annealing temperatures ordered according to the left edge of the curves.

and T_h from the relation,

$$\Delta H(T) = \left[\int_{T_0}^{T_h} \left(\frac{dH}{dT} \right) dT \right]_{\text{unannealed}} - \left[\int_{T_0}^{T_h} \left(\frac{dH}{dT} \right) dT \right]_{\text{annealed}} \quad (2.13)$$

$$\Delta S(T) = \left[\int_{T_0}^{T_h} \left(\frac{dH}{dT} \right) d \ln T \right]_{\text{unannealed}} - \left[\int_{T_0}^{T_h} \left(\frac{dH}{dT} \right) d \ln T \right]_{\text{annealed}} \quad (2.14)$$

where (dH/dT) is determined from DSC. Thus the $\Delta H(T)$ and $\Delta S(T)$ plots against T for all t_a and T_a condition would merge in the equilibrium liquid state. The recovery of the enthalpy and entropy on heating the metallic glasses in Figs. 2.31 – 2.33 shows a more rapid increase in H and S for the annealed sample than that for the unannealed one. The difference between the curves for the unannealed sample and the annealed sample vanishes at annealing temperatures near T_g , where metastable, supercooled sample reaches its state of a thermodynamic equilibrium on heating at 20 K/min. Above this temperature, the sample's properties become time-invariant on heating at 20 K/min and independent of thermal history.

2.4.5 Dependence of Structural Relaxation on the Annealing Time at a Fixed Annealing Temperature

The decrease in ΔH and ΔS on structural relaxation during annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ samples at a fixed T_a for different t_a s is determined from the area of the curves in Figs. 2.20B – 2.25B using Eqs. (2.5) and (2.6) and is tabulated in Table 2.6. The results for ΔH and ΔS on similar annealing were qualitatively similar for the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses. For

Table 2.6. The enthalpy and entropy loss during isothermal annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass at several fixed annealing temperature and different annealing times.

T_a (K)	t_a (min)	Enthalpy (J/mol)	Entropy (J/mol K)
363	5	7.98 ± 0.05	0.020 ± 0.005
	10	12.91 ± 0.05	0.032 ± 0.005
	20	17.81 ± 0.05	0.043 ± 0.005
	60	22.73 ± 0.05	0.055 ± 0.005
	120	29.60 ± 0.05	0.072 ± 0.005
373	5	21.47 ± 0.05	0.054 ± 0.005
	10	31.81 ± 0.05	0.079 ± 0.005
	20	45.89 ± 0.05	0.113 ± 0.005
	60	59.99 ± 0.05	0.146 ± 0.005
	120	74.07 ± 0.05	0.179 ± 0.005
383	5	24.06 ± 0.05	0.058 ± 0.005
	10	48.13 ± 0.05	0.116 ± 0.005
	20	78.49 ± 0.05	0.189 ± 0.005
	60	107.81 ± 0.05	0.259 ± 0.005
	120	137.44 ± 0.05	0.330 ± 0.005
393	5	53.35 ± 0.05	0.126 ± 0.005
	10	70.67 ± 0.05	0.171 ± 0.005
	20	96.17 ± 0.05	0.214 ± 0.005
	60	118.54 ± 0.05	0.283 ± 0.005
	120	144.01 ± 0.05	0.332 ± 0.005
403	5	52.88 ± 0.05	0.125 ± 0.005
	10	71.75 ± 0.05	0.169 ± 0.005
	20	90.91 ± 0.05	0.213 ± 0.005
	60	111.84 ± 0.05	0.261 ± 0.005
	120	132.74 ± 0.05	0.310 ± 0.005
413	5	21.27 ± 0.05	0.050 ± 0.005
	10	21.99 ± 0.05	0.052 ± 0.005
	20	21.91 ± 0.05	0.052 ± 0.005
	60	22.57 ± 0.05	0.053 ± 0.005
	120	23.24 ± 0.05	0.055 ± 0.005

maintaining brevity, those data and multiple figures are not shown here. Those data have been plotted in the figures given later here from which the values may be read.

The decrease in ΔH and ΔS on structural relaxation during annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ samples at various T_a s for different t_a s is plotted against annealing time in Figs. 2.34 – 2.37. The continuous lines through the data points for the enthalpy and entropy loss, ΔH and ΔS , were calculated using Eqs. (2.7) and (2.8) and the values of the fitting parameter are shown in Table 2.7, 2.8, 2.9, and 2.10 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, respectively. The decrease in ΔH and ΔS on annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ is plotted against temperature on heating in Figs. 2.38 – 2.43. In these figures, the curve labeled 0 is for the unannealed sample and the curves labeled 5, 10, 20, 60, and 120 are for the annealed samples referring to the annealing time in minutes at a certain annealing temperature.

2.4.6 Theoretical Consideration for Structural Relaxation

In 1937, Bernal had concluded that C_p in the liquid state varies with T partly due to change in the liquid's structure and partly due to change in the molecular vibrational frequency. The change in the H and S observed on heating a glass are therefore attributable to an increase in the configurational and vibrational contributions at a fixed T . The decrease in H and S on structural relaxation at a fixed T_a is therefore due to attainment of configurationally low energy state as well as vibrationally different, less anharmonic (low-energy) state of lower C_p . On heating a glass, the configurational and vibrational contributions decrease due to structural relaxation, and increase with increase

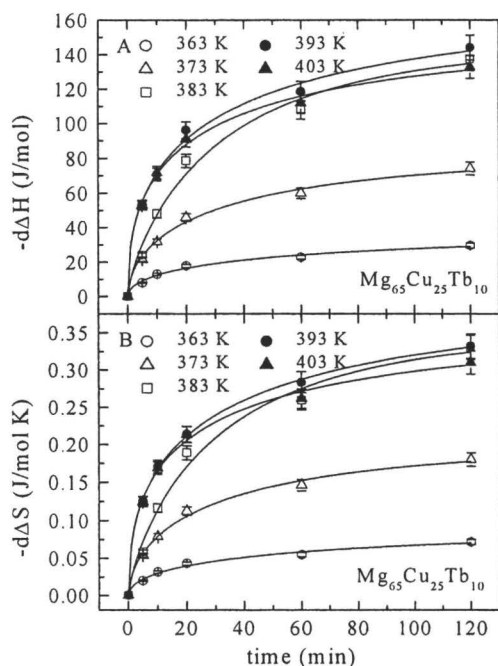


Fig. 2.34. The enthalpy and entropy loss are plotted against the annealing time during isothermal annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass at annealing temperature of 363 K, 373 K, 383 K, 393 K, and 403 K.

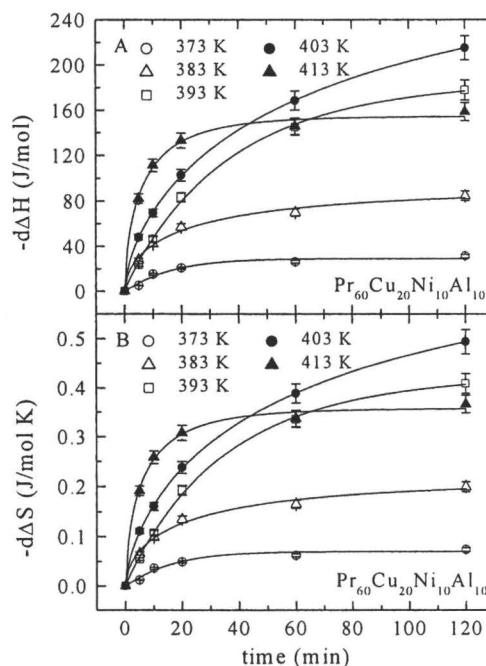


Fig. 2.35. The enthalpy and entropy loss are plotted against the annealing time during isothermal annealing of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass at annealing temperatures of 373 K, 383 K, 393 K, 403 K, and 413 K.

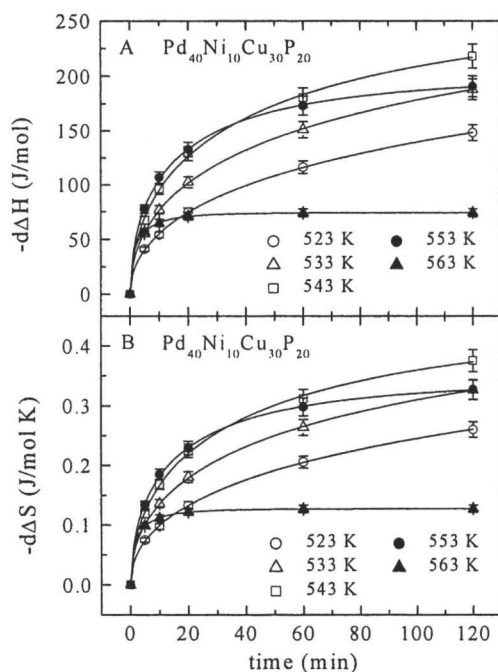


Fig. 2.36. The enthalpy and entropy loss are plotted against the annealing time during isothermal annealing of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass at annealing temperatures of 523 K, 533 K, 543 K, 553 K, and 563 K.

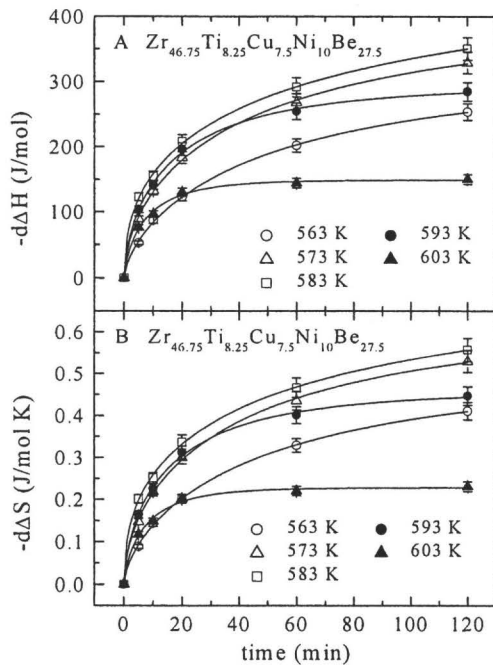


Fig. 2.37. The enthalpy and entropy loss are plotted against the annealing time during isothermal annealing of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass at annealing temperatures of 563 K, 573 K, 583 K, 593 K, and 603 K.

Table 2.7. The fitting parameters of the enthalpy and entropy loss during isothermal annealing of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass at a fixed annealing temperature for different annealing times.

$T_a \text{ (K)}$	$t_a \text{ (min)}$	$\Delta H_a \text{ (J/mol)}$	$\Delta S_a \text{ (J/mol K)}$	$\tau \text{ (min)}$	β
363	5, 10, 20, 60, 120	37.99 ± 0.03	0.09 ± 0.02	59.04 ± 0.01	0.52 ± 0.01
373	5, 10, 20, 60, 120	83.12 ± 0.03	0.20 ± 0.02	33.96 ± 0.01	0.58 ± 0.01
383	5, 10, 20, 60, 120	145.31 ± 0.03	0.35 ± 0.02	33.86 ± 0.01	0.76 ± 0.01
393	5, 10, 20, 60, 120	169.96 ± 0.03	0.39 ± 0.02	35.04 ± 0.01	0.48 ± 0.01
403	5, 10, 20, 60, 120	151.76 ± 0.03	0.36 ± 0.02	27.42 ± 0.01	0.47 ± 0.01
413	5, 10, 20, 60, 120	31.03 ± 0.03	0.07 ± 0.02	0.24 ± 0.01	0.05 ± 0.01

Table 2.8. The fitting parameters of the enthalpy and entropy loss during isothermal annealing of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass at a fixed annealing temperature for different annealing times.

T_a (K)	t_a (min)	ΔH_a (J/mol)	ΔS_a (J/mol K)	τ (min)	β
373	5, 10, 20, 60, 120	29.14 ± 0.03	0.07 ± 0.02	16.15 ± 0.01	0.54 ± 0.01
383	5, 10, 20, 60, 120	89.44 ± 0.03	0.21 ± 0.02	23.11 ± 0.01	0.58 ± 0.01
393	5, 10, 20, 60, 120	185.75 ± 0.03	0.43 ± 0.02	37.03 ± 0.01	0.64 ± 0.01
403	5, 10, 20, 60, 120	287.88 ± 0.03	0.65 ± 0.02	73.05 ± 0.01	0.64 ± 0.01
413	5, 10, 20, 60, 120	154.52 ± 0.03	0.36 ± 0.02	7.29 ± 0.01	0.65 ± 0.01

Table 2.9. The fitting parameters of the enthalpy and entropy loss during isothermal annealing of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass at a fixed annealing temperature for different annealing times.

T_a (K)	t_a (min)	ΔH_a (J/mol)	ΔS_a (J/mol K)	τ (min)	β
523	5, 10, 20, 60, 120	284.68 ± 0.03	0.49 ± 0.02	222.34 ± 0.01	0.49 ± 0.01
533	5, 10, 20, 60, 120	282.13 ± 0.03	0.48 ± 0.02	100.10 ± 0.01	0.50 ± 0.01
543	5, 10, 20, 60, 120	263.50 ± 0.03	0.45 ± 0.02	43.71 ± 0.01	0.55 ± 0.01
553	5, 10, 20, 60, 120	200.09 ± 0.03	0.34 ± 0.02	17.05 ± 0.01	0.57 ± 0.01
563	5, 10, 20, 60, 120	74.05 ± 0.03	0.13 ± 0.02	2.47 ± 0.01	0.54 ± 0.01

Table 2.10. The fitting parameters of the enthalpy and entropy loss during isothermal annealing of $\text{Zr}_{46.75}\text{Ti}_{18.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass at a fixed annealing temperature for different annealing times.

T_a (K)	t_a (min)	ΔH_a (J/mol)	ΔS_a (J/mol K)	τ (min)	β
563	5, 10, 20, 60, 120	309.25 ± 0.03	0.49 ± 0.02	54.53 ± 0.01	0.67 ± 0.01
573	5, 10, 20, 60, 120	398.62 ± 0.03	0.63 ± 0.02	47.75 ± 0.01	0.59 ± 0.01
583	5, 10, 20, 60, 120	491.19 ± 0.03	0.76 ± 0.02	74.65 ± 0.01	0.47 ± 0.01
593	5, 10, 20, 60, 120	293.72 ± 0.03	0.46 ± 0.02	18.46 ± 0.01	0.64 ± 0.01
603	5, 10, 20, 60, 120	148.88 ± 0.03	0.23 ± 0.02	8.40 ± 0.01	0.73 ± 0.01

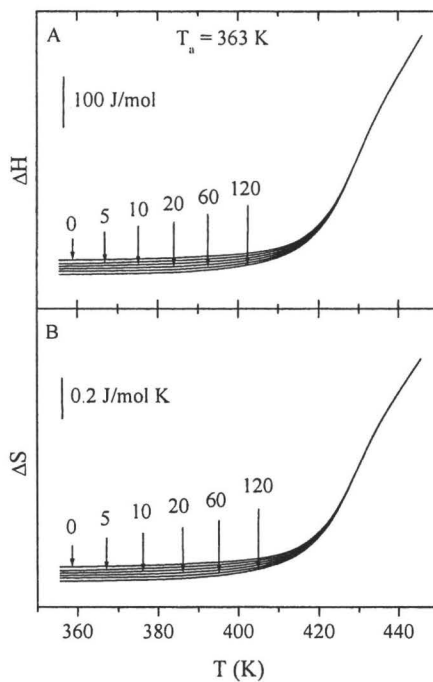


Fig. 2.38. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 363 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

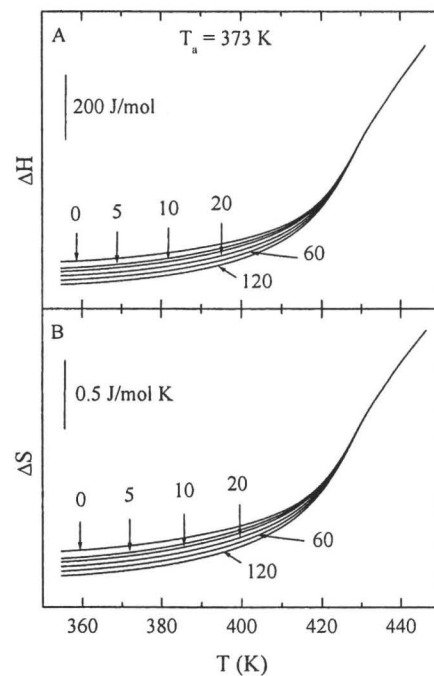


Fig. 2.39. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 373 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

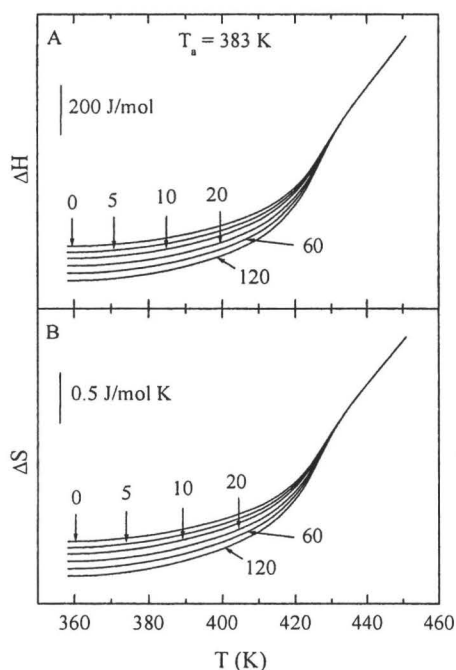


Fig. 2.40. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 383 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

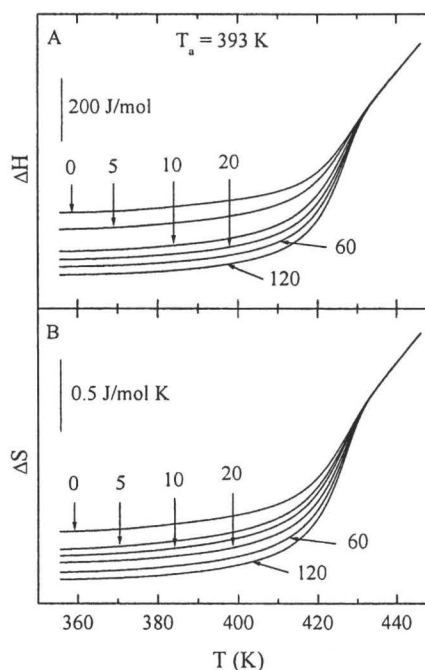


Fig. 2.41. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 393 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

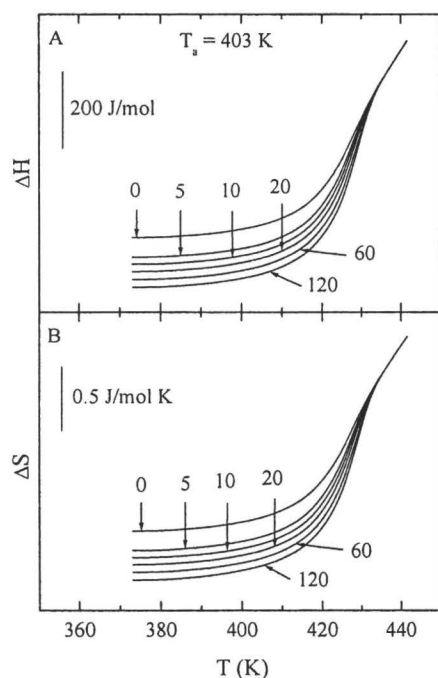


Fig. 2.42. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 403 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

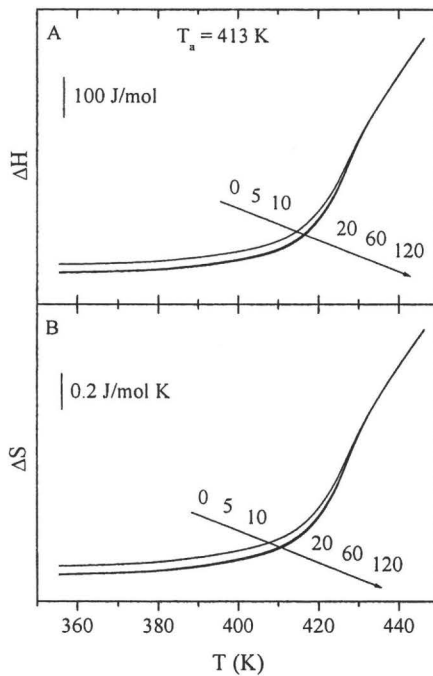


Fig. 2.43. The enthalpy and entropy loss of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 413 K for different annealing times are plotted against the temperature. The numbers labeled to the curves refer to the annealing time in minutes.

in T . The first dominates initially and the second dominates in the later stage and their rates cancel out at T where the peak appears in the plots in Figs. 2.27 – 2.30. While the physical origins of the two effects are common to all glasses, the vibrational contribution is usually ignored, even though it is significant because configurational states of high energy also have low vibrational frequencies and hence a large vibrational contribution.

For a metallic glass, there is also an entropy of mixing that is a part of the configurational entropy, and both would change with short range ordering of the structure, and both would kinetically freeze on cooling at the same temperature and unfreeze on heating. The maximum entropy of mixing for this glass is equal to $-R \sum_i x_i \ln x_i$, where R is the gas constant and x_i is the mole fraction of the component i .

Its value for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and

Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5} glasses is 7.12, 9.05, 10.64, and 11.15 J mol⁻¹ K⁻¹, respectively.

In earlier studies where the effect of the distribution of relaxation times was investigated in the glassy state (Shim and Johari 1999, Johari and Shim 2000), several metallic glasses and polymers were cooled from $T < T_g$, annealed and then heated back to the same $T < T_g$, i.e., thermally cycled in a T range below T_g , a similar but much smaller endothermic peak was observed. That endothermic peak was attributed to the unfreezing of the faster relaxation modes in the distribution of the main or the α -relaxation process. If Johari-Goldstein (JG) relaxation occurs at a rate comparable to these faster modes, its own strength would decrease on annealing, as is already known (Johari and Goldstein 1970, Johari 1982, Power et al 2002, Casalani and Roland 2009), and would be recovered on heating the glass. The recovery would appear as an overshoot of the type usually observed at $T > T_g$ and attributed to the α -relaxation. But when the rate of the JG relaxation is close to that of the α -relaxation or they appear at temperatures relatively close to each other, recovery of the JG relaxation configurations would be accompanied by the recovery of the faster modes in a distribution of the α -relaxation contributions. Thus the JG relaxation in a DSC scan can be distinguished only if its relaxation rate is much faster than that of the faster modes of the α -relaxation and its magnitude is relatively large.

The similarity of structural relaxation observed in glassy polymers and in metallic glasses (Shim and Johari 1999, Johari and Shim 2000) indicates that the concept and mathematical models which are used currently for interpreting the structural relaxation in

other glasses can be extended to metallic glasses. The atomic level processes on structural relaxation in all glasses are expected to be similar, where localized diffusion that allows a spontaneous decrease in H and S of a glass is a reflection of the approach of either the overall glass structure to a lower configurational H and S state, or of only those group of atoms in it that have been trapped in a high-energy minimum during the cooling of the glass. In one model, without configuring the atomic or molecular details, developed by Perez and coworkers (Perez 1988, 1992, Cavaille et al 1989, Johari and Perez 1994), the high energy sites in configurational space are termed defects, that is local groups of atoms whose potential energy corresponds to a point on either the attractive side of the potential energy minimum or the repulsive side of it. There are also alternative representations containing numerous minima of varying depths (Goldstein 1969, Johari 1982, Stlinger and Weber 1984, Frauenfelder et al 1994) with a possible of time dependence of the potential energy landscapes (Johari and Sartor 1996, Johari et al 2006a). Ichitsubo et al (2003, 2005, 2006) have found evidence for inter-dispersed regions of low and high densities in the structure of a glass. Thus they envisaged the structure of a glass as a composite of weakly bonded and strongly bonded regions. By studying accelerated crystallization caused by high-energy ultrasonic waves traveling through metallic glasses, they deduced that atoms in the weakly bonded regions or “islands of mobility” in the glass structure have a lower vibrational frequency. As these regions do not resist a shear stress, they argued that when the volume fraction of such regions is large their Poisson’s ratio is large. Since annealing decreases the fractional population of such regions, it would decrease the Poisson’s ratio. Based on Johari and

Shim (2000) discussions, the variations in the atomic environment in a glass structure leads to a distribution of diffusion coefficients, which may be expressed as a distribution of mainly the activation energy, E , in the Arrhenius equation, $D = D_0 \exp (-E/kT)$, where D_0 is the pre-exponential term and k the Boltzmann constant. On cooling, those atoms, which diffuse too slowly approaching their lowest configurational H and S state of their equilibrium disorder structure, become kinetically frozen-in. As the self-diffusion coefficient decreases progressively more rapidly on cooling, the majority of the atoms in the glass structure become kinetically frozen-in just below T_g . A relatively small fraction of atoms remains mobile at all temperature below T_g . Only the mobility of this small fraction contributes to the configurational H and S . Thus, the gradual decrease in C_p , H and S of a glass over a temperature range extending to 0 K is seen as a reflection of the fraction of the atoms population that ceases to contribute to a thermodynamic function during the cooling of a glass. On isothermal annealing, only those atoms that diffuse sufficiently rapid approach an equilibrium structure within a given annealing time. On heating an annealed glass, self diffusion in the local regions in the glass structure becomes faster according to the same Arrhenius equation as on cooling and the increase in C_p , H and S is as a result of the contributions from all states that achieve configurational equilibrium on heating and the vibrational contributions from all.

We envisage that when the majority of the atoms in a glass structure at $T < T_g$ are kinetically frozen-in, the rapid approach towards an equilibrium of a small, but increasing number of locally diffusing atoms produces a small overshoot at a temperature determined by its diffusion rate and the rate of heating. In this view, the endothermic

peak observed on heating an annealed glass is a reflection of the sum of a multitude of C_p overshoots, each corresponding to a “mini glass–liquid transition” of the localized groups of atoms. Superposed on it is the recovery of configurations of atoms in local regions that produce a JG relaxation without causing the glass to show viscous flow over a short period. The entropy of mixing of 7.12, 9.05, 10.64, and 11.15 Jmol⁻¹ K⁻¹ for Mg₆₅Cu₂₅Tb₁₀, Pr₆₀Cu₂₀Ni₁₀Al₁₀, Pd₄₀Ni₁₀Cu₃₀P₂₀, and Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5} glasses, respectively, would also unfreeze on heating to the liquid state, and some of it may also unfreeze at a lower T where JG relaxation within the localized group of atoms unfreezes at $T < T_g$. The fraction of that entropy loss would be relatively small. This contribution is absent in a mono-component glass.

2.4.7 Modeling of Structural Relaxation

Hodge (1994, 1995) and Johari and Sartor (1996) reviewed various models usually used for mathematically describing structural relaxation, either empirical or theoretical. These models have two common features: (i) the relaxation time is distributed with a stretched-exponential function, and (ii) the relaxation time increases as the annealing time increases.

Hodge (1983, 1994) has simulated the structural relaxation of organic and inorganic polymers from DSC data. In his simulation, he incorporated the concept of a distribution of relaxation times and the non-linearity of the relaxation time. Kohlrausch (1854) and Williams and Watts (1970) have formulated the relaxation function which incorporates a distribution of relaxation times as,

$$\phi(t) = \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right] \quad (2.15)$$

where $\phi(t) = \frac{H(t) - H(\infty)}{H(0) - H(\infty)}$, ($H(t)$ is the value of enthalpy at time t , $H(\infty)$ is the value of the enthalpy at equilibrium (infinite time), $H(0)$ is the value of the enthalpy at initial time ($t = 0$)), τ is characteristic relaxation time, β is a parameter that expresses the breadth of the distribution of relaxation time ($0 < \beta < 1$). A single relaxation time is denoted by $\beta = 1$. Eq. (2.15) is equivalent to a set of separate relaxation mechanisms for the various relaxation time components of $g(\tau)$ which represents the distribution of times:

$$\phi(t) = \int_0^\infty g(\tau) \exp \left(- \frac{t}{\tau} \right) d\tau \quad (2.16)$$

for $\int_0^\infty g(\tau) d\tau = 1$, and,

$$\tau(T, T_f) = A \exp \left[\left(\frac{x\Delta h^*}{RT} \right) + \left(\frac{(1-x)\Delta h^*}{RT_f} \right) \right] \quad (2.17)$$

where T_f is the fictive temperature, Δh^* is the activation energy, A is a parameter equal to τ when both T and T_f are formally infinity, and $x < 1$ is an empirical parameter referred to as the non-linearity parameter. For $x = 1$, Eq. (2.17) becomes the Arrhenius equation.

For the simulation of the DSC curves, by using Boltzmann superposition principle and Eqs. (2.15) and (2.17), the summation over all instantaneous temperature jumps results the fictive temperature formalism as (DeBolt et al 1976, Berens and Hodge 1982),

$$T_f(T) = T_0 + \int_{T_0}^T dT'' \left[1 - \exp \left\{ - \left[\int_{T'}^T \left(\frac{dT''}{q_h \tau(T, T_f)} \right) \right]^\beta \right\} \right] \quad (2.18)$$

where T_0 is a starting temperature in the supercooled liquid and T' and T'' are the dummy temperatures at each instantaneous jump. Fictive temperature is related to the heat capacity by its normalized heat capacity as (DeBolt et al 1976),

$$C_p^{norm} = \frac{dT_f}{dT} \quad (2.19)$$

To fit the model to experimental data, the heat capacity data must be converted into a normalized heat capacity by using the relation,

$$C_p^{norm} = \left(\frac{C_{p, meas}(T) - C_p^{glass}(T)}{C_p^{liq}(T) - C_p^{glass}(T)} \right) \quad (2.20)$$

where $C_{p, meas}(T)$ is either taken as the measured (dH/dt) in a DSC scan divided by $q_h = dT/dt$, or else all C_p values taken as equivalent to $(dH/dt)_q$, C_p^{glass} is the C_p in the glassy state, and C_p^{liquid} is the C_p in the supercooled liquid state. The normalized C_p is zero in the glassy state and unity in the supercooled liquid state. For simulation, four parameters: A , x , β , and Δh^* , are chosen to generate a calculated normalized C_p . This calculated normalized C_p is fitted to the measured normalized C_p of the experimental data. For this simulation, a computer program as a dynamic link library (dll) was written in Fortran for numerical computation. This library was called by a computer program written in Visual Basic for displaying the curves of both calculated and measured normalized C_p . For optimization, a method of Nelder-Mead Simplex algorithm was used.

The simulation was performed for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass. The best fitting parameters used are: $\ln A = -118$, $x = 0.47$, $\beta = 0.60$ and $\Delta h^* = 423,000$ J/mol. The simulated curves are shown in Fig. 2.44 for the unannealed and annealed sample at 403 K for t_{as} of 5, 10, 20, 60 and 120 min. In the simulation, a glass was cooled at 20 K/min from 443 K, 28 K above T_g of 415 K, to 363 K and heated to 403 K at 20 K/min then held at 403 K for a certain annealing time. The heating curve of annealed glass thus could be obtained. These parameters should describe the curves for all the samples, whether annealed or unannealed.

It is evident in Fig. 2.44 that a good fit is obtained for the sample after annealing for 10 min, and somewhat satisfactory fit is obtained for the unannealed sample and for the sample annealed for 5 min. But the fit is quite unsatisfactory for the samples that were annealed for 20, 60 and 120 min. The discrepancy between the simulated results and the experimental data for the metallic glasses seems to support the premise that only for a few cases structural relaxation of a metallic glass may be described in terms of a distribution of relaxation times and Eqs. (2.13) and (2.15). The above-given comparison of simulation of the DSC scans for metallic glasses, even though they fail to predict the structural relaxation or annealing over a long time period, shows that the structural relaxation observed in metallic glasses, whether irreversible or reversible, has a broad distribution of atomic diffusion time. Formalisms used for glasses in general can be used to describe the structural relaxation in metallic glasses, as concluded by Johari and coworker (1999, 2000).

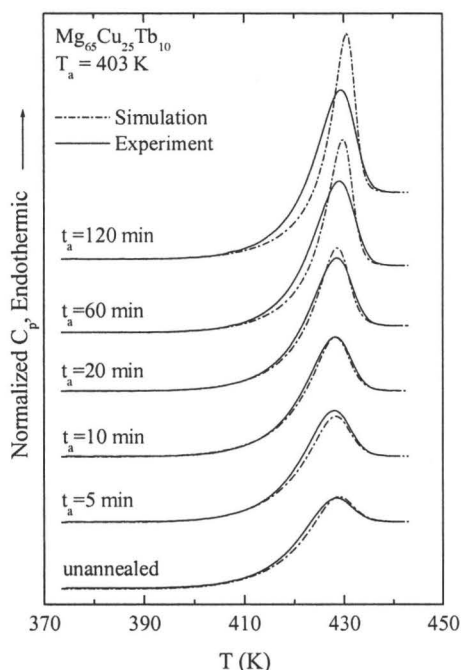


Fig. 2.44. The TNM simulation of heating curves for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass after isothermal annealing at 403 K for different annealing times. The parameters for simulation are $\ln A = -118$, $x = 0.47$, $\beta = 0.60$, and $\Delta H = 423,000$ J/mol.

To express the fit of the equations to the experimental data in an alternative manner, we calculated the relaxation time, τ , from the simulated plots in Fig. 2.44. It is plotted logarithmically (to the base 10) against $1/T$ in Fig. 2.45A and for clarity against T in Fig. 2.45B. The plot in Fig. 2.45A is non-linear at T up to 10 K below T_g , and is expected to become linear at lower temperatures when the effect of distribution of times is reduced. This is a characteristic of an Arrhenius temperature dependence and is expected from Eq. (2.17) when $T = T_f^H$ in the equilibrium state.

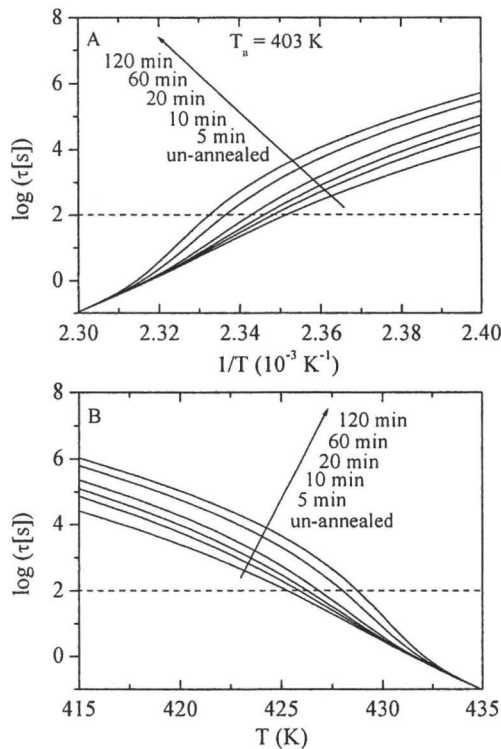


Fig. 2.45. Plots of the calculated relaxation time from the fitted curves in Fig. 2.44. A Plots against $1/T$. B. Plots against T .

Also, τ for the annealed sample cannot be reliably estimated when the fit-parameters for unannealed sample are used. In summary, the fit parameters for the annealed samples in Fig. 2.44 do not yield reliable value for the enthalpy regain on heating the annealed sample. For that reason, Eqs. (2.1), (2.2), (2.7) and (2.8) seems to be a better description of structural relaxation, than a structural relaxation model. There seems to be no independent manner of determining τ from the DSC data to determine if the calculations yield the correct value of τ , but modulated calorimetry data provide such values (Boller et al 1995, Simon 2001, Tombari et al 2009). Nevertheless, they show that the structural relaxation of the glass has a broad distribution also of atomic diffusion time.

The poor fit of the model to the data may also be due to the approximations made in developing and using these models, which we briefly note below:

(i) For calculating $C_{p,norm}$ from Eq. (2.20) one uses linear extrapolation of C_p^{liq} from $T \gg T_g$ to $T \ll T_g$, and of C_p^{glass} from $T \ll T_g$ to $T \gg T_g$. But C_p^{glass} itself increases non-linearly with T because contributions from anharmonic forces of the potential function and from JG relaxation configurations increase rapidly with increase in T . As a result, the slope of C_p^{glass} against T plot increases as T_g is approached on heating and linear extrapolation becomes questionable. Also, plots of C_p^{liq} against T for ultraviscous liquids at $T > T_g$ are curved, and either $C_p^{liq}/dT < 0$, as for 1-butene an N-type liquid, or $(dC_p^{liq}/dT) > 0$, as for *o*-terphenyl, a P-type liquid. For metallic glasses, the high temperature data are insufficient for C_p^{liq} extrapolation.

(ii) The quantity dT_f^H/dT of liquid is taken to be equal to 1. This means that, on extrapolation, T_f^H would reach zero at $T > 0$ K. By extrapolating a supercooled liquid's entropy to $T < T_g$, Kauzmann (1948) had suggested that its entropy may become equal to that of a crystal at a temperature T_K . The Adam-Gibbs theory (1965) that relies on the Kauzmann extrapolation but instead of the excess entropy, S_{exc} , of the liquid over the crystal phase, uses the configurational entropy, S_{conf} , that is zero at T_K , even though $S_{conf} < S_{exc}$. As an alternative to Kauzmann and Adam-Gibbs extrapolations, interpolation of C_p between 0 K and T_g has been suggested (Johari 2000, 2001) following the argument given by Simon (1930). In this interpolation, S_{exc} tends to zero at 0 K. An analysis of the

C_p data of amorphous polyethylene provide support for the absence of the T_K (Pyda and Wunderlich 2000), and an analysis of the DSC data on a polymer (Huang et al 2003) has suggested a similar absence of T_K . The extra contributions from anharmonic forces (Johari 2000, 2002a, 2002b), and from motion of atoms or molecules occupying higher volume sites in the glass structure would not allow S_{exc} to become zero at T_K . In summary, dT_f^H/dT would not approach zero at $T > 0$ K. Rather it would decrease slowly from its value of 1 to zero at 0 K. The plot of T_f^H against T therefore would be curved and would flatten out as $T \rightarrow 0$ K.

(iii) The parameter β is assumed to remain constant with t_a , T and T_a , although it is acknowledged that β is expected to change. The studies here and earlier (Fransson and Backstrom 1987, O'Reilly and Hodge 1991, Fujimori et al 1992, Hanaya et al 1994, Johari 2002b) show that β changes, thus confirming Douglas's 1966 finding (Douglas 1966) that β changes with t_a .

(iv) It is assumed that there is no contribution to C_p from the increasing strength of the JG relaxation on heating a glass.

Nevertheless, these models are found to be adequate for fitting a DSC scan over a narrow temperature range, implying that the combined effects of the above-given approximations are insignificant in comparison with the experimental errors. The parameters obtained are useful for a self-consistent analysis of the DSC data. If the above-given effects were to be included, it would add to adjustable parameters.

Fig. 2.34 also provides a direct analysis of the data on time dependence of the enthalpy and entropy change at fixed T_a . This is in contrast to the normalized C_p change observed on heating when the TNM model is fitted to a DSC scan and the two cannot be compared. Also, in their studies, Hodge and Berens (1982) used a temperature-step of 1 K for all simulations of the TNM model and found it to be satisfactory. We have used the step as 0.1 K for greater accuracy and yet we have found large differences between the measured and simulated DSC scans here for annealed samples.

2.5 Conclusions

Structural relaxation studies of metallic glasses lead to the following conclusions:

1. There are two types of relaxation observed in the metallic glasses. The first relaxation is irreversible relaxation and the second is reversible relaxation. The irreversible relaxation is observed as an exothermic feature during the first heating of the as-cast sample. The exotherm is due to the very large enthalpy frozen-in during the relatively rapid cooling in the preparation of the metallic glass and release of this enthalpy during the slower heating of the first heating in the DSC.
2. Bulk metallic glasses stored at ambient conditions shows an endothermic peak in dH/dT on heating at $T < T_g$ and the usual dH/dT overshoot at $T > T_g$. This peak is due partly to the unfreezing of the JG relaxation in the glassy state and partly to the unfreezing of the faster modes in the distribution of the α -relaxation times. It may be seen as the sum of a multitude of 'overshoots' in the apparent C_p still in the glassy

state, and to correspond to localized motions when localized group of atoms kinetically unfreeze. This is qualitatively similar to the overshoot observed in a DSC heating scan. This is one aspect of the distribution of diffusion times in local regions that arises from spatial and temporal distinctions of the atomic environment in the structure of a glass. Similarity of the structural relaxation effects with polymers and other glasses show that thermodynamics and kinetics provides no distinction between the changes in the topological and chemical short range orders in the metallic glass.

3. Isothermal annealing of a sample at a certain temperature and a certain time produces also endothermic effect during the sample's heating, which are the reversible relaxations. The peak's area is larger than that for the unannealed sample. For a fixed annealing time but different annealing temperature the peak areas increase, reach a maximum at a certain temperature, and then decrease. For a fixed annealing temperature but different annealing times, the peak areas continuously increase as annealing time increases. These features correspond to the enthalpy and entropy loss during annealing.
4. The curves for enthalpy and entropy loss of the bulk metallic glasses with different annealing conditions merge on heating to the equilibrium liquid state. The temperature at which this occurs increases with increase in the annealing temperature for a fixed annealing time as well as with increase in the annealing time for a fixed annealing temperature.
5. Isothermal structural relaxation of metallic glasses, in which atomic diffusion determines the kinetics, follows a stretched exponential relation with a parameter that

remains constant with the annealing time. For the same annealing period at different annealing temperatures, the decrease in H and S shows a peak as the sample reaches an equilibrium state for that annealing period.

6. The fictive temperature estimated from the $C_p dT$ integral is the same as that estimated from the $C_p d\ln T$ integral.
7. Simulation of the heat capacity curves obtained from the DSC scans in terms of a non-exponential and non-linear relaxation concept for metallic glasses fit satisfactorily for some isothermal annealing experiment results but do not do so for other experimental results. Even so, the simulation shows that the origin of the reversible relaxation is an important aspect of a distribution of diffusion times due to the temporal and spatial variation in the environments of atoms.

CHAPTER 3

MEMORY EFFECT IN METALIC GLASSES

3.1 Introduction

Before describing the study of the memory effect of bulk metallic glasses, we note that, in addition to the distribution of relaxation times, change in the properties of structural relaxation of glasses has several characteristics, as summarized by Kovacs et al (1979). These are, (1) non-linearity with respect to the magnitude of the initial departure from equilibrium, (2) asymmetry with respect to heating and cooling a glass, and (3) the so-called, “memory effect” or “cross-over” effect, observed when a glass is subjected to two or more successive isothermally annealing steps. Since they determine the manner in which the magnitude of a glass property changes with time, these features have consequences for the technological use of a material in the glassy state.

As described in Chapter 2, structural relaxation of a glass during its storage at a temperature below T_g decreases the volume, enthalpy and entropy of the glass towards its equilibrium liquid state. Its optical, elastic, electrical and deformation properties change with time accordingly. This is referred to as physical ageing.

Memory effect or cross-over effect is another manifestation of structural relaxation of a glass. It is observed when the temperature of an isothermally annealed glass is quickly raised to just below its fictive temperature and allowed to anneal. The volume, enthalpy and entropy at this temperature first increase with time, reach a

maximum value and then decrease towards that of the equilibrium liquid state. For the laboratory study of this effect, the sample is held first at a certain annealing temperature and allowed to structurally relax for a certain time. It is then held at a higher annealing temperature. When measured with time, its properties first show recovery in a direction opposite to the usual effect of structural relaxation in the glassy state and then in a direction toward structural relaxation.

The phenomena of memory effect was described by Alfrey in terms of the time-dependent loss of torsional deformation of a polymer in a monograph on the mechanical properties of the glassy state of high polymers (Alfrey 1948) published in 1948. In a section on complex phenomenon resulting from distribution of retardation times, Alfrey describes the elastic memory of a high polymer (Alfrey 1948, page 130): “If the configurational elasticity of a polymer actually represents several mechanisms with different retardation times, then the material will exhibit several interesting properties which cannot be explained on the basis of Model A. One such phenomenon is *elastic memory*.” (Model A on page 104 (Alfrey 1948) refers to the simplest, two springs and two dashpots model with instantaneous elasticity, retarded elasticity and flow.) By using an illustration of the memory effect in his Fig. 61 (Alfrey 1948) (after Kohlrausch), Alfrey described a simple experiment: “Twist a rod θ_1 degrees in one direction, and hold it for a long time. Then twist it back beyond its equilibrium position to θ_2 degrees in the opposite sense and release rather quickly.” The twist angle will increase first beyond the equilibrium value in the (positive) direction of θ_1 and then decrease towards zero, the equilibrium value. The crossing-over of the zero deformation and then return to zero

deformation in the time-dependent manner is the elastic memory of a polymer. Alfrey emphasized: “Such ‘memory effects’ are commonly observed in high polymers” (Alfrey 1948), and attributed the effect to a distribution of relaxation times.

After the Tool’s concept (Tool and Eichlin 1931, Tool 1946) of fictive temperature, T_f , came into wider use for describing the effects of heat treatment on properties of commercial glasses, Ritland (1956) showed that such a one-parameter description has only a limited quantitative significance. He reported that the room temperature refractive index of borosilicate crown optical glass (Corning code 8370) varied with the annealing or treatment time at 803 K such that its value for an unstabilized glass sample first decreased, reached a broad minimum and then increased slowly toward the initial equilibrium value. Ritland (1956) also noted that other workers had observed similar effects and he recognized Tool’s suggestion that a non-equilibrium state may not be identical with the equilibrium state at T_f . The simplest model in which Tool’s concept may not apply, he noted, would be a multiparameter model for “a microscopically inhomogeneous structure in which both the average size and the distribution of sizes of the sub-units are affected by thermal history.” (Ritland 1956). Since refractive index had been found to be already a unique function of volume, it was expected that a similar effect would be observed in volume measurements; the volume would first increase and then decrease toward the equilibrium value.

Kovacs (1958, 1963) performed a detailed and comprehensive study of the volume of poly(vinyl acetate). He found that, in addition to the known volume decrease on isothermal annealing at a low temperature and subsequent (asymmetric) volume

recovery at a higher temperature, the volume first increased and then decreased to the equilibrium value when a preannealed sample was further isothermally annealed at certain high temperatures, as was to be expected from Ritland's experiment (1956). In its plot against time, the fractional change in volume crossed the equilibrium value, reached a peak and then slowly decreased toward the equilibrium value at the annealing temperature. Kovacs et al (1963) further studied the viscoelastic properties of poly(vinyl acetate) by varying the thermal history of the sample and related it to the volume changes. In his 1964 article, Goldstein has discussed the findings of Kovacs in the light of other studies of the volume and elastic behavior of polymers. In the current literature, the phenomenon observed by Ritland (1956) and by Kovacs (1958, 1963) is referred to as both 'memory effect' and 'cross-over effect', and it has been figuratively stated, that the sample "remembers that at a time t_2 as a result of its previous thermal history it does not possess a structure corresponding to the equilibrium properties at any temperature. Hence its properties evolve in a different fashion..." (Moynihan et al 1976b). Here, we have used the original term 'memory effect', after Alfrey (1948).

Spinner and Napolitano (1976) have found memory effect in a borosilicate glass by measuring refractive index, n , by using a refractometer in their experiments. The plot of n against the time t during the isothermal hold first decreased, reached a minimum, and then increased to an equilibrium value of n . The phenomena has been found also in the volume and enthalpy measurement by Hojumi et al (1970) and Hojumi (1971) and by Adachi and Kotaka (1982), who used adiabatic microcalorimetry to measure the rate of enthalpy release of polystyrene and a dilatometer to measure the volume change. They

plotted the rate of increase or of decrease in the enthalpy against the annealing time and the absolute change in volume against time to show the appearance of the memory effect.

Due to the small magnitude of the decrease and increase of the enthalpy in the memory effect experiment, the detection of memory effect in glasses using Differential Scanning Calorimetry (DSC) had not been achieved until Hofer et al (1991) reported a study of this effect in the enthalpy by using a new procedure of anneal-and-scan in the DSC technique in our laboratory. They studied an inorganic network structure glass, a linear-chain polymer and a nonpolar rigid molecular glass to show the general occurrence of the effect. In their procedure, the sample was heated to a temperature (T_{a1}) near T_g , kept at this temperature for a certain time period (t_{a1}) and then heated rapidly to a higher temperature (T_{a2}) near its fictive temperature and kept at this temperature. During isothermal holding at this temperature (T_{a2}), the enthalpy plotted against time showed first an increase towards a maximum value, then a decrease towards its equilibrium state value. Adachi and Kotaka (1982) described the memory effect phenomena on the basis of a model in which the bulk volume consists of many sub-volumes, each having a different relaxation time but each sub-volume varying with temperature in the same manner as the volume of the bulk material. Hodge (1984) explained mathematically that the memory effect of a glass is a consequence of stretched exponential character of structural relaxation. If the behavior of structural relaxation were exponential, the two-step temperature-jump experiment would not show a peak, but only a monotonic decrease.

Here we describe a study of the memory effect in bulk metallic glasses by using the method by Hofer et al (1991):

- (i) $\text{Mg}_{65}\text{Cu}_{26}\text{Tb}_{10}$
- (ii) $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$
- (iii) $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$
- (iv) $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$

One paper on the study has been published in Journal of Non-Crystalline Solids (Aji et al 2007).

3.2 Experimental Methods

The samples of four bulk metallic glasses (BMGs) of compositions $\text{Mg}_{65}\text{Cu}_{26}\text{Tb}_{10}$, $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_2$, and $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ used for the experiments were cut from the specimens by using the same procedure as described in Chapter 2. The instrument used was Pyris Diamond DSC, the same as the one used for structural relaxation studies in Chapter 2.

For enthalpy change studies in the memory effect, two different experiments were performed. In the first experiments the annealing time t_{a1} at temperature T_{a1} is varied, while the temperatures T_{a1} and T_{a2} are kept fixed, and in the second experiments the temperature T_{a1} is varied, while the annealing time t_{a1} and T_{a2} are kept fixed. Fig. 3.1 illustrates the procedure for both memory effect experiments: (i) First the glass is

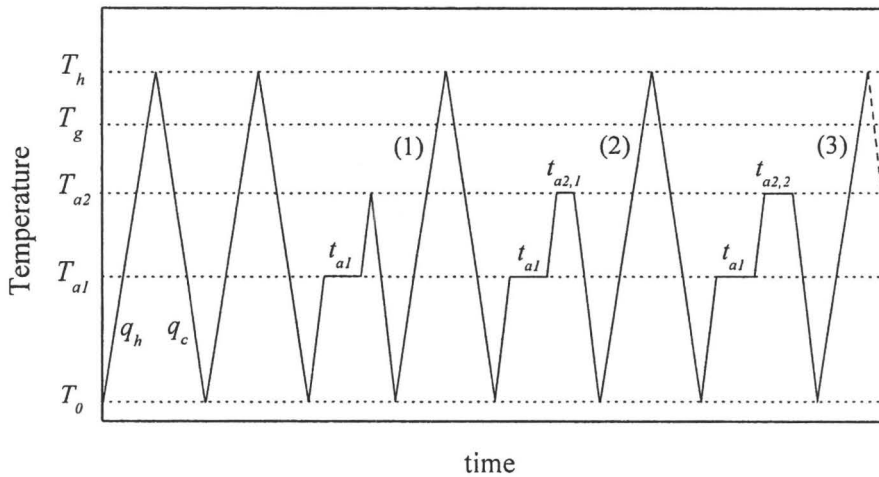


Fig. 3.1. Temperature – time diagram of thermal cycling used for studying the memory effect. The heating rate (q_h) from T_0 to T_h is 20 K/min, from T_0 to T_{a1} is 80 K/min, and from T_{a1} to T_{a2} is 50 K/min. Cooling rate (q_c) from T_h to T_0 is 20 K/min and from T_{a2} to T_0 is 80 K/min.

conditioned to achieve a reproducible thermal history by heating it at a rate q_h from an arbitrarily chosen temperature T_0 to a temperature of its equilibrium liquid state T_h , and is then rapidly cooled at a high rate q_c to T_0 in order to produce its high-enthalpy, high- T_f state. The heating and cooling are repeated to check the reversibility of the sample. (ii) The sample is then heated again at the maximum possible rate to a temperature T_{a1} . (iii) It is kept at T_{a1} for a predetermined period t_{a1} . (iv) It is then heated to a temperature T_{a2} and immediately cooled back to T_0 at the maximum possible rate. (v) The sample is then heated from T_0 to T_h at a rate q_h and the first scan labeled 1 for the sample annealed for a period t_{a1} at T_{a1} but *not* annealed at the second temperature T_{a2} is obtained, which is used for constructing the C_p against T plot. The sample is cooled back from T_h to T_0 at rate q_c , and immediately heated to T_{a1} and annealed for the same period, t_{a1} . (vi) It is then heated to T_{a2} , and annealed at T_{a2} for a period t_{a2} , cooled back to T_0 and finally heated to T_h at the rate q_h and the second scan labeled 2 for the sample annealed for a period t_{a1} at T_{a1} , as

before, and additionally annealed at the second temperature T_{a2} for a period t_{a2} is obtained, which is used for constructing the C_p against T plot. The difference between the areas of scans 1 and 2 yields the enthalpy lost on structural relaxation in a time t_{a2} at a temperature T_{a2} , i.e., one data point. Procedures (i) to (vi) are repeated for preselected t_{a2} at T_{a2} , while keeping T_0 , T_h , q_c , q_h , T_{a1} , T_{a2} and t_{a1} fixed and thus one memory effect plot is obtained for a given t_{a1} at a fixed T_{a1} . In the second experiment, t_{a1} is kept fixed and T_{a1} is varied. Hence the memory effect plots are obtained for different T_{a1} s in which T_0 , T_h , q_c , q_h , T_{a2} and t_{a1} are all kept fixed.

In particular the procedure for the memory effect study of $\text{Mg}_{65}\text{Cu}_{26}\text{Tb}_{10}$ glass is as follows. First, the sample was heated from 363 K to 443 K at a rate of 20 K/min and then cooled from 443 K to 363 K at 20 K/min two times. After this, the sample was heated from 363 K (T_0) to 408 K (T_{a1}) at 80 K/min, held for 4 min (t_{a1}), then heated rapidly at 50 K/min to 411 K (T_{a2}) and cooled immediately to 363 K at 80 K/min. Thereafter, the sample was heated from 363 K to 443 K at 20 K/min and cooled from 443 K to 363 K at 20 K/min. This heating curve is the first DSC scan for zero annealing time (t_{a2}) or the curve for the unannealed sample. The procedure was repeated for the same T_{a1} , t_{a1} , and T_{a2} with different annealing time (t_{a2}) at temperature T_{a2} . The second DSC scan, which is the heating after annealing at T_{a2} for annealing time t_{a2} , is obtained. The procedure is repeated for other annealing times (t_{a2}) for one set of measurements. The procedure described above is for condition 1 ($T_{a1} = 408$ K, $t_{a1} = 4$ min, and $T_{a2} = 411$ K) of the memory effect experiments. The conditions of the memory effect experiments for $\text{Mg}_{65}\text{Cu}_{26}\text{Tb}_{10}$ glass are shown in Table 3.1.

Table 3.1. Details of the time-temperature conditions for the memory effect and physical ageing experiments of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass.

Condition	T_{a1} (K)	t_{a1} (min)	T_{a2} (K)	t_{a2} (min)
1	408	4	411	0, 0.2, 0.3, 1, 2, 3, 5, 10, 20, 60, 120
2	408	5	411	0, 0.2, 1, 2, 5, 10, 20, 60, 120
3	408	10	411	0, 0.2, 1, 2, 5, 10, 60, 120
4	407	10	411	0, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, 60, 120
5	406	10	411	0, 0.1, 0.3, 0.8, 2, 3, 5, 10, 20, 60, 120
6	405	10	411	0, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 5, 10, 20, 60, 120
Physical Ageing	-	-	411	0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5, 2, 3.5, 5, 10, 20, 60, 120

In addition to performing memory effect experiments, physical ageing experiments, in which only one annealing temperature, were also performed. The procedure for these experiments is similar to the procedure described in Chapter 2, in which the samples were annealed at T_{a2} for a period t_{a2} . For one set of measurements, T_{a2} was fixed but the annealing time, t_{a2} was varied. It is illustrated in Fig. 2.5 of Chapter 2.

The procedure for studying the memory effect in the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_2$, and $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ glasses was the same as that for the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass. Only the time-temperature conditions were different.

3.3 Results

The DSC scans obtained for studying the memory effect in $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ for condition 5 in Table 3.1 ($T_{a1} = 406$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K, $t_{a2} = 0, 0.1, 0.3, 0.8, 2, 3, 5, 10, 20, 60, 120$ min) are shown in Fig. 3.2A. The DSC scans obtained for other

conditions are similar and therefore are not shown in this thesis. Fig. 3.2B is the enlargement of the endothermic peak portion in Fig. 3.2A. It shows that the maximum or peak value first decreases, reaches a minimum value, and then increases.

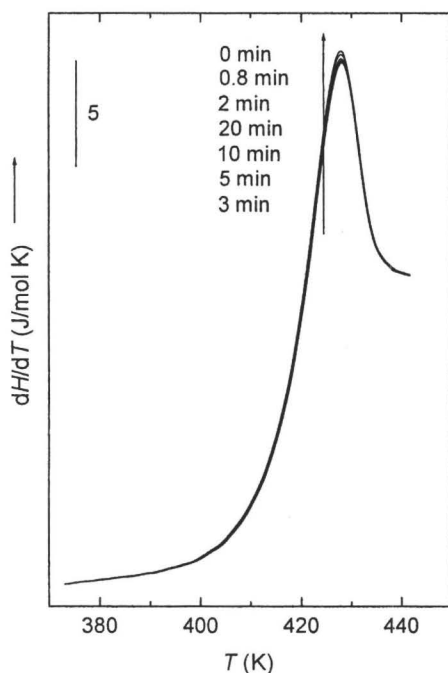


Fig. 3.2. A. The DSC scans for the memory effect experiments obtained on heating at a rate of 20 K/min for condition 5 ($T_{a1} = 406$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K, $t_{a2} = 0, 0.1, 0.3, 0.8, 2, 3, 5, 10, 20, 60, 120$ min) of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass. The annealing times labeled next to the curves are in order of the increasing maximum value of dH/dT of the curves.

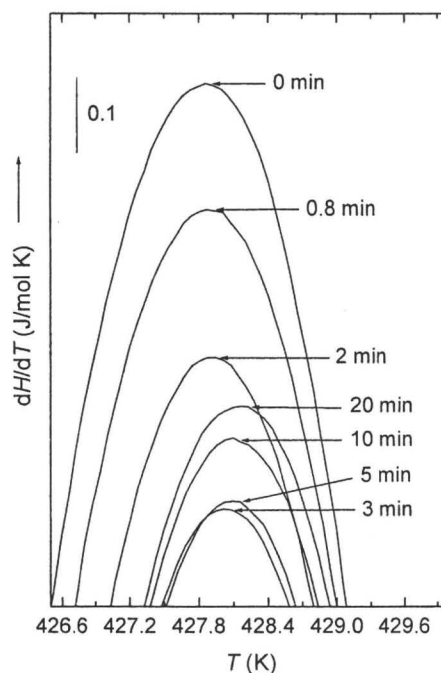


Fig. 3.2. B. Enlargement of Fig. 3.2A.

The difference between the areas of the first heating scan ($t_{a2} = 0$) and the heating scans of annealed sample were calculated and the enthalpy differences ($H_0 - H(t_{a2})$) were determined. The enthalpy difference is the same with the enthalpy decrease or increase that occurs during annealing for a period t_{a2} at temperature T_{a2} . The enthalpy change on structural relaxation for studying both the memory effect and physical ageing of

$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass are plotted against time in Figs. 3.3 and 3.4. Fig. 3.3 shows enthalpy change against annealing time for the memory effect experiments for conditions 1, 2, 3, and for physical ageing experiment ($T_{a2} = 411$ K and $t_{a2} = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5, 2, 3.5, 5, 10, 20, 60, 120$ min.). Fig. 3.4 shows enthalpy change against the annealing time for the memory effect experiments for conditions 3, 4, 5, 6 in Table 3.1, and for physical ageing ($T_{a2} = 411$ K and $t_{a2} = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5, 2, 3.5, 5, 10, 20, 60, 120$ min.). Figs. 3.3 and 3.4 show that the enthalpy change first increases, reaches maximum, and then decreases following the enthalpy change of physical ageing curve as expected for

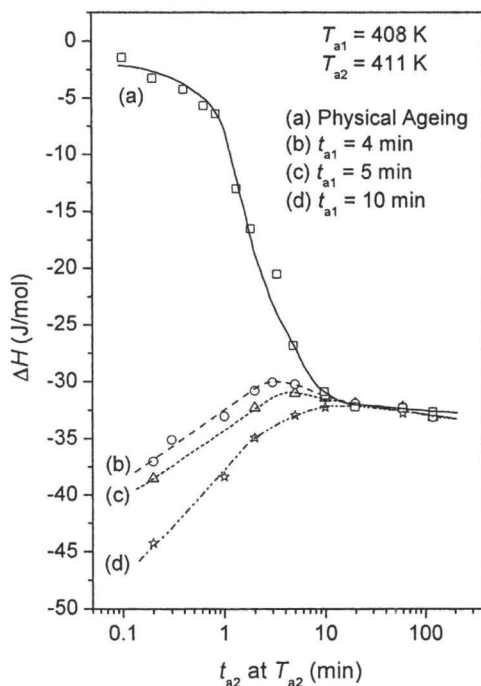


Fig. 3.3. The plots of enthalpy against the annealing time (t_{a2}) of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass for the memory effect experiments for condition 1 ($T_{a1} = 408$ K, $t_{a1} = 4$ min, $T_{a2} = 411$ K), 2 ($T_{a1} = 408$ K, $t_{a1} = 5$ min, $T_{a2} = 411$ K), 3 ($T_{a1} = 408$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K), and physical ageing ($T_{a2} = 411$ K and $t_{a2} = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5, 2, 3.5, 5, 10, 20, 60, 120$ min.).

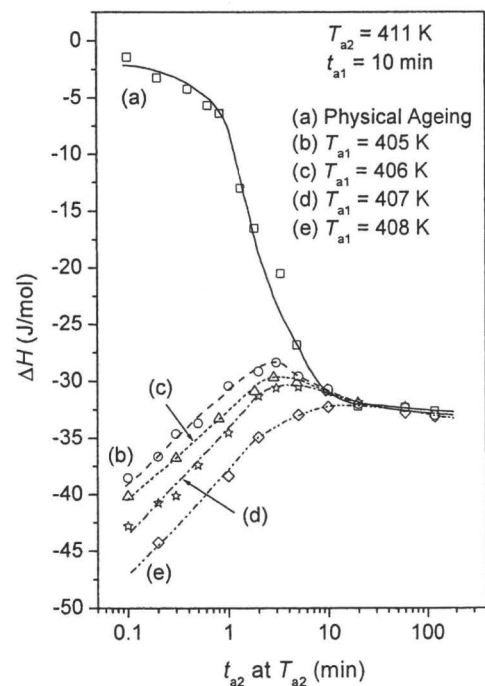


Fig. 3.4. The plots of enthalpy against the annealing time (t_{a2}) of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass for the memory effect experiments for condition 3 ($T_{a1} = 408$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K), 4 ($T_{a1} = 407$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K), 5 ($T_{a1} = 406$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K), 6 ($T_{a1} = 405$ K, $t_{a1} = 10$ min, $T_{a2} = 411$ K), and physical ageing ($T_{a2} = 411$ K and $t_{a2} = 0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5, 2, 3.5, 5, 10, 20, 60, 120$ min.).

the memory effect. For the fixed first and second annealing temperatures, T_{a1} and T_{a2} in Fig. 3.3, the enthalpy change peak increases in height and shifts to shorter time as the t_{a1} is decreased. For fixed t_{a1} and fixed T_{a2} in Fig. 3.4 the peak value of the enthalpy change also increases and shifts to shorter time but now as T_{a1} is decreased.

Fig. 3.5 shows the results of two sets of memory effect experiments performed on $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass. Fig. 3.5A is for the condition: $T_{a1} = 418$ K, $T_{a2} = 423$ K and $t_{a1} = 10$ min and Fig. 3.5B is for the condition: $T_{a1} = 418$ K, $T_{a2} = 423$ K and $t_{a1} = 5$ min. The decrease in the endothermic peak height and in the values for the equilibrium state show that the glassy sample partially crystallized on heating after the unannealed sample. Experiments were repeated several times with the new samples and for varied conditions. In all experiments, the DSC scans show partial crystallization, as shown in Figs. 3.6 and 3.7.

Fig. 3.8 shows the DSC scans for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_2$ and Fig. 3.9 shows those for $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$. Fig. 3.8A is for the scans obtained for the condition: T_{a1} of 567 K, T_{a2} of 571 K and t_{a1} of 5 min and Fig. 3.8B is for the condition: T_{a1} of 568 K, T_{a2} of 571 K and t_{a1} of 5 min. Fig. 3.9 is for condition: T_{a1} of 337 K, T_{a2} of 340 K and t_{a1} of 5 min. Similar to the result obtained for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass, the plots show that partial crystallization occurred during the heating and also after the heating of the unannealed samples. The experiments were repeated several times with new samples taken from the stock and various temperature-time conditions were used. But partial crystallization still occurred during the DSC measurement.

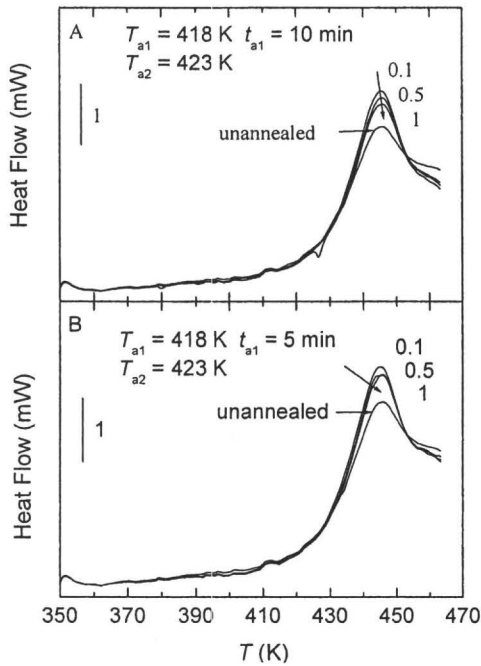


Fig. 3.5. The DSC scans of the memory effect experiments of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass at heating rate of 20 K/min for a certain condition: A. $T_{a1} = 418$ K, $t_{a1} = 10$ min, $T_{a2} = 423$ K, $t_{a2} = 0, 0.1, 0.5, 1$ min, B. $T_{a1} = 418$ K, $t_{a1} = 5$ min, $T_{a2} = 423$ K, $t_{a2} = 0, 0.1, 0.5, 1$ min. The annealing times labeled next to the curves are ordered according to the maximum value of the curves.

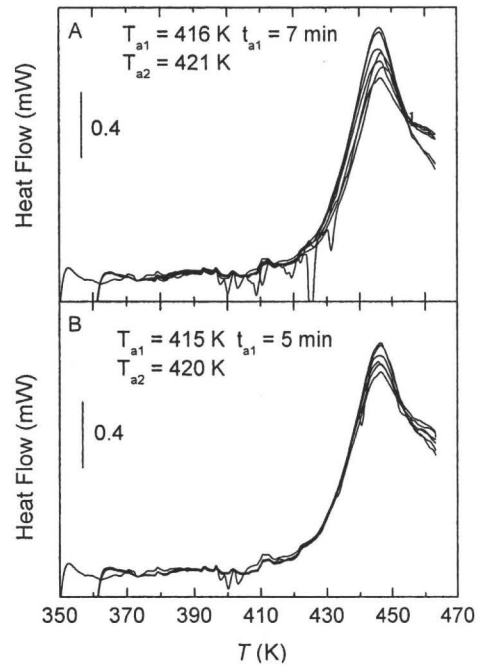


Fig. 3.6. The DSC scans of the memory effect experiments of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass at heating rate of 20 K/min for a certain condition: A. $T_{a1} = 416$ K, $t_{a1} = 7$ min, $T_{a2} = 421$ K, $t_{a2} = 0, 0.5, 0.8, 1.5, 2, 3.5, 5$ min, B. $T_{a1} = 415$ K, $t_{a1} = 5$ min, $T_{a2} = 420$ K, $t_{a2} = 0, 0.5, 0.8, 1.5, 2, 3.5, 5$ min.

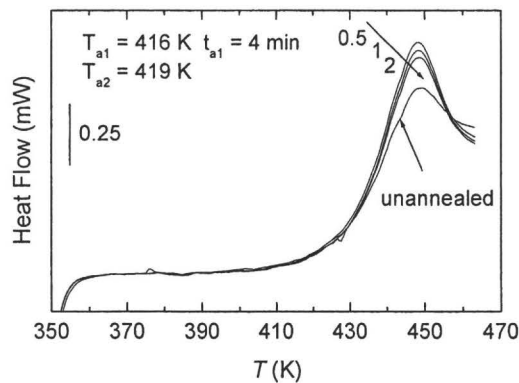


Fig. 3.7. The DSC scans of the memory effect experiments of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass at heating rate of 20 K/min for a certain condition: $T_{a1} = 416$ K, $t_{a1} = 4$ min, $T_{a2} = 419$ K, $t_{a2} = 0, 0.5, 1, 2$ min. The annealing times labeled next to the curves are ordered according to the maximum value of the curves.

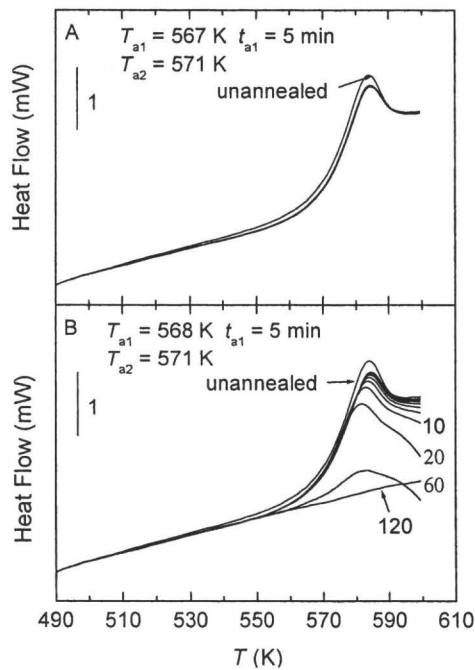


Fig. 3.8. The DSC scans of the memory effect experiments of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass at heating rate of 20 K/min for a certain condition: A. $T_{a1} = 567$ K, $t_{a1} = 10$ min, $T_{a2} = 571$ K, $t_{a2} = 0, 0.2, 0.5, 1, 2, 3, 5, 10,$ and 20 min, B. $T_{a1} = 568$ K, $t_{a1} = 5$ min, $T_{a2} = 571$ K, $t_{a2} = 0, 0.2, 0.5, 1, 2, 3, 5, 10, 20, 60,$ and 120 min.

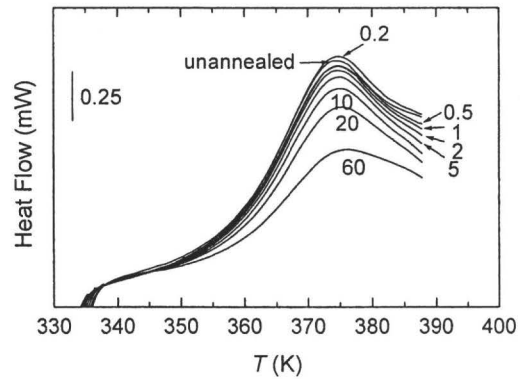


Fig. 3.9. The DSC scans of the memory effect experiments of $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ glass at heating rate of 20 K/min for a certain condition: $T_{a1} = 337$ K, $t_{a1} = 5$ min, $T_{a2} = 340$ K, $t_{a2} = 0, 0.2, 0.5, 1, 2, 5, 10, 20,$ and 60 min.

In an attempt to determine whether or not the DSC scans of partially-crystallized samples could still be used, the data were rescaled as follows. The total change in the heat flow, dH/dT on crystallization was determined from the difference between the heat flow of the first scan (0 % glass, scan-1), and the scan for its crystal state (100 % crystals, scan-2). By assuming the fraction of crystals is constant during the heating, the rescaled DSC scan can be calculated by first calculating the crystallized fraction in the supercooled liquid state. This fraction was calculated by comparing the heat flow values in the supercooled liquid state of scan-1 to scan-2. The rescaled DSC scan then can be calculated by multiplying the DSC scan to the crystallized fraction. The result of the

rescaling for $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ scans with condition as shown in Fig. 3.9 is shown in Fig. 3.10 for the annealing time, t_{a2} , of 5 and 20 min. The procedure is not correct because during the heating, the fraction of crystals formed is not constant. Because of determining the fraction of crystals formed during the heating is not possible, the rescaling of partial crystallized DSC scans is not possible as well.

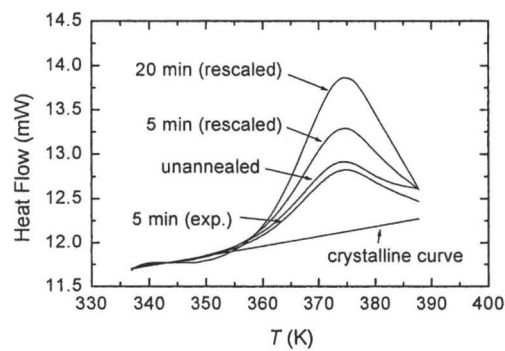


Fig. 3.10. The rescaled DSC scans of the memory effect experiments of $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ glass of Fig. 3.9.

3.4 Discussion

The main purpose of the study was to determine whether memory effect may be observed for glasses in which the shape of the entities are spheres, as are used in computer-simulation, and to extend our earlier study in which a decrease in enthalpy and its regain was observed when the glass was thermally cycled over a temperature range restricted to $T < T_g$. Both purposes have been fulfilled by this study. Nevertheless there are certain aspects of metallic glasses that have been found in this study which are worthy of discussion. This is done in the following.

Since the non-linear parameters, distribution of relaxation times and relaxation time that determine the change in the properties of glass can not be determined by

independent methods, we interpret the finding of the memory effect in glasses qualitatively. Similar to Adachi and Kotaka (1982) we assume that the relaxation time has a broad distribution that does not depend upon the thermal history or structure. The peak in the enthalpy resulting from the memory effect as seen in Figs. 3.3 and 3.4 may be interpreted on the basis of the following four assumptions:

1. The relaxation times have a box-type distribution, as shown in Fig. 3.11B, where n is the number of the relaxing components in the range from $\log \tau$ to $\log \tau + d \log \tau$ and $\Delta H_i (= H_i - H_\infty)$ is the deviation of the enthalpy from the equilibrium value.
2. Each component in the system relaxes exponentially after being brought to a non-equilibrium state. The deviation in the enthalpy of the i th component ($\Delta H_{t,i}$) from the equilibrium value is given by,

$$\Delta H_{t,i} = \Delta H_{t,i0} \exp\left(-\frac{t}{\tau_i}\right) \quad (3.1)$$

where $\Delta H_{t,i0}$ is the initial value of $\Delta H_{t,i}$.

3. The total deviation in the enthalpy from equilibrium of a bulk sample is the summation of all the components, given by $\sum n_i \Delta H_{t,i}$.
4. The temperature dependence of the enthalpy of each component is the same as that of bulk sample, as schematically shown in Fig. 3.11B. Therefore, Eq. (3.1) can be approximated by a step function.

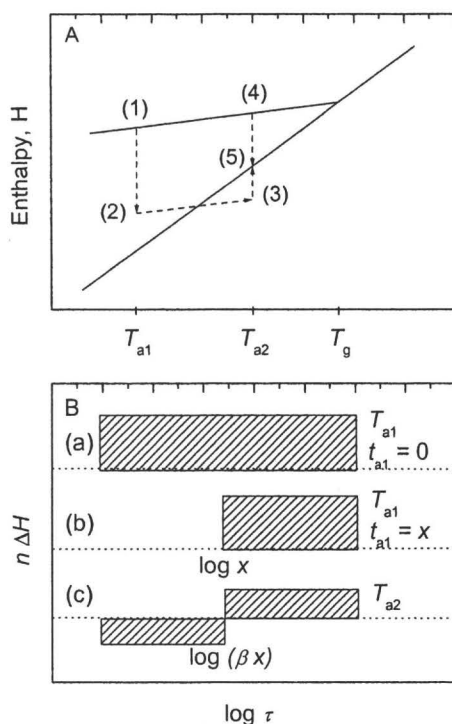


Fig. 3.11. Schematic diagram for the explanation of memory effect phenomena. A. Enthalpy versus temperature, B. Spectrum of $n\Delta H$ at T_{a1} immediately following the physical ageing curve (a), the spectrum after annealing for x min at T_{a1} (b), and the spectrum immediately following the second temperature jump from T_{a1} to T_{a2} . The parameter β is the factor that would lead to correct temperature dependence of the relaxation time.

When the sample is first heated from a temperature below T_g to T_{a1} and held at T_{a1} for $t = t_{a1}$ in Fig. 3.11A, the spectrum of relaxation times is as illustrated by the bar (a) in Fig. 3.11B. Annealing at T_{a1} for t_{a1} of x min changes the spectrum as shown by the bar (b) in Fig. 3.11B. During this, the components with τ_i longer than x remain at point (1) in the enthalpy versus temperature diagram in Fig. 3.11A, while the components with τ_i shorter than t_{a1} are at point (2). When the temperature is instantaneously increased from T_{a1} to T_{a2} , the state of the unannealed glass shifts from point (1) to (4), and for the annealed glass shifts from point (2) to point (3). As a consequence, $n\Delta H_{t,i}$ of the relaxing components which have been at point (2) become negative, as shown by the positive and negative components of the bar (c) in Fig. 3.11B according to the assumption 4. Since the components of relaxation that cause $\Delta H_{t,i0}$ to become negative and enthalpy to increase

have relatively shorter relaxation time than those components that cause $\Delta H_{t,i0}$ to become positive and enthalpy to decrease, the enthalpy recovery occurs faster than the enthalpy decrease. As a result, the enthalpy initially increases with time, deviating from the equilibrium enthalpy at T_{a2} . When the recoveries resulting from faster motions is approaching completion, the slower components begin to decrease the enthalpy and hence there is reversion in the path. In the time domain, the enthalpy would show broad peak at a time when the effect of longer relaxation time begins to dominate.

The same effect may be described in terms of the distribution of relaxation times and in that case, annealing at T_{a2} would cause the enthalpy to increase by the faster modes first and then would decrease by the slower modes. Hodge (1984) has considered the memory effect in general terms of a distribution of time. Also if a well annealed sample is heated at a relatively fast rate, its C_p and enthalpy would first increase as the fictive temperature is being approached and would then decrease during the heating thereby showing a sub- T_g peak as observed for the aged $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass here.

Kovacs and coworkers (1963, 1977, 1979) had discussed the change in the properties of a glass with time in terms of a quantity δ , defined by $(\nu - \nu_\infty)/\nu_\infty$, where ν is the volume at a certain time and ν_∞ is its equilibrium value. Both the enthalpy, H , and ν of a glass are partly configurational in origin; H is additionally determined by the vibrational frequency and anharmonic effects and ν only by the anharmonic effects. Despite that we use δ_H defined as $(H - H_\infty)/H_\infty$ where H_∞ is the equilibrium value to express our data in Kovacs' manner. For the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass in our study ($T_g = 414 \text{ K}$

for 20 K/min heating) the plots in Figs. 3.3 and 3.4 show that δ_H is negative initially. For example, the values are -37, -38.5, and -44.3 J/mol for curves (b), (c) (d) in Fig. 3.3. In the memory effect study in which the preannealing temperature is varied, the δ_H values are -38.5, -42.4, -42.8 and -44.2 J/mol for curves (b), (c), (d) and (e), respectively in Fig. 3.4. This means that the enthalpy of the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass sample initially at the memory effect temperature of 411 K, is lower than the equilibrium enthalpy of the sample at 411 K. Therefore the initial value of H in the memory effect experiment at 411 K is less than H_∞ .

It has been often stated that memory effect is observed when the glass preannealed at a lower temperature has been rapidly heated to its equilibrium temperature T_{eq} , which is its fictive temperature T_f . But this is neither the case here nor in earlier studies by Hofer et al (1991). Kovacs (1963) had found memory effect at $T > T_{eq}$ and at $T = T_{eq}$ and had modeled it for $T < T_{eq}$ (Kovacs et al 1977, 1979). In his study (Kovacs 1963, Kovacs et al 1977, 1979), the initial value for δ is zero, when $T = T_{eq}$, negative when $T > T_{eq}$, and positive when $T < T_{eq}$. The memory effect peak is highest when $T = T_{eq}$. It gradually vanishes as T is decreased because the rise in δ gradually vanishes. It also vanishes when T is increased, because the decline in δ gradually vanishes.

An initial negative value of δ or δ_H can occur only when the annealing temperature is higher than T_{eq} . Therefore, the enthalpy data for the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass in Figs. 3.3 and 3.4 show that its annealing temperature of 411 K is higher than T_{eq} . In contrast, initially positive values of δ or δ_H can occur only when the annealing

temperature is lower than T_{eq} , as shown by Aji et al (2007) in their Figs. 9 and 10 for the enthalpy data for the $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ glass.

The observations of the memory effect put into question the description of structural relaxation in terms of change in T_f . It has been known that the same value of a physical property of a glass can be reached by a large number of temperature-time paths, but it is not certain whether the structure of the glass thus reached is the same. The opposite signs of the time derivative of a property on the two sides of the memory effect peak show that the structure of two glasses of different thermal history differ when their macroscopic property do not. As the structure of the state at T_f is unique, we argue that structural relaxation of a glass may not be appropriately treated in terms of change in T_f with time and/or temperature.

When a peak appears in the plot of a property changing with time, it is an indication of two processes whose time derivatives, which are opposite in sign become equal in magnitude at the peak position, with the slower processes dominating as $t \rightarrow \infty$. It is significant that not only the peak height of the memory effect, but also the time for its appearance varies with the preannealing conditions.

The memory effect was explained by Kovacs (1963) and Kovacs et al (1977, 1979) in terms of a distribution of relaxation times using the free volume concepts and later showing that the same concepts would apply if the entropy or enthalpy were considered. Rotiashvilli et al (1984) modeled it by assuming the existence of regions of small and large fluctuations with different mechanism for dissipation. It has been modeled by including a distribution of relaxation times, expressed by stretched

exponential parameter, β , for the decay and rise of the relaxation function in macroscopic time (Sartor et al 1996). A distribution of relaxation times written as $\beta < 1$ is almost always observed when DSC scans are analyzed. It has been observed directly in the C_p spectra (Pascheto et al 1994) and from measurements of the real and imaginary components of the C_p at a fixed frequency (Tombari et al 2002, 2006). But β of the α -relaxation process in an ultraviscous liquid differs from β of a structural relaxation of a glass, because of its non-equilibrium state. Accordingly, a glass with small β at $T = T_{eq}$ is expected to show a larger memory effect than a glass with large β , and glassy state of a liquid with a single relaxation time, or $\beta = 1$ would not show the memory effect. In this sense Ngai's conviction that a successful theory for glass-formation should include the distribution of relaxation times (Ngai 1999) is a good guide. Ngai's original coupling model has also been extended to describe the non-equilibrium structural recovery (Rendell et al 1987). Irreversible change in volume is not only due to a change in free volume or in the number of configurations available to a glass structure but also due to a significant change in the anharmonic effects.

In the potential energy barrier picture of viscous flow which is now known as potential energy landscape, Goldstein (1969) had concluded that in ultraviscous liquids there is a distribution of relaxation times and that some degree of faster molecular motions would persist in the glassy state at $T < T_g$. Structural relaxation also decreases the strength of dielectric (Johari 1973, 1982) and mechanically observed JG relaxation (Muzeau and Johari 1990, Cavaille et al 1999), which indicates that the number of

molecules or group of molecules contributing to the JG relaxation decreases (Johari et al 2002c, Power et al 2003, 2006) and the plot of its dielectric relaxation strength against T has shown a change in slope at T_g (Johari et al 2002a, 2002b, 2006b), similar to that in the plots of enthalpy and volume. Structural relaxation also changes the vibrational and electronic properties of a glass. All of these are recovered at a temperature of the memory effect and this needs to be taken into account. Nevertheless, in the enthalpy recovery, the memory effect peak height is as high as 14.8 % of the enthalpy decrease on structural relaxation, which indicates that a large fraction of the enthalpy increase in memory effect would be configurational.

There are other consequences of the relaxation time distribution. For example, it has been deduced that faster modes in this distribution contribute to C_p , H and S of a glass at T below its T_g and cease to contribute only at low temperatures. On that basis it has been suggested that the slope of the DSC scan at temperatures below T_g would be more when the β value is less and that the T_g -endotherm for glasses of very low β value would become so broad as to be undiscernible. A distribution of relaxation times has been analyzed as a sum of single relaxation times (Majumdar 1971) and this has been supported by hole-burning experiments that have led to the inference for heterogeneous dynamics of a liquid and glass (Richert 2001).

As a supplementary part of this study, we use the Tool-Narayanaswamy-Moynihan formalism for modeling the DSC scans used for studying the memory effect. The equation has been described in Section 2.4.7 of Chapter 2. It is used to produce a simulated plot for both isothermal annealing and the time-temperature dependence of the

heat capacity or of the DSC scan on heating and cooling. The procedure for simulation is given in Chapter 2. The algorithm for the memory effect simulation uses two annealing temperatures instead of one. Fig. 3.12 shows the simulation results of heating curves for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass. The heating rate used was 20 K/min for conditions: (A) $T_{a1} = 418$ K, $t_{a1} = 10$ min, $T_{a2} = 423$ K, $t_{a2} = 0.1, 0.5$, and 1 min, and (B) $T_{a1} = 418$ K, $t_{a1} = 5$ min, $T_{a2} = 423$ K, $t_{a2} = 0.1, 0.5, 1$, and 2 min. The parameters for simulation are: $\ln A = -116.1$, $x = 0.51$, $\beta = 0.54$, $\Delta H = 429.9$ kJ/mol. The parameters were chosen first to fit the unannealed curve then with these parameters, the simulation curves were obtained for the curves of memory effect experiments.

For simulation of the DSC scans for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass, the parameters for simulation are: $\ln A = -87$, $x = 0.68$, $\beta = 0.8$, $\Delta H = 429.9$ kJ/mol. The heating rate used was of 40 K/min for conditions: (A) $T_{a1} = 577$ K, $t_{a1} = 10$ min, $T_{a2} = 581$ K, $t_{a2} = 0.5$ min, and (B) $T_{a1} = 578$ K, $t_{a1} = 5$ min, $T_{a2} = 581$ K, $t_{a2} = 0.2$ min. The simulation curves are shown in Fig. 3.13. Fig. 3.14 shows the simulation of the DSC scans of $\text{Ce}_{66}\text{Al}_{10}\text{Cu}_{20}\text{Co}_4$ glass at heating rate of 20 K/min for conditions: $T_{a1} = 337$ K, $t_{a1} = 10$ min, $T_{a2} = 340$ K, and $t_{a2} = 0.5$ min. The parameters for simulation are $\ln A = -137.7$, $x = 0.51$, $\beta = 0.55$, $\Delta H = 428.7$ kJ/mol.

As is seen in Figs. 3.12, 3.13, and 3.14, the fit is quite unsatisfactorily for the curves of memory effect experiments. Similar conclusion for simulation of results were obtained from isothermal annealing experiments in Chapter 2. The discrepancy between the simulation and data shows that only in a few cases can structural relaxation of a metallic glass be described in terms of a distribution of relaxation times and Eqs. (2.15)

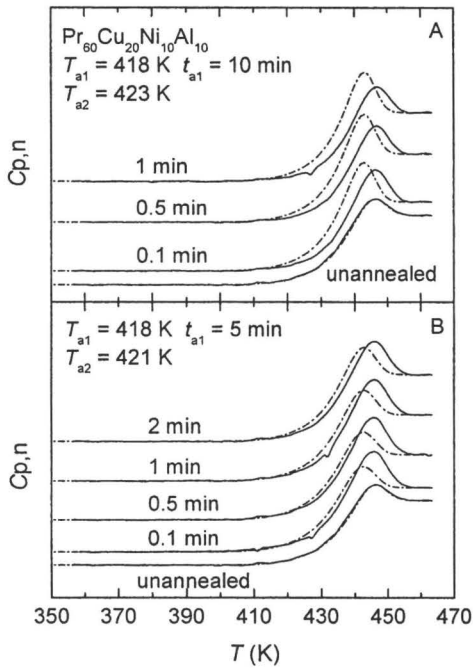


Fig. 3.12. The TNM simulation of heating curves of Pr₆₀Cu₂₀Ni₁₀Al₁₀ at heating rate of 20 K/min for conditions: A. $T_{a1} = 418 \text{ K}$, $t_{a1} = 10 \text{ min}$, $T_{a2} = 423 \text{ K}$, $t_{a2} = 0.1, 0.5, 1 \text{ min}$, B. $T_{a1} = 418 \text{ K}$, $t_{a1} = 5 \text{ min}$, $T_{a2} = 423 \text{ K}$, $t_{a2} = 0.1, 0.5, 1 \text{ min}$. The parameters for simulation are $\ln A = -116.1$, $x = 0.51$, $\beta = 0.54$, $\Delta H = 429.9 \text{ kJ/mol}$. The dash dot lines are the simulation curves and the solid lines are the experimental data.

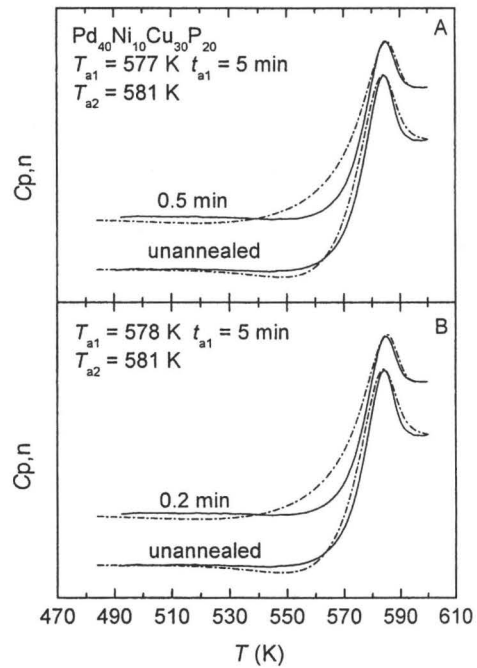


Fig. 3.13. The TNM simulation of heating curves of Pd₄₀Ni₁₀Cu₃₀P₂₀ at heating rate of 40 K/min for conditions: A. $T_{a1} = 577 \text{ K}$, $t_{a1} = 10 \text{ min}$, $T_{a2} = 581 \text{ K}$, $t_{a2} = 0.5 \text{ min}$, B. $T_{a1} = 578 \text{ K}$, $t_{a1} = 5 \text{ min}$, $T_{a2} = 581 \text{ K}$, $t_{a2} = 0.2 \text{ min}$. The parameters for simulation are $\ln A = -87$, $x = 0.68$, $\beta = 0.8$, $\Delta H = 429.9 \text{ kJ/mol}$. The dash dot lines are the simulation curves and the solid lines are the experimental data.

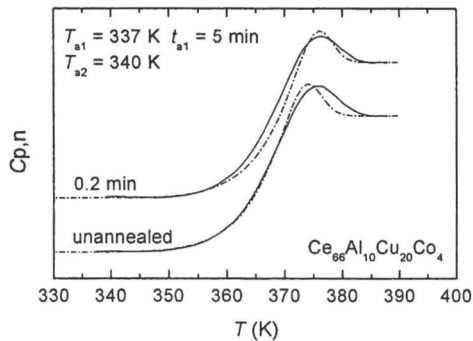


Fig. 3.14. The TNM simulation of heating curves of Ce₆₆Al₁₀Cu₂₀Co₄ at heating rate of 20 K/min for conditions: $T_{a1} = 337 \text{ K}$, $t_{a1} = 10 \text{ min}$, $T_{a2} = 340 \text{ K}$, $t_{a2} = 0.2 \text{ min}$. The parameters for simulation are $\ln A = -137.7$, $x = 0.51$, $\beta = 0.55$, $\Delta H = 428.7 \text{ kJ/mol}$. The dash dot lines are the simulation curves and the solid lines are the experimental data.

and (2.17). It may also be pointed out that the fictive temperature of a glass depends upon the property being measured and use of fictive temperature would be useful only for describing the change in the relevant property of a glass.

3.5 Conclusions

Study of the memory effect of bulk metallic glasses presented in this chapter lead to the conclusion that the memory effect phenomena of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ bulk metallic glass can be detected successfully using differential scanning calorimetry. The convenient method in memory effect study using differential scanning calorimetry can be applied to other glasses. The phenomena of memory effect in glasses can be explained using a model in which the enthalpy of the bulk consists of many ‘sub-enthalpies’ of components in the bulk, each component has a different relaxation time and varies with temperature in the same manner as the relaxation time of the bulk.

We did not analyze our data in detail enough to obtain parameters of the various structural relaxation models: Firstly, the time-temperature superposition of the plots of the measured properties used in such analysis is not expected to be valid, because (i) the magnitude of the equilibrium property varies with T , (ii) contribution and rate of the faster or JG relaxation changes and (iii) the non-exponential parameter β varies. Secondly, irreversible change in volume and enthalpy is not only due to a change in free volume and configurational C_p , but also from a significant change in the anharmonic effects, vibrational frequencies and the strength of the localized motions of the JG

relaxation. The role of localized motions was mentioned in an earlier study of memory effect by dynamic mechanical measurements of polymer blends (Cavaille et al 1986), but has not been considered further. Thirdly, T_f itself has been known to depend upon the property being measured, and finally, T_f alone is insufficient for describing the properties of a glass. If it becomes established that a non-exponential relaxation represents merely the sum of a large number of independent exponential relaxation processes, then there would be a T_g and a T_f for each process, i.e., a distribution of also T_g s and T_f s. Without considering such a distribution, it is difficult to explain how enthalpy recovery of a glass can occur in a closed thermal cycle at $T < T_g$ (Shim and Johari 1999, Johari and Shim 2000).

CHAPTER 4

CRYSTALLIZATION KINETICS OF METALLIC GLASSES

4.1 Introduction

Crystallization kinetics of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ bulk metallic glasses are most accurately studied by using differential scanning calorimetry (DSC) methods in both isothermal and non-isothermal modes. In the isothermal mode, the sample is held at a certain fixed temperature for a certain period and in the non-isothermal crystallization the sample is heated at a certain rate. Crystallization occurs in the metastable state of a supercooled ultraviscous liquid. It is irreversible, and since it is an exothermic process, the volume fraction of the crystals formed as a function of time or temperature is determined by measuring the heat liberated during the course of irreversible phase change. When crystallization occurs, an exothermic minimum is observed in experiments performed by using DSC. This indicates the rate of crystallization increasing from zero to a maximum value and then decreasing to zero.

In addition to the interest in crystal nucleation and growth in an amorphous solid, crystallization of metallic glasses has been studied extensively because of their technically useful physical properties, such as magnetic permeability and coercivity, are lost on crystallization. Since even partial crystallization occasionally causes the end of their usefulness in commercial applications (Bletry and Sador 1975, Luborsky et al

1975), an understanding of crystallization process of such glasses is important and their thermal stability need to be documented.

Partial or total crystallization of a metallic glass, may also produce useful states of different microstructures that are unobtainable by other means (Scott 1978). In such cases, knowledge of the kinetics of the process involved in crystallization is a prerequisite. Therefore, crystallization kinetics studies have also been performed not only to determine the stability of selected phases but also to determine the rates at which new crystal phases evolve on heating, or on other thermal treatments (Kelton 1993). For this purpose, crystal nucleation and growth rates of the new phase have been also investigated by studies of phase transformations kinetics (Kelton 1993).

It is known that the accuracy of the heat measurements by DSC is often high, but the data analysis necessary for understanding the crystallization kinetics have been based on certain assumptions. Therefore, the parameters obtained from the analysis often seem to bear little resemblance to their correct values for nucleation and growth (Kelton 1993). The rates of crystallization have been investigated by DSC methods for a large number of glasses, and the kinetics of the transformation has been analyzed through the use of the generalized theory of phase transformation (Kolmogorov 1937, Johnson and Mehl 1939, Avrami 1939, Turnbull 1956, and Christian 1965), that leads to, $x = 1 - \exp(-kt^m)$ where x is the fraction of volume transformed after time t , k is a rate constant, and the exponent m describes the transformation mode. This equation has been known as Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation. It has been found that for crystallization of glasses, m ranges from 2.5 to 4 for Pd-Si glasses (Burton and Ray 1971, Chou and

Turnbull 1975), and from 3 to 5 for Fe-based glasses (Scott and Ramachandrarao 1977, Shingu et al 1978). The value of m which is equal to 1 has been obtained for a Pd-Ag-Si alloy (Funakoshi et al 1977). On the basis of these studies, it was proposed that transformations for which m is between 3 and 4 may indicate a diffusion-controlled process with decreasing crystal nucleation rate with time, while for transformations for which m is equal to 1, only a one-dimensional growth of needle- or plate-like crystal form from a fixed number of nuclei after saturation.

The activation energy for crystallization has been found to vary widely with the composition and temperature of transformation of a glass. For metallic glasses with high thermal stability, such as $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ (Bagley and Vogel 1975), $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{82}\text{P}_{18}$ (Boswell 1977), and $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (Luborsky 1977), in which crystallization occurs at a temperature above the glass-liquid transformation temperature, T_g , or in the ultraviscous supercooled liquid state, the activation energy is higher than 385 kJ/mol and is seen as comparable to the activation energy for the viscous flow of an ultraviscous melt. Activation energy of $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ and $\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$ glasses, which have high thermal stability, has been found to be equal to the activation energy for viscous flow and it decreases with increasing temperature of crystallization (Chen 1978b). Therefore, it has been suggested that viscosity of the ultraviscous liquid is the rate-controlling factor in crystallization of such glasses.

Based on the crystallization study of $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$ bulk metallic glass, Wang et al (2000b) found that the apparent activation energy of crystallization is markedly changed when the glass was preannealed, especially under a high-pressure.

They concluded that the pressure annealing near glass transition temperature results in the microstructural change from short-range order to medium-range order, which affects the nucleation and diffusion. In their studies, the high diffusivity of Be atoms has a significant role in the crystallization kinetics. The study reported here is on crystallization of several non-beryllium based bulk metallic glasses and was performed to investigate the features of their crystallization kinetics.

The purpose of this study was also to investigate the nature of crystallization kinetics of an ultraviscous melt at a fixed temperature and of that of a glass on rate-heating (non-isothermal) through its melt state. The study may be useful in extrapolating how a metallic glass may partially or fully crystallize in storage and thereby cause its physical properties to change spontaneously to the detriment of its commercial use. Briefly, the study would be useful for estimating the useful life of a device containing metallic glass component subjected to high temperatures. One paper on the study has been published (Aji and Johari 2010).

4.2 Experimental Methods

Samples of three bulk metallic glasses, (i) $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, (ii) $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and (iii) $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ were used for crystallization kinetics study in this chapter. Thin samples which weighed between 7 to 15 mg used for this study were cut from the same specimens for structural relaxation study as described in Chapter 2. The instrument used for crystallization kinetics was also the same as the one used for structural relaxation study in Chapter 2, which is Pyris Diamond DSC.

For isothermal crystallization studies at a fixed temperature, a DSC scan was first obtained by heating a sample at a heating rate, q_h , of 20 K/min from 363 K to a certain temperature, T_{max} , 723 K for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, 693 K for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and 703 K for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. The basis for selecting T_{max} was that the glass should crystallize completely at that temperature. From the profile of this scan, several temperatures were selected for crystallization studies and these temperatures were specific to a glass. The as-cast metallic glass samples were heated from 363 K at 100 K/min rate to the fixed temperature, T_{crys} , and then held at T_{crys} for a certain time, t_{crys} . To investigate whether or not isothermal precrystallization has an effect on non-isothermal crystallization kinetics, the samples were subsequently cooled to 363 K and thereafter heated to T_{max} . The heat flow was recorded as a function of time. For each study of crystallization kinetics at a selected T_{crys} , a new sample was used. These temperatures as well T_g determined at 20 K/min heating rate and the onset temperature of crystallization T_x are listed in Table 4.1.

Table 4.1. Annealing temperatures, T_{crys} , for isothermal crystallization studies of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses.

Metallic Glass	T_g (K) $q_h = 20$ K/min	T_x (K) $q_h = 20$ K/min	T_{crys} (K)
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	569	647	593, 603, 613, 623, 633
$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$	415	481	448, 453, 458, 463, 468
$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	423	499	448, 453, 458, 463, 468, 473

For non-isothermal crystallization studies, the as-cast samples were heated at various rates from 363 K to T_{max} , then cooled to 363 K at the same rate as heating, and thereafter reheated to T_{max} . The second heating of the crystallized sample was performed in order to determine whether or not the glass sample had completely crystallized. During

the second heating no exothermic heat flow was observed. The heating rates selected are 5, 10, 20, 40 and 80 K/min for all glasses.

4.3 Results and Data Analysis

4.3.1 Isothermal Crystallization of Bulk Metallic Glasses

As the data analysis for isothermal crystallization is relatively simple, we first describe this study. The heat flow against temperature plots obtained from the DSC scans during isothermal crystallization are shown for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ in Fig. 4.1, for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ in Fig. 4.2, and for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ in Fig. 4.3. These figures show that for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glasses only one minimum is observed and for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ two minima are observed. Also, the figures show, as expected from the thermally activated crystallization and phase transformation, the higher the selected T_{crys} , the higher is the depth of the exothermic minimum, the smaller is the minimum's width, the lesser is the onset (or starting) time for crystallization, and shorter is the time for complete crystallization.

To determine the crystallized volume fraction during isothermal annealing, we assumed, as by other investigators (Borchard and Daniel 1957, Henderson 1979) that the area of the minimum is proportional to the crystallized volume fraction. Therefore, at the onset time of crystallization this fraction is zero and for the final time of crystallization the fraction is one. Fig. 4.4 shows as an example how the crystallized volume fraction, x , was determined for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass annealed at 453 K.

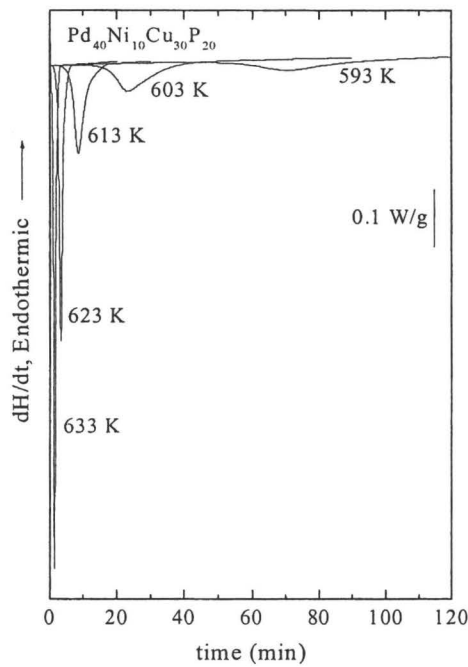


Fig. 4.1. The DSC curves of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass during isothermal annealing at T_{crys} of 593 K, 603 K, 613 K, 623 K, and 633 K.

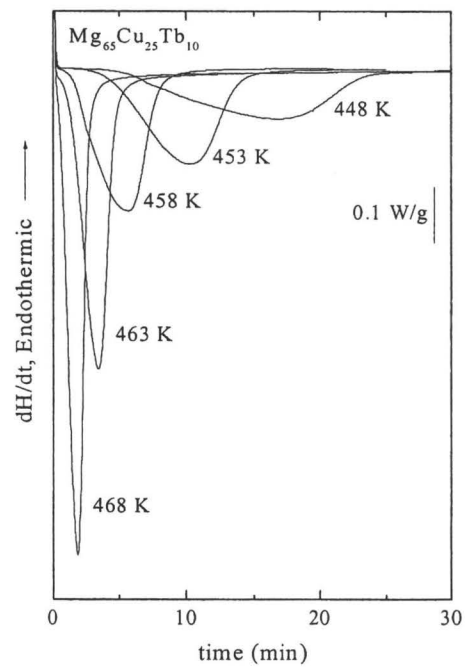


Fig. 4.2. The DSC curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during isothermal annealing at T_{crys} of 448 K, 453 K, 458 K, 463 K, and 468 K.

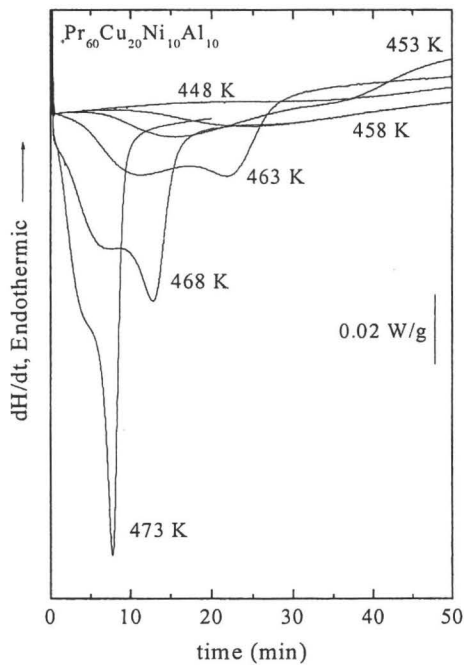


Fig. 4.3. The DSC curves of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass during isothermal annealing at T_{crys} of 448 K, 453 K, 458 K, 463 K, 468 K and 473 K.

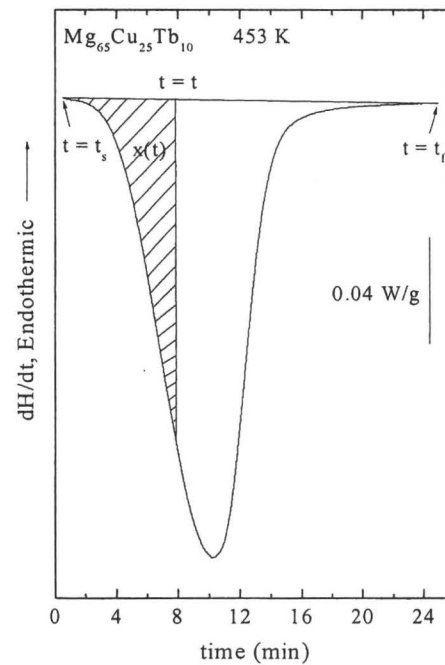


Fig. 4.4. Typical exothermic minimum for isothermal crystallization of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass at T_{crys} of 453 K. The hatched area represents crystallization fraction at time t . t_s is the starting time of crystallization and t_f is the final time of crystallization.

The crystallized volume fraction at time, t , at the relevant temperature is,

$$x(t) = \frac{1}{\Delta H_{cryst}} \int_{t=0}^t \left(\frac{dH}{dt} \right) dt \quad (4.1)$$

where ΔH_{cryst} is equal to the total area of the crystallization exotherm. The values of ΔH_{cryst} obtained from isothermal crystallization of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ melts are listed in Table 4.2. Figs. 4.5A, 4.5B, and 4.6 show the crystallized volume fraction versus annealing time for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, respectively.

Table 4.2. The fixed temperature of crystallization and the enthalpy of crystallization for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses.

Metallic Glass	Minimum	T_{crys} (K)	ΔH_{cryst} (kJ/mol)
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	1	593	1.96 ± 0.05
		603	2.39 ± 0.05
		613	2.81 ± 0.05
		623	2.92 ± 0.05
		633	2.97 ± 0.05
$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$	1	448	2.81 ± 0.05
		453	2.92 ± 0.05
		458	2.96 ± 0.05
		463	3.23 ± 0.05
		468	3.61 ± 0.05
$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	1	453	1.33 ± 0.05
		458	1.37 ± 0.05
		463	1.45 ± 0.05
		468	1.49 ± 0.05
		473	1.55 ± 0.05
	2	458	1.54 ± 0.05
		463	1.58 ± 0.05
		468	1.61 ± 0.05
		473	1.64 ± 0.05

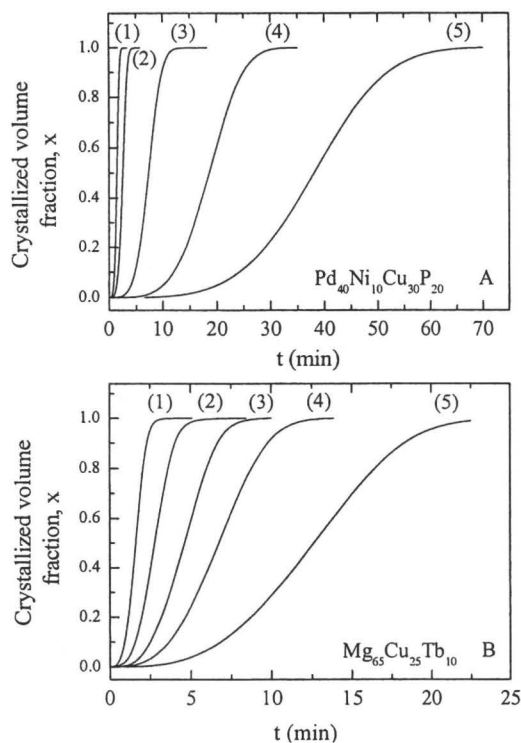


Fig. 4.5. The crystallized volume fraction curves against annealing time at different annealing temperatures. A. $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ at annealing temperatures: (1) 633 K, (2) 623 K, (3) 613 K, (4) 603 K, and (5) 593 K. B. $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ at annealing temperatures: (1) 468 K, (2) 463 K, (3) 458 K, (4) 453 K, and (5) 448 K.

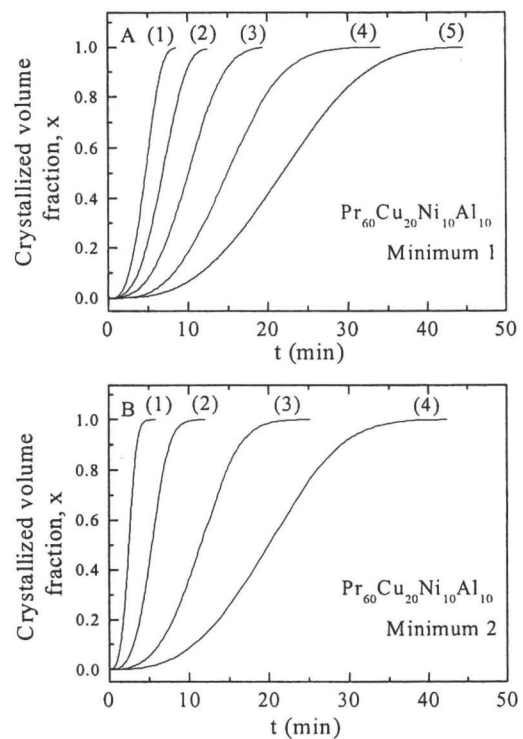


Fig. 4.6. The crystallized volume fraction curves against annealing time at different annealing temperatures of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. A. First exothermic minima at annealing temperatures: (1) 753 K, (2) 468 K, (3) 463 K, (4) 458 K, and (5) 453 K. B. Second exothermic minima at annealing temperatures: (1) 753 K, (2) 468 K, (3) 463 K, and (4) 458 K.

4.3.2 Non-isothermal Crystallization of Bulk Metallic Glasses

On the basis of the data obtained from isothermal crystallization studies, we now consider the non-isothermal crystallization during the heating of the bulk metallic glasses. Fig. 4.7 shows the heat flow against temperature plots obtained from the DSC curves for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, as measured during its heating at different rates, Fig. 4.8 shows the corresponding plots for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and Fig. 4.9 shows the corresponding plots for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. There are two distinguishable exothermic minima observed for all three

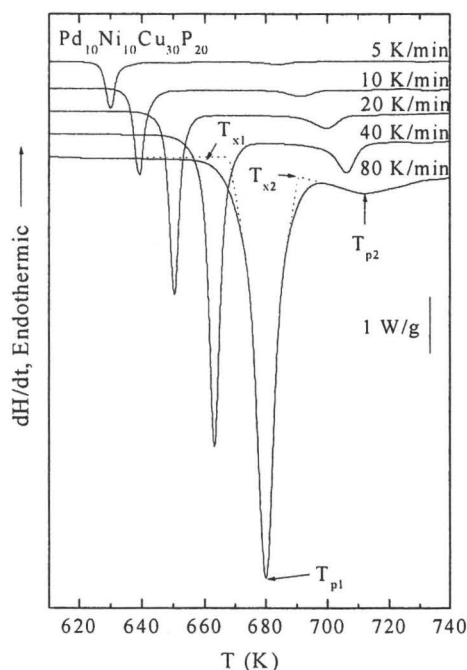


Fig. 4.7. The DSC curves of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass during heating at rates of 5, 10, 20, 40, and 80 K/min. T_{x1} and T_{x2} are the onset crystallization temperatures for minimum 1 and minimum 2, respectively. T_{p1} and T_{p2} are the minimum temperatures for minimum 1 and minimum 2, respectively.

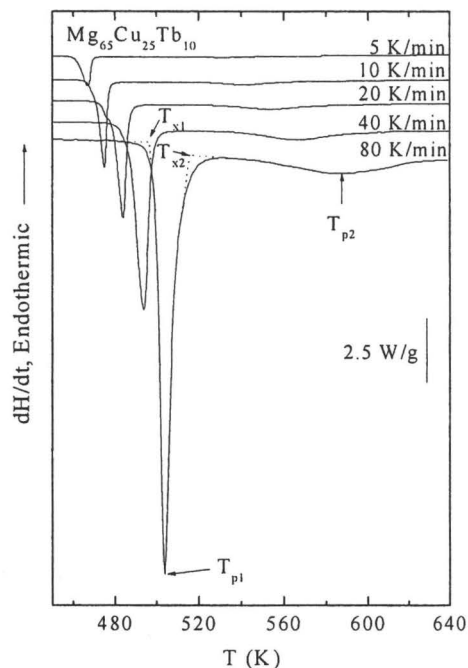


Fig. 4.8. The DSC curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at rates of 5, 10, 20, 40, and 80 K/min. T_{x1} and T_{x2} are the onset crystallization temperatures for minimum 1 and minimum 2, respectively. T_{p1} and T_{p2} are the minimum temperatures for minimum 1 and minimum 2, respectively.

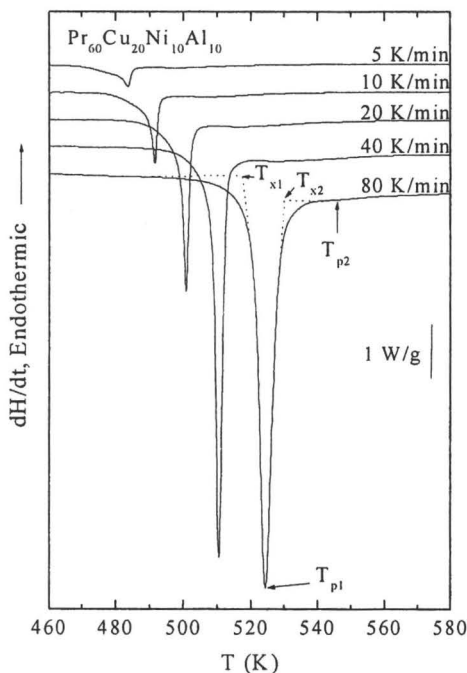


Fig. 4.9. The DSC curves of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass during heating at rates of 5, 10, 20, 40, and 80 K/min. T_{x1} and T_{x2} are the onset crystallization temperatures for minimum 1 and minimum 2, respectively. T_{p1} and T_{p2} are the minimum temperatures for minimum 1 and minimum 2, respectively.

glasses. In the first exothermic minimum labeled 1, the onset and the end temperature of the first exothermic minima can be discerned. The plots also show that the higher the heating rate of a glass and ultraviscous melt, the higher is the crystallization temperature, T_x , the temperature of the local minimum T_p , and its depth, and the minimum's width at half-depth.

To further analyze these features of the crystallization exotherm, the glasses were isothermally annealed at a certain temperature and thereafter their non-isothermal crystallization studied by heating at fixed rate. Fig. 4.10 shows the heating curves for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass after isothermal annealing at, (i) 593 K for 150 min, (ii) 603 K for 90 min, (iii) 613 K for 30 min, (iv) 623 K for 20 min, and (v) 633 K for 10 min. These annealing times were considered as sufficient for the samples to reach complete crystallization, as is seen in Fig. 4.1.

Fig. 4.11 shows the heating curve for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ after isothermal annealing at, (i) 448 K for 40 min, (ii) 453 K for 25 min, (iii) 458 K for 20 min, (v) 463 K for 15 min, and (vi) 468 K for 10 min. These annealing times were sufficient also for the samples to reach complete crystallization as is seen in Fig. 4.2. Fig. 4.12 shows the heating curve for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ after isothermal annealing at, (i) 448 K for 90 min, (ii) 453 K for 120 min, (iii) 458 K for 90 min, (iv) 463 K for 50 min, (iv) 468 K for 30 min, and (v) 473 K for 20 min. These annealing times were sufficient also for the samples to reach complete crystallization, as is seen in the plots in Fig. 4.3, except for the plot for the annealing temperature of 448 K and time of 90 min.

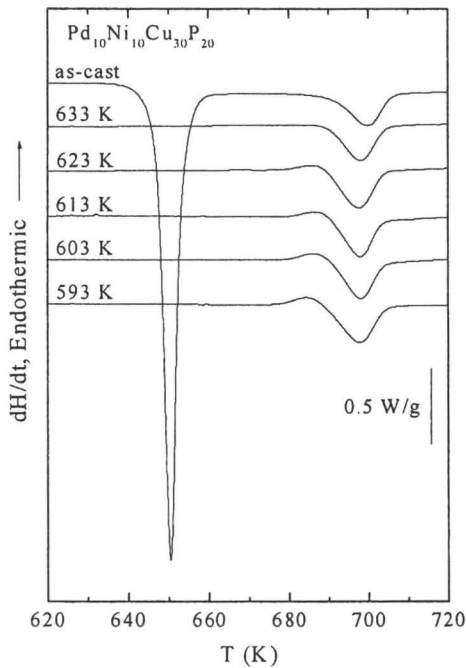


Fig. 4.10. The DSC curves of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass during heating at rate of 20 K/min of the as-cast sample and after isothermal annealing at annealing temperatures of 593 K for 150 min, 603 K for 90 min, 613 K for 30 min, 623 K for 20 min, and 633 K for 10 min.

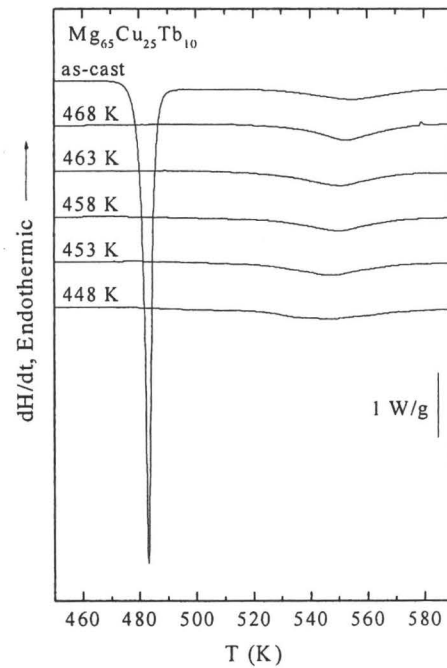


Fig. 4.11. The DSC curves of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass during heating at rates of 20 K/min of the as-cast sample and after isothermal annealing at annealing temperatures of 448 K for 40 min, 453 K for 25 min, 458 K for 20 min, 463 K for 15 min, and 468 K for 10 min.

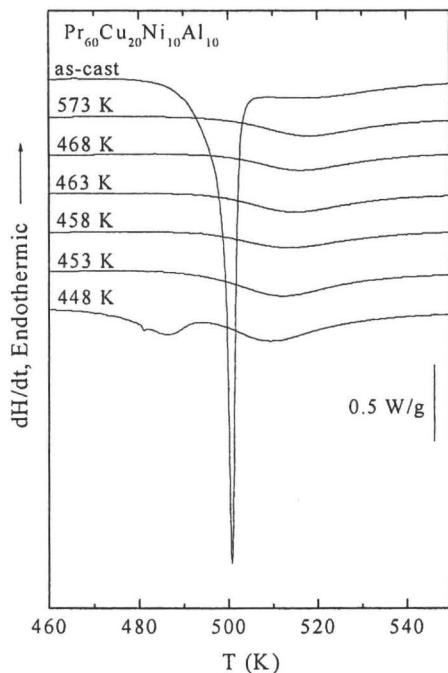


Fig. 4.12. The DSC curves of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass during heating at rates of 20 K/min of the as-cast sample and after isothermal annealing at annealing temperatures of 448 K for 90 min, 453 K for 120 min, 458 K for 90 min, 463 K for 50 min, 468 K for 30 min, and 473 K for 20 min.

The crystallized volume fraction, x , at a certain temperature T is again taken as proportional to the fractional area of the exothermic minimum, as shown in Fig. 4.13. Therefore,

$$x(T) = \frac{1}{\Delta H_{cryst}} \int_{T_0}^T \frac{1}{q_h} \left(\frac{dH}{dt} \right) dT \quad (4.2)$$

where ΔH_{cryst} is equal to the total exothermic minimum area in the plot of $(dH/dt)/q_h$ in the temperature plane, and T_0 is a reference temperature below $T_{x,1}$ or $T_{x,2}$. The values of ΔH_{cryst} obtained from isothermal crystallization of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ melts are listed in Table 4.3. Figs. 4.14A and 4.15A show the plots of the crystallized volume fraction against the temperature at different heating rate for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ minima 1 and minima 2, respectively. Figs. 4.16A and 4.17A show the plots of the crystallized volume fraction against the temperature at different heating rate for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ minima 1 and minima 2, respectively, and Fig. 4.18A shows the plots of the crystallized volume fraction against the temperature at different heating rate for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ minima 1. The crystallization rate, dx/dt , is calculated by,

$$\frac{dx}{dt} = \frac{dx}{dT} \times \frac{dT}{dt} \quad (4.3)$$

Figs. 4.14B and 4.15B show the plots of crystallization rate against the temperature at different heating rates for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ minima 1 and minima 2, respectively. Figs. 4.16B and 4.17B show the corresponding plots at different heating rates for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ minima 1 and minima 2, respectively, and Fig. 4.18B shows the corresponding plots at different heating rate for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ minima 1.

Table 4.3. The heating rate, the onset and peak temperatures, the enthalpy of crystallization $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ melts for the first and second exothermic features.

Metallic Glass	q_h (K/min)	$T_{x,1}$ (K)	$T_{p,1}$ (K)	$\Delta H_{cryst,1}$ (kJ/mol)	$T_{x,2}$ (K)	$T_{p,2}$ (K)	$\Delta H_{cryst,2}$ (kJ/mol)
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	5	626.3	630.1	3.15 ± 0.05	676.6	683.7	0.31 ± 0.05
	10	635.2	639.4	3.19 ± 0.05	684.1	691.3	0.43 ± 0.05
	20	645.5	650.4	3.31 ± 0.05	690.1	700.1	0.51 ± 0.05
	40	655.7	663.3	3.43 ± 0.05	695.3	706.1	0.55 ± 0.05
	80	667.8	679.9	3.48 ± 0.05	700.2	711.9	0.59 ± 0.05
$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$	5	461.9	466.9	3.47 ± 0.05	469.5	530.7	0.76 ± 0.05
	10	469.8	475.2	3.51 ± 0.05	477.5	541.6	0.85 ± 0.05
	20	478.2	483.2	3.58 ± 0.05	487.1	553.5	0.89 ± 0.05
	40	484.3	493.9	3.74 ± 0.05	498.8	565.9	0.97 ± 0.05
	80	496.1	503.8	4.05 ± 0.05	515.7	585.9	0.99 ± 0.05
$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	5	474.7	483.6	3.01 ± 0.05	483.7	498.5	1.47 ± 0.05
	10	481.4	491.4	3.36 ± 0.05	493.2	506.5	1.51 ± 0.05
	20	494.1	500.8	3.42 ± 0.05	502.4	516.5	1.58 ± 0.05
	40	505.3	510.6	3.49 ± 0.05	512.7	528.8	1.61 ± 0.05
	80	517.4	524.4	3.61 ± 0.05	529.8	545.7	1.65 ± 0.05

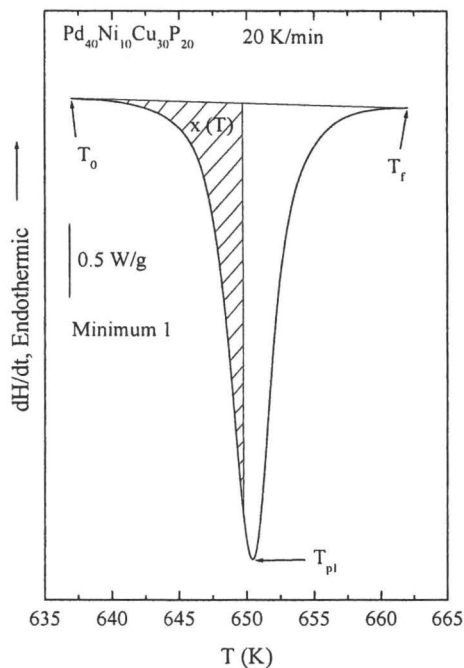


Fig. 4.13. Typical exothermic minimum for non-isothermal crystallization of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass at a heating rate of 20 K/min. The hatched area represents the crystallized fraction at temperature T . T_0 is the starting point of crystallization and T_f is the final temperature of crystallization.

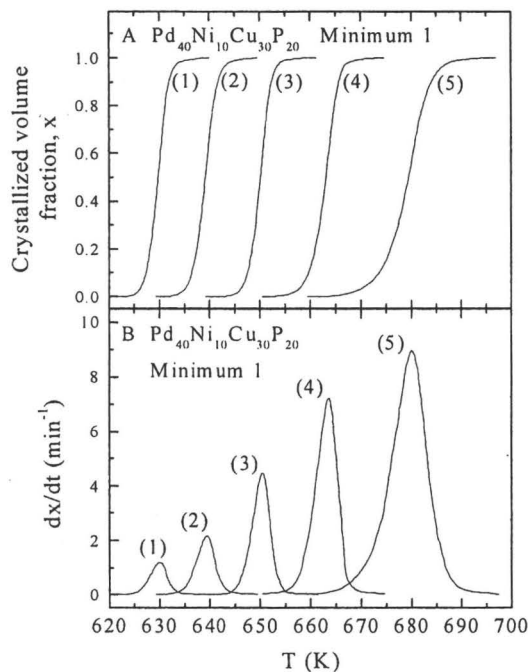


Fig. 4.14. The crystallized volume fraction curves (A) and the crystallization rate (B) against temperature of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ first minima at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min.

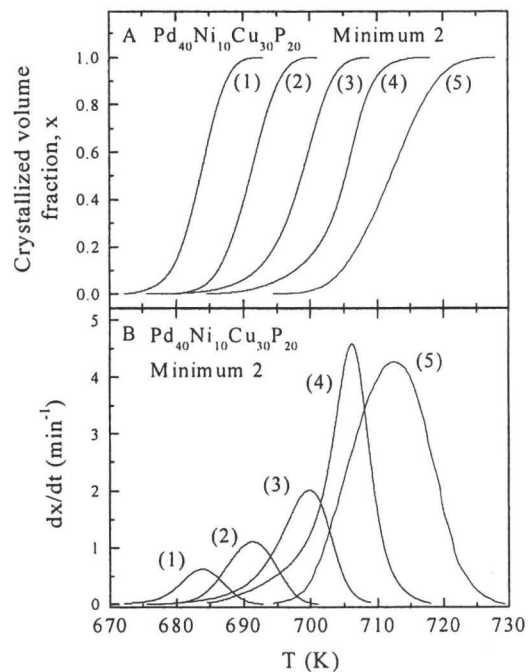


Fig. 4.15. The crystallized volume fraction curves (A) and the crystallization rate (B) against temperature of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ second minima at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min.

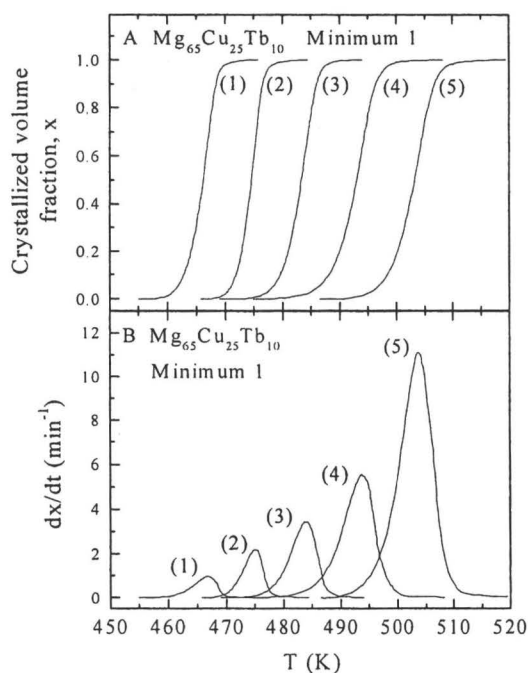


Fig. 4.16. The crystallized volume fraction curves (A) and the crystallization rate (B) against temperature of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ first minima at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min.

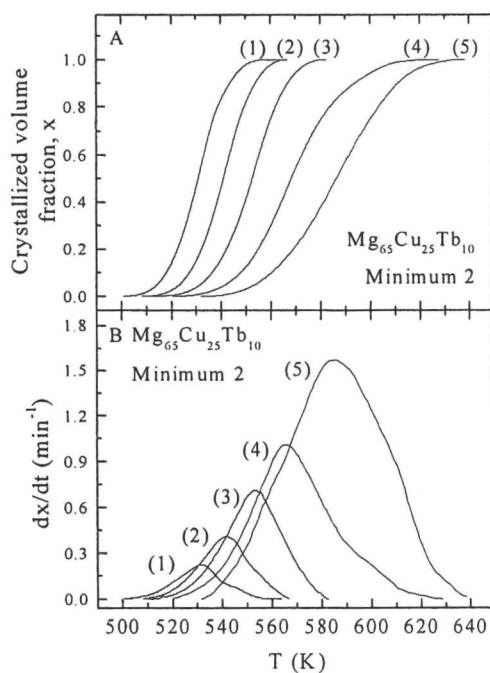


Fig. 4.17. The crystallized volume fraction curves (A) and the crystallization rate (B) against temperature of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ second minima at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min.

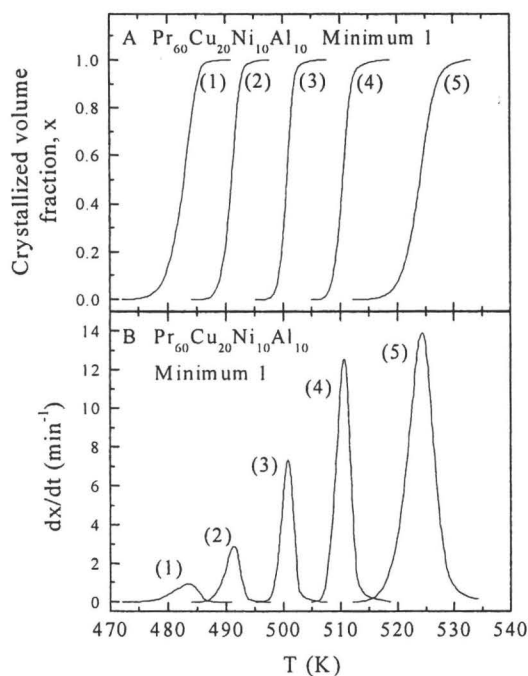


Fig. 4.18. The crystallized volume fraction curves (A) and the crystallization rate (B) against temperature of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ first minima at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min.

4.4 Discussion

4.4.1 General Features and Formalisms Used for Crystallization Kinetics

It appears that the general concepts and analysis that had been developed for congruent crystallization of (mono-component or eutectic composition) glasses and melts have been used for crystallization of multi-component non-eutectic compositions. In as much as these concepts are used for interpreting the data for metallic glasses, it seems worth mentioning their theoretical and experimental context, and their limitations: According to Turnbull and Fisher's theory of crystal growth (Turnbull and Fischer 1949, Christian 1975, Gutzow and Schmelzer 1995, Schmelzer 2008, Schmelzer et al 2010), the rate of homogeneous nucleation is determined by two quantities, (i) the extent of supercooling denoted by $(T_m - T)$, where T_m is the equilibrium freezing point of the melt, and (ii) the excess entropy of supercooled melt over the crystal phase. Kinetic equations for the nucleation rate require also the solid-melt interfacial energy and the free energy barrier for molecular diffusion across the interface, and this barrier may change with both t and T when crystal formed do not have the same composition as the melt. As the melt is cooled, the term $(T_m - T)^2$, that appears in the denominator of the negative exponential term for the nucleation rate, increases rapidly and hence the nucleation rate increases from a low to a high value over a small temperature range. The assumption of constant excess entropy with increasing supercooling restricts the use of the Turnbull-Fisher equation to a small extent of supercooling. For deep supercooling to T far below T_m , the excess entropy becomes significantly less than that at T_m . This lessening not only has a significant effect on the nucleation rate, but also on the crystal growth rate if the

excess entropy were to determine the viscosity, as in thermodynamic theories of glass formation (Adam and Gibbs 1965). (Multi-component glasses also have entropy of mixing that does not change on cooling.) In the terminology of thermodynamic and kinetic driving forces for crystallization, (i) the effect of increase in $(T_m - T)^2$ is relatively small at T just below T_m and large in the ultraviscous melt, particularly on cooling toward the vitrification range and (ii) the effect of reduction in the excess entropy is large at T just below T_m and small in the ultraviscous melt on cooling toward the vitrification range. Nucleation rate is zero at T_m and crystal-growth rate is vanishingly small in the vitrified state. Plots of both the nucleation and crystal-growth rates against T show a peak. Their widths and shapes differ and the plots often partly overlap.

The above mentioned separation between the time scales of nucleation and crystal-growth, recognized already by Tammann (1933) as two consecutive stages of crystallization. In the first stage crystallization centers or nuclei form and in the second the nuclei grow. Plots of the nucleation and crystal growth rates against T also have different shapes, and when an ultraviscous melt obtained by heating a glassy state crystallizes, the crystal nuclei, if already present, are expected to grow before new nuclei may form preferably in the localized regions in the glassy state or else form randomly in the volume of an ultraviscous melt. Both the nucleation and crystal-growth rates determine the crystallization kinetics of the melt but the slower of the two rates dominates the observed thermal effects. In contrast, crystallization of metal alloy glasses by Ichitsubo et al (2005, 2006, 2008), by use of radio-frequency ultrasonic energy absorption has shown that mechanical instability due to the resulting shear in local

regions, where the faster process of JG relaxation occurs (Johari 1973), causes crystallization. Also, as nucleation and crystal-growth occur in the same volume of a melt, the amount of melt available for nucleation decreases as crystals grow. The situation becomes further complicated for incongruent crystallization, because in this case the composition and properties of the remaining melt also change.

Molecular diffusion dynamics that is needed for crystallization of an ultraviscous melt and glass is distinguished from that of a low-viscosity melt. In the ultraviscous melt, it is said to be co-operative and is described in terms of either the characteristic time for the α -relaxation process or viscosity, both of which show a non-Arrhenius variation with T . Their apparent activation energies decrease as T is increased. There is also a dynamics of localized motions that shows up as the β - or the JG relaxation (Johari 1973), and whose characteristic time varies with T according to the Arrhenius equation. In the glassy state, the co-operative dynamics is too slow and only the JG relaxation dynamics is observed and yet heat treatment of metallic glass changes its shear modulus (Kahl et al 2009). Localized modes of motions are also recognized as the source of the unexpectedly rapid nucleation and growth in the glassy and ultraviscous states of small molecule organic substances (Hikima et al 1996, 1999, Norimaru and Oguni 1996, Hatase et al 2003, Paladi and Oguni 2002, 2003), and there are indications that the overall crystallization rate is most rapid in a viscous melt far below its freezing point (Power and Vij 2004), at the Donth temperature (Donth 2001), where the α -relaxation process evolves from the JG relaxation process (Johari 1973, Ngai and Paluch 2004).

4.4.2 Thermodynamic Aspects

In Table 4.2, ΔH_{cryst} of $Mg_{65}Cu_{25}Tb_{10}$ melt increases from 2.81 kJ/mol from T_{cryst} of 448 K to 3.61 kJ/mol for T_{cryst} of 468 K. In Table 4.3, ΔH_{cryst} for minimum 1 increases from 3.47 kJ/mol for q_h of 5 K/min to 4.05 kJ/mol for q_h of 80 K/min and the minimum itself shifts from 466.9 K to 503.8 K. Also, ΔH_{cryst} for minimum 2 increases from 0.76 kJ/mol for q_h of 5 K/min to 0.99 kJ/mol for q_h of 80 K/min and the minimum shifts from 530.7 K to 585.9 K. If crystallization occurred congruently and there were no other thermodynamic occurrences, the ΔH_{cryst} values would be closely similar for the five temperatures listed in Table 4.2. Also, the total ΔH_{cryst} value for minima 1 and 2 would be similar for the five heating rates. Moreover, the ΔH_{cryst} value determined from isothermal crystallization would be similar to that determined from non-isothermal crystallization. Any difference in the total heat of crystallization per mol of the original compositions ($Mg_{65}Cu_{25}Tb_{10}$) in isothermal and non-isothermal measurements would be a consequence of incongruent crystallization to compositionally different phases. The differences observed here indicate that crystallization is incongruent and the calculations based on per mol of the original composition of $Mg_{65}Cu_{25}Tb_{10}$ are not directly comparable. As in $Mg_{65}Cu_{25}Tb_{10}$, the analysis above also observed in $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and $Pr_{60}Cu_{20}Ni_{10}Al_{10}$. This behavior also has been observed in Fe-based metallic glass (Shingu et al 1978).

4.4.3 Isothermal Crystallization of Bulk Metal Glasses

Kolmogorov (1937) had calculated the probability of nucleation in a certain volume that remains available at a certain time after crystallization has begun. Gutzow and Schmelzer (1995) have provided a detailed discussion of the subject and compared the Kolmogorov's probability calculation with Poisson's probability calculation of a mathematically similar problem. They also discussed the formal treatments of the volume available for nucleation in a partially-crystallized melt by Johnson and Mehl (1939) and by Avrami (1939, 1940). More recent experiments (Hikima et al 1996, 1999, Norimaru and Oguni 1996, Hatase et al 2003, Paladi and Oguni 2002, 2003, Ichitsubo et al 2005, 2006, 2008) showing that nucleation and crystal growth occurs in local regions imply that these processes are not necessarily as random as is implicit in the Poisson distribution. It has not been possible to incorporate it in the kinetics of nucleation and crystal-growth, and the incongruent crystallization of metal alloy glasses makes it more difficult to mathematically interpret crystallization kinetics. As we are unable to take these aspects into account, we analyze our data, as in numerous earlier studies of phase transformation in crystalline metals, and crystallization of molecular and polymeric and metal-alloy glasses, by using the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation (Kolmogorov 1937, Johnson and Mehl 1939, Avrami 1939, 1940) for overall crystallization. Accordingly, the quantity x is written as,

$$x_n(t) = 1 - \exp[-Y_n(t)], \text{ and } Y_n(t) = \omega_n J v^n \int_0^t (t-t')^n dt' \quad (4.4)$$

where Y_n is the new phase formed until time t , J is the nucleation rate, v is the linear growth velocity and ω_n is a geometrical factor equal to $4\pi/3$ for spheres. The parameter n has different values for different nucleation and growth mechanisms and for dimensions of space in which transformation occurs. After substitution for the integral for $Y_n(t)$, the final equation is now known as Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation. Burbelko et al (2005) have reviewed its progress since Kolmogorov's original paper. We follow the description in the monograph by Gutzow and Schmelzer (1995):

$$x_n(t) = 1 - \exp\left[-\frac{\omega_n}{(n+1)} J v^n t^{n+1}\right] \quad (4.5)$$

or,
$$x_n(t) = 1 - \exp[-k_n t^{n+1}], \text{ where } k_n = \frac{\omega_n}{(n+1)} J v^n \quad (4.5)$$

The quantity $n+1$ is written as equal to m , which is known as the KJMA coefficient for phase transformation. The quantity k_n is known as KJMA kinetic coefficient. Macroscopically, it is the temperature-dependent rate constant for crystallization in this study. The value of m is usually an integer, which depends upon the dimensionality and morphology of the crystal-growth.

In the formalism for nucleation and crystal growth in molten metals, interactions between atoms have a spherical symmetry, i.e., there is no directional bias, and in molecular melts interactions are also taken to be spherical but in terms of the Van der Waals forces. Any change in these interactions may be seen as a process occurring concurrently to crystal growth and this change is expected to show up as a decrease in the enthalpy.

In practice the form of KJMA equation used for fitting the overall crystallization kinetics data is:

$$x(t) = 1 - \exp[-kt^m] \quad (4.6)$$

By differentiating Eq. (4.6) with respect to t one obtains the condition at which the rate of crystallization reaches a maximum value,

$$\frac{dx}{dt} = mkt^{m-1}\exp(-kt^m) \quad (4.7)$$

Eq. (4.6) was fitted to the plots of x against t in Figs. 4.5 and 4.6 and the values of m and k were obtained. These values are listed in Table 4.4. The k values in turn were used to determine the rate constant k_0 and the activation energy E from the relation,

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (4.8)$$

The values of E are 252 kJ/mol for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, 169 kJ/mol for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and 116 and 217 kJ/mol for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ for exothermic minima 1 and 2, respectively, and the corresponding k_0 values are 1.12×10^{87} , 1.53×10^{59} , 9.51×10^{37} , and $3.98 \times 10^{77} \text{ s}^{-1}$. The fitted and experimental curves of x and dx/dt are shown in Fig. 4.19 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, Fig. 4.20 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and Fig. 4.21 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$.

4.4.4 Non-isothermal Crystallization of Bulk Metal Glasses

The parameters for the non-isothermal crystallization kinetics are obtained also by fitting the KJMA equation modified for the purpose. There are several methods (Ozawa 1971, Takhor 1972, Augis and Bennet 1978, and Henderson 1979) for such an analysis, but one suggested by Greer (1982) seems most appropriate for use here. Greer assumed that the crystallization at different T will vary only in the time scale, i.e., that the

Table 4.4. The fixed temperature of crystallization, the enthalpy of crystallization, and the parameters of crystallization kinetics for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses as obtained by fitting the KJMA equation.

Metallic glass	Minimum	T_{crys} (K)	$k(\text{s})^{-m}$	m	E (kJ/mol)
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	1	593	1.8×10^{-14}	4.04 ± 0.05	252 ± 2
		603	1.2×10^{-13}	4.17 ± 0.05	
		613	4.7×10^{-12}	4.22 ± 0.05	
		623	2.4×10^{-10}	4.33 ± 0.05	
		633	1.7×10^{-9}	4.41 ± 0.05	
$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$	1	448	7.7×10^{-10}	3.11 ± 0.05	169 ± 2
		453	4.3×10^{-9}	3.15 ± 0.05	
		458	1.3×10^{-8}	3.17 ± 0.05	
		463	5.09×10^{-8}	3.21 ± 0.05	
		468	2.5×10^{-7}	3.25 ± 0.05	
$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	1	453	1.7×10^{-8}	3.01 ± 0.05	116 ± 2
		458	3.5×10^{-8}	3.07 ± 0.05	
		463	7.5×10^{-8}	3.15 ± 0.05	
		468	1.4×10^{-7}	3.24 ± 0.05	
		473	2.4×10^{-7}	3.36 ± 0.05	
	2	458	1.4×10^{-8}	3.08 ± 0.05	217 ± 2
		463	3.6×10^{-8}	3.23 ± 0.05	
		468	1.2×10^{-7}	3.41 ± 0.05	
		473	8.6×10^{-7}	3.53 ± 0.05	

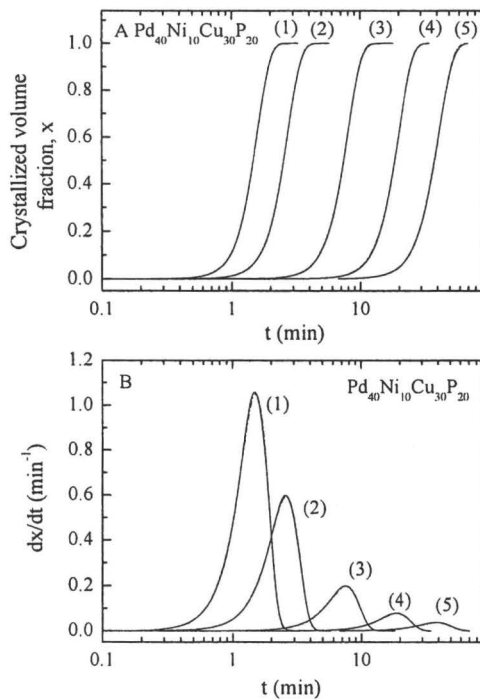


Fig. 4.19. A. The JMAK equation fitting of x for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ at T_{cryst} of: (1) 633 K, (2) 623 K, (3) 613 K, (4) 603 K, and (5) 593 K. B. The corresponding dx/dt . The solid lines are the experiment data and the dash lines are the fitting curves.

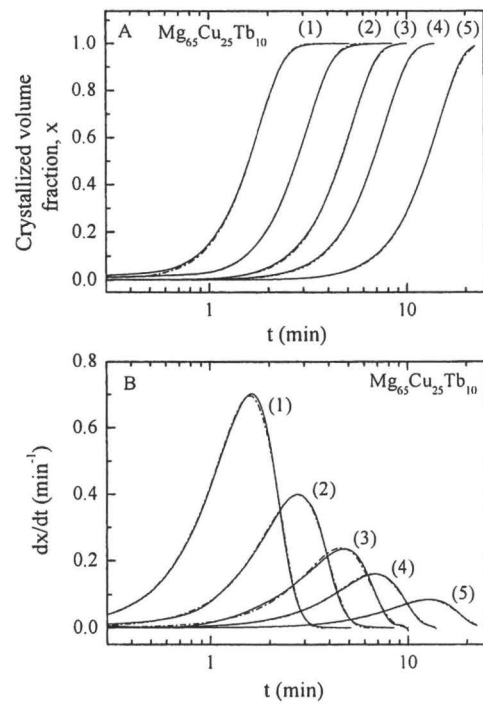


Fig. 4.20. A. The JMAK equation fitting of x for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ at T_{cryst} of: (1) 468 K, (2) 463 K, (3) 458 K, (4) 453 K, and (5) 448 K. B. The corresponding dx/dt . The solid lines are the experiment data and the dash lines are the fitting curves.

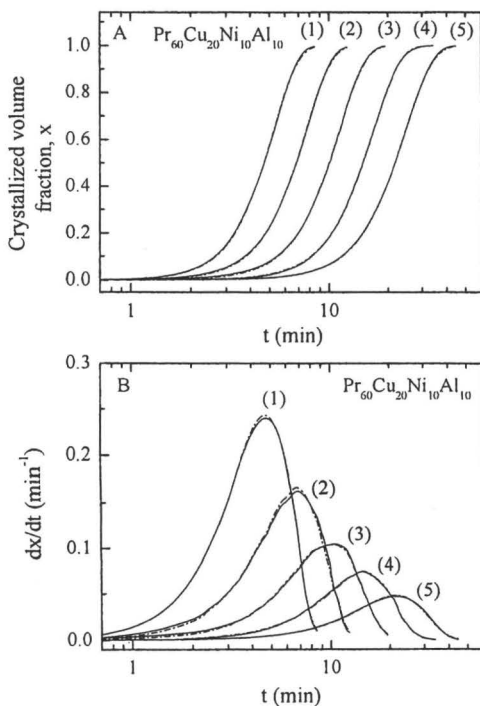


Fig. 4.21 A. The JMAK equation fitting of x for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ first exothermic minima at T_{cryst} of: (1) 473 K, (2) 468 K, (3) 463 K, (4) 458 K, and (5) 453 K. B. The corresponding dx/dt . The solid lines are the experiment data and the dash lines are the fitting curves.

transformation is iso-kinetic and its rate at any instant depends only on T and x at that instant. It is independent of prior thermal history of the sample, as would be the case for a melt in which crystals of only one composition form. In this study, direct use is made of the isothermal KJMA equation by approximating the linear heating profile as a series of short isothermal anneals. Consider a material transformed at T_1 for a time of t_1 . The transformed fraction at T_1 is $x = f_1(t')$, where t' is the time from the start of the transformation at T_1 . At the end of transformation at T_1 , the transformed fraction is $x = f_1(t_1)$. The transformation continues at T_2 for a time of t_2 at which $x = f_2(t'')$, where t'' is the time from the start of transformation at T_2 . The course of the transformation at T_2 is precisely the same as if the initial transformed fraction at T_2 , $f_1(t_1)$, had been formed at T_2 . If $t_{1'}$ is the time it would have taken at T_2 to produce $x = f_1(t_1)$, i.e., $f_1(t_1) = f_2(t_{1'})$, the transformation at T_2 is given by,

$$x = f_2(t + t_{1'} - t_1) \quad (4.9)$$

where t is the time from the start of the transformation at T_1 (or T_2). At the end of transformation at T_2 , $x = f_2(t_2 + t_{1'} - t_1)$. The calculations had been performed by using a computer program for anneals at uniformly incremented temperature. At the end of the rate-heating, values of x are obtained and dx/dt is evaluated at the midpoints of temperature step. For the i th increment, dx/dt at $T = (T_i + T_{i+1})/2$ is taken to be $(x_{i+1} - x_i)/(t_{i+1} - t_i)$. The fitted parameters of crystallization kinetics for all three glasses are listed in Table 4.5. The data for $\ln(k)$ obtained are plotted against $1/T$ in Fig. 4.22 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, Fig. 4.23 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and Fig. 4.24 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, where the values obtained from isothermal crystallization studies are shown by circles. Figs.

4.25, 4.26A, and 4.26B show the fitting result of non-isothermal crystallization at different heating rates for exothermic minima 1 of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses, respectively.

Table 4.5. The parameters of non-isothermal crystallization kinetics obtained by fitting the KJMA equation to the data for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses obtained at different heating rates.

Metallic Glass	Minimum	q_h (K/min)	T_p (K)	E (kJ/mol)	$\ln k_0$	m
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	Minimum 1	5	630.3	249 ± 2	178.60	4.10 ± 0.05
		10	639.4		177.96	4.09 ± 0.05
		20	650.4		177.10	4.07 ± 0.05
		40	663.3		174.80	4.05 ± 0.05
		80	680.0		171.20	4.02 ± 0.05
$\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$	Minimum 1	5	466.9	246 ± 2	191.90	3.30 ± 0.05
		10	475.2		190.10	3.28 ± 0.05
		20	483.2		187.01	3.26 ± 0.05
		40	493.9		183.25	3.23 ± 0.05
		80	503.8		180.30	3.20 ± 0.05
$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$	Minimum 1	5	484.3	241 ± 2	180.70	3.29 ± 0.05
		10	491.5		180.30	3.27 ± 0.05
		20	500.7		177.80	3.23 ± 0.05
		40	510.5		174.10	3.19 ± 0.05
		80	524.5		169.04	3.17 ± 0.05

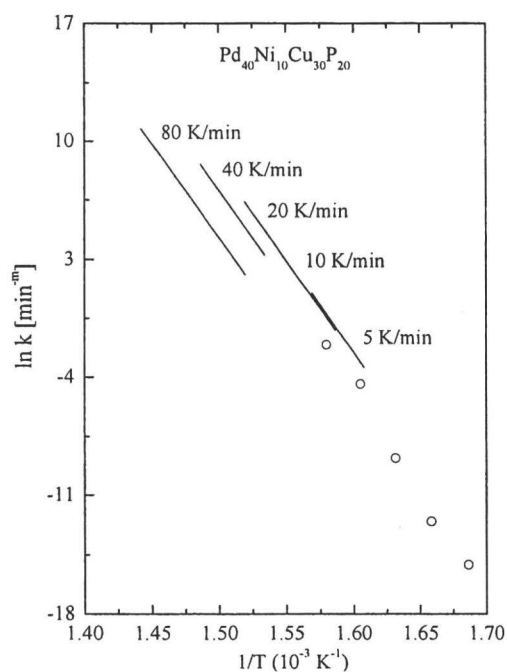


Fig. 4.22. The plots of $\ln(k)$ against the reciprocal temperature for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$. Circles are data from isothermal kinetics, and lines from the non-isothermal kinetics.

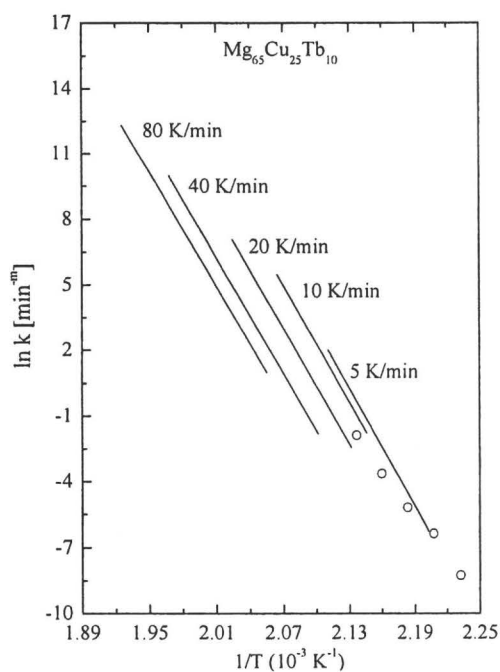


Fig. 4.23. The plots of $\ln(k)$ against the reciprocal temperature for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$. Circles are data from isothermal kinetics, and lines from the non-isothermal kinetics.

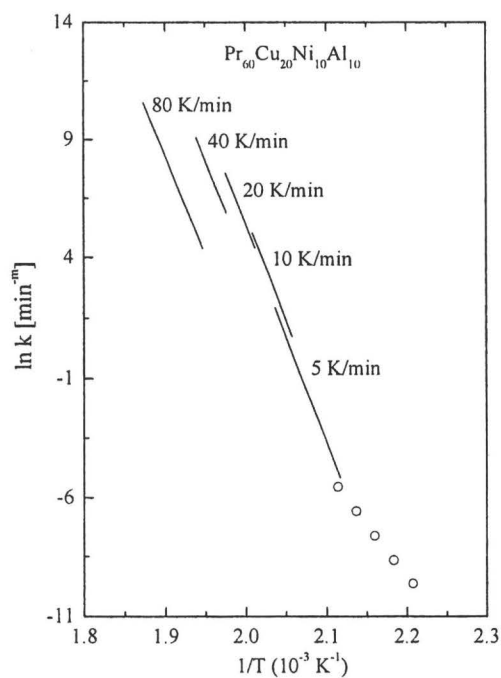


Fig. 4.24. The plots of $\ln(k)$ against the reciprocal temperature for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. Circles are data from isothermal kinetics, and lines from the non-isothermal kinetics.

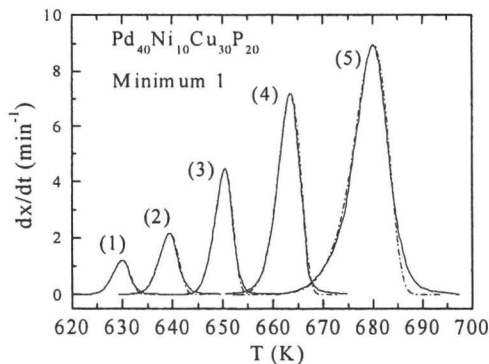


Fig. 4.25. The KJMA equation fitting to the first stage crystallization rate of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, that have been observed as the first minima for non-isothermal crystallization at the heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min. The solid lines are the experiment data and the dash-dot lines are the fitted curves.

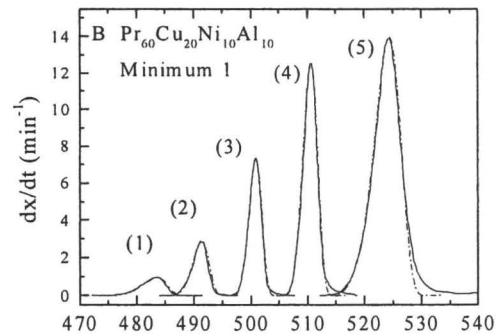
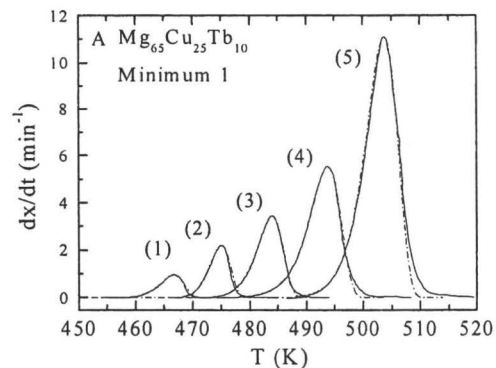


Fig. 4.26. The KJMA equation fitting of the crystallization rate of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ (A) and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ (B) first minima for non-isothermal crystallization at heating rates of: (1) 5 K/min, (2) 10 K/min, (3) 20 K/min, (4) 40 K/min, and (5) 80 K/min. The solid lines are the experiment data and the dash-dot lines are the fitting curves.

The activation energies obtained by the two methods differ, but both values are considerably high. Still these values are lower than those observed for molecular ultraviscous melts, e.g., the activation energy for isothermal crystallization for syndiotactic Polystyrene is 792 kJ/mol (Lu and Nutt 2003). In earlier studies, the activation energies of several relatively stable metallic glasses, $\text{Pd}_{77}\text{Cu}_6\text{Si}_{17}$ and $\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$ (Chen 1978b), were determined by using crystallization kinetics data obtained by rate-heating (non-isothermal mode). These values were found to be equal to the activation energy for viscous flow and which decreased when the crystallization

temperature was increased. This equality led to the conclusion that crystallization rate is controlled by viscosity. It was also suggested that crystallization in the amorphous state (Turnbull and Bagley 1975) may occur by diffusion-less mechanism and in such a case the activation energy is low and hence the crystallization rate is slow. This is reminiscent of the crystallization occurring as a result of localized motions of the JG relaxation, as mentioned here earlier. However, it is now established that the processes of crystallization as well as of structural relaxation in metallic glasses is diffusion-controlled.

4.4.5 Differences between the Isothermal and Non-isothermal Crystallization

One finding here is that crystallization occurs in one step isothermally in Figs 4.1 and 4.2 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, respectively, in two step isothermally in Fig. 4.3 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, and in two steps on rate-heating (non-isothermal), i.e., only one peak is observed in Figs. 4.1 and 4.2 and two in Fig. 4.3 and Figs. 4.7 – 4.9. For $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, a small further broadening to the left (shorter times) of the already broad peak, but only for isothermal crystallization at 448 K in Fig. 4.2. As this feature appears before the main crystallization exotherm it would corresponds to a faster kinetics. Therefore, we expect that a correspondingly small feature from this faster process would appear at the low-temperature side of the first peak in the non-isothermal experiment. But no such feature was observed in Fig. 4.8. As isothermal crystallization at 468 K is complete in less than 10 min according to the plot in Fig. 4.2, and 468 K is considerably below 510 – 580 K range at which $T_{p,2}$ appears in Fig. 4.8, we may estimate the

temperature $T_{p,2}$ at which the second peak might appear at zero heating rate i.e., isothermally, by extrapolation. This temperature is 525 K.

The exponent, m , is interpreted such as to determine the manner in which nuclei grow to form crystals. Its magnitude is seen to indicate the mechanism of crystal-growth (Christian 1975). The value of m for isothermal crystallization obtained here varies, as listed in Table 4.4, from 4.04 – 4.41 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, 3.11 – 3.25 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, 3.01 – 3.36 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ of minima 1. The value of m for non-isothermal crystallization of minima 1, as listed in Table 4.5, ranges from 4.02 – 4.10 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, 3.2 – 3.3 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, 3.17 – 3.29 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. This would suggest that crystallization occurs by interface-controlled growth with increasing nucleation rate for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ but decreasing nucleation rate for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. Since our study is focused on thermal effects of crystallization, we did not confirm the validity of these interpretations by x-ray diffraction and electron microscopy studies.

4.4.6 Deviations from the KJMA Equation and Crystallization Kinetics

The plots in Figs. 4.19 – 4.21 show that in the beginning of isothermal crystallization, the measured x deviates from the best fit of the KJMA equation. There are also deviations in the plots of the rate of crystallization, but the deviations are small and negligible in view of the measurements and analysis errors. The plots in Figs. 4.25 and 4.26 show for non-isothermal crystallization at different heating rates the crystallization rate (dx/dt) deviates considerably from the best fit of the KJMA equation. The deviation seems to be highest at high temperatures where the measured values are more spread out

than the calculated values. The calculated values also show, as expected for a thermally activated process, a relatively sharp decrease. It should be noted that in comparison with the deviations from the KJMA equation observed for other metallic glasses in several earlier studies (Greer 1982, Shen et al 2005, Kou et al 2008), deviations from the KJMA equation observed for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ are much smaller and seem negligible in this study.

To investigate the source of this deviation, we determined the ratio of the measured rate of crystallization to that calculated, for both isothermal and non-isothermal crystallizations. This ratio is plotted in Figs. 4.27 for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, 4.28 for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and 4.29 for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. For isothermal crystallization, the plots in Fig. 4.28A show a positive deviation by at most 25 % at short times when crystallization occurs at 468 K. For higher temperatures, the deviation is less. This may be partly due to the errors in the fitting as well as in experiments and these errors are more pronounced in dx/dt than in the value of x .

For non-isothermal crystallization, the maximum deviation of the plots of measured $(dx/dT)_q$ against T in Fig. 4.28B is much greater, reaching a factor of 1.4 relative to calculated values at the highest temperatures. In the absence of any effects that may increase the heat evolution and thus add to $-dH/dt$, this would indicate that crystallization of the melt becomes faster than expected from the KJMA equation as $x \rightarrow 1$. Alternatively, it may indicate additional heat evolution if (i) micron-size crystal grains formed initially grew rapidly as T increased, (ii) some or all of the inter-granular melt crystallized more slowly than the bulk, (iii) the melt composition changed on incongruent

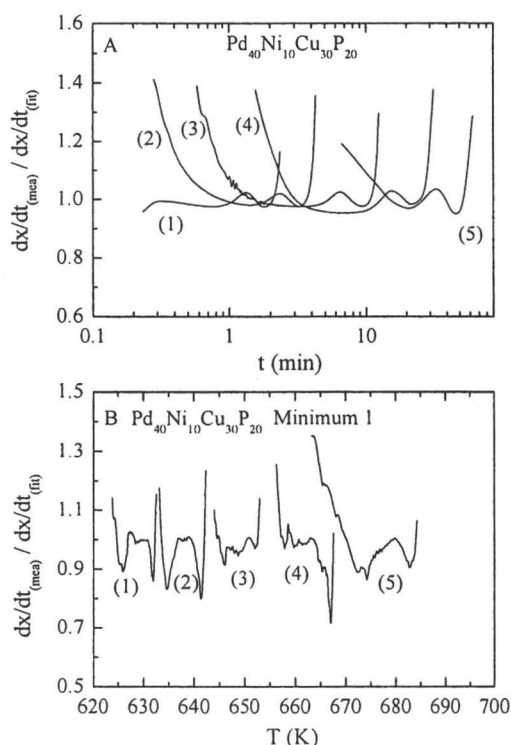


Fig. 4.27. A. The ratio of the measured rate of crystallization to that calculated from fitting the KJMA equation is plotted against time for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$. B. The corresponding plots against the temperature.

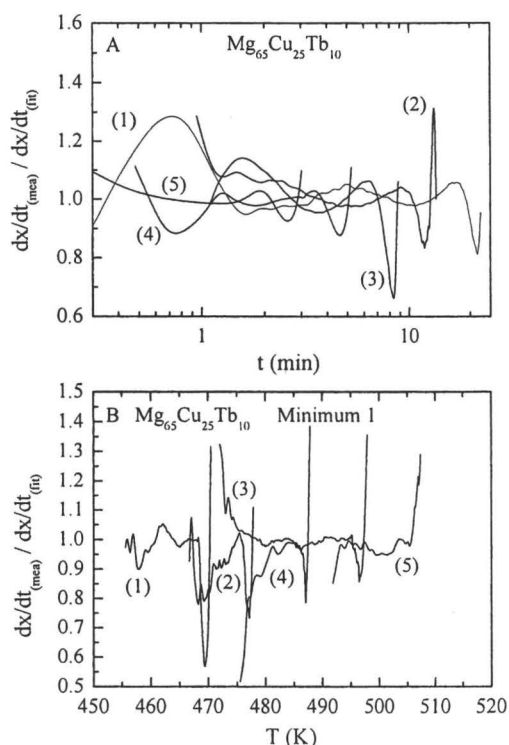


Fig. 4.28. A. The ratio of the measured rate of crystallization to that calculated from fitting the KJMA equation is plotted against time for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$. B. The corresponding plots against the temperature.

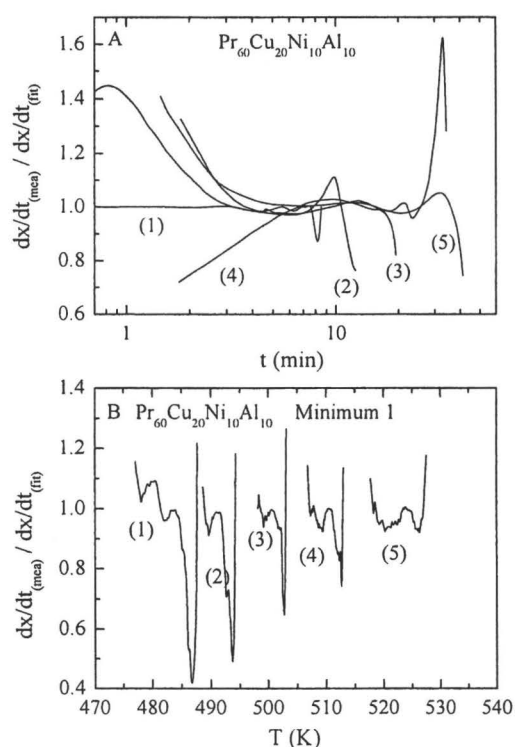


Fig. 4.29. A. The ratio of the measured rate of crystallization to that calculated from fitting the KJMA equation is plotted against time for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. B. The corresponding plots against the temperature.

crystallization and it slowed the crystallization process more when $x \rightarrow 1$, and (iv) the crystals formed underwent a solid-solid transformation.

We also investigate how the rates of isothermal and of non-isothermal crystallization change with the extent of crystallization. Figs. 30A, 31A, and 32A show the plots of $(dx/dt)_T$ against x isothermally and Figs. 30B, 31B, and 32B shows the corresponding plots for heating at different rates. According to Eq. (4.7), a plot of $(dx/dt)_T$ against t would show a peak only when $m > 1$, which of course is roughly evident from the sigmoid-shaped plots of x against t in Figs. 4.5 and 4.6. The plots of $(dx/dt)_T$ against x in Figs. 30A, 31A, and 32A show a hump-like feature whose peak shifts from $x = 0.52$ at 663 K to $x = 0.51$ at 593 K for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, from $x = 0.52$ at 448 K to $x = 0.53$ at 468 K for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and from $x = 0.54$ at 468 K to $x = 0.61$ at 453 K for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, as indicated by the arrows. The relatively small shift is mainly due to change in m with the crystallization temperature. In contrast a broad peak is observed in Figs. 30B, 31B, and 32B, and this peak shifts from $x = 0.59$ at 5 K/min to $x = 0.57$ at 80 K/min for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, from $x = 0.62$ at 5 K/min to $x = 0.56$ at 80 K/min for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and from $x = 0.49$ at 5 K/min to $x = 0.38$ at 80 K/min for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, as indicated by the arrows.

4.4.7 Origin of the Second Peak on Non-isothermal Crystallization

In Figs. 4.7 – 4.9 and Table 4.3, the high temperature and low-intensity exothermic peak shifts to higher temperatures as the heating rate q_h is increased. In contrast, the first peak shifts much more. This indicates irreversible occurrence of an additional process in the ultraviscous melt or in the crystal formed in the first

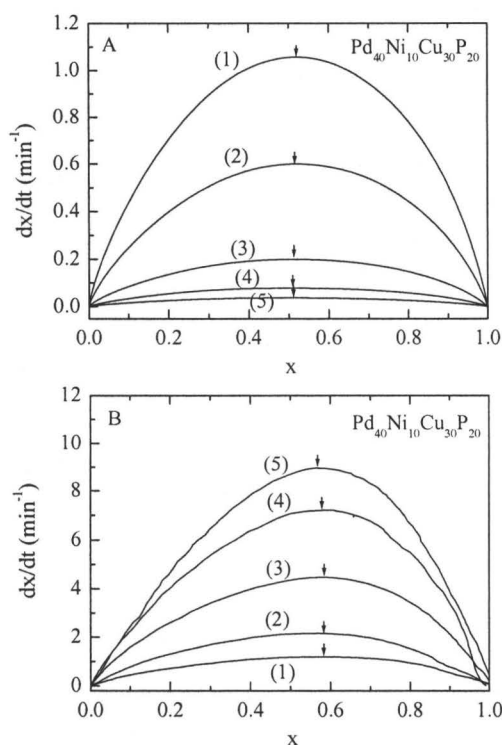


Fig. 4.30. A. The rate of crystallization is plotted against the extent of crystallization for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ at, (1) 633, (2) 623, (3) 613, (4) 603, and (5) 593 K. B. The corresponding plots from the data obtained for heating at, (1) 5, (2) 10, (3) 20, (4) 40, and (5) 80 K/min.

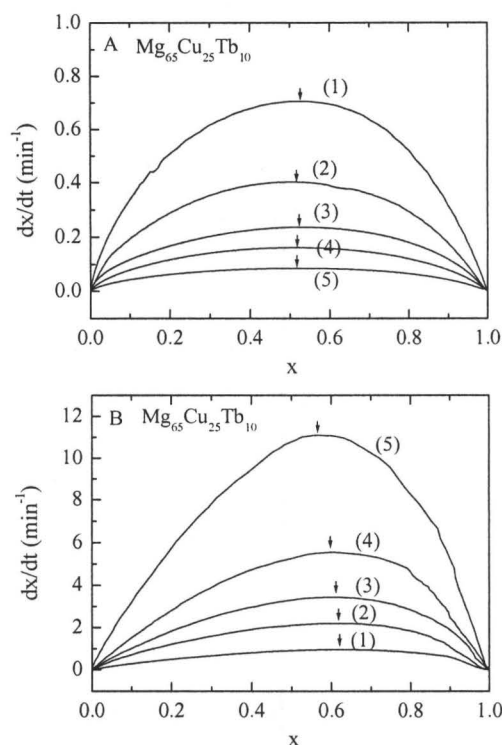


Fig. 4.31. A. The rate of crystallization is plotted against the extent of crystallization for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ at, (1) 468, (2) 463, (3) 458, (4) 453, and (5) 448 K. B. The corresponding plots from the data obtained for heating at, (1) 5, (2) 10, (3) 20, (4) 40, and (5) 80 K/min.

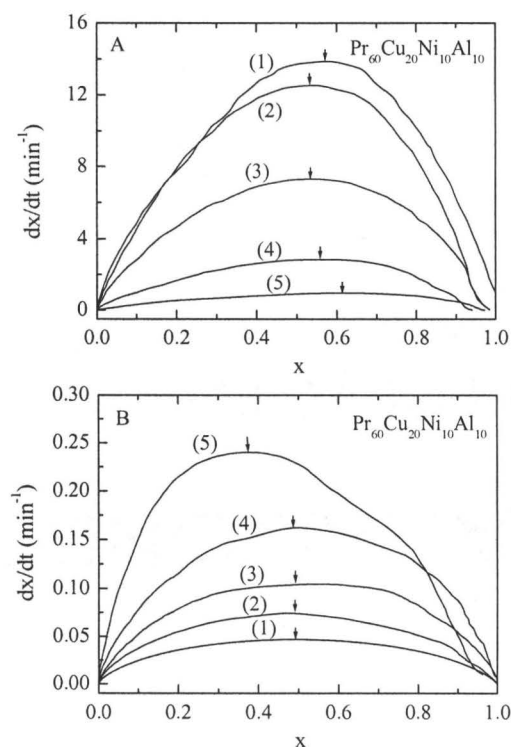


Fig. 4.32. A. The rate of crystallization is plotted against the extent of crystallization for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ at, (1) 473, (2) 468, (3) 463, (4) 458, and (5) 453 K. B. The corresponding plots from the data obtained for heating at, (1) 5, (2) 10, (3) 20, (4) 40, and (5) 80 K/min.

crystallization. If such a second exotherm were observed for a one-component melt, it would indicate, (i) grain growth in some of the fine structure or nanocrystalline phases formed as a result of the first crystallization, or (ii) a solid-solid transformation to a more stable crystalline phase. These processes may also occur here. But they seem unlikely for a ternary melt of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and quaternary melts of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ unless their crystals melted and froze congruently. It is also conceivable that the melt initially crystallized non-congruently to form an inter-metallic compound, leaving behind a melt rich in one component. If nucleation and growth in this latter melt were slow, its crystallization would produce a broad exothermic peak at higher temperatures.

The enthalpy decrease associated with the second exotherm minimum 2 is 0.89 kJ/mol for heating rate of 20 K/min for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$. The enthalpy released in the first crystallization minimum is 3.58 kJ/mol for heating rate of 20 K/min as in Table 4.3, and for the isothermal crystallization is 2.81 – 3.61 kJ/mol, as given in Table 4.2. This is only ~78 to 85 % of the enthalpy released in the first minimum observed in Fig. 4.8, and it seems to be a substantial thermal effect. But we point out that such comparisons may be misleading because when incongruent crystallization occurs, the original composition of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ can not be used for determining the per mole amount of ΔH_{cryst} for either the first peak or the second peak. Also, in a case where the surface of compositionally different crystals acts as a heterogeneous nucleation site, crystallization of the remaining melt would be faster than that observed from homogeneous nucleation and its rate would vary with the amount of crystals present and distribution of the crystal size. This is not

observed in the data for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ here. As in $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, the analysis above also applies to $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. For that reason we may use the KJMA equation also for the second exothermic minimum, but its broadness makes it difficult to separate it satisfactorily from the low-temperature minimum.

To resolve the origin of the second exothermic peak seen in Figs. 4.7 – 4.9, we performed a further experiment. For $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, a new as-cast sample was heated to T_a of 458 K (~ 44 K above the T_g of 414 K) and then kept isothermally for t_a of 10 min. Thereafter, the sample was reheated from 458 K to 620 K at a rate of 20 K/min. The curve obtained is shown as curve 1 in Fig. 4.33. It shows no features until a temperature of 480 K is reached and thereafter an exotherm appears as in Fig. 4.11. This shows that annealing of the ultraviscous melt at 458 K for 10 min does not remove the second exothermic peak. Since annealing was done at ~ 44 K above its T_g , it is unlikely that a significant amount of melt would have persisted after 10 min. (When compared against the plot at 458 K in Fig. 4.8, this annealing condition amounts to extending the isothermal experiment for 10 more minutes at 458 K.) The sample was then cooled back to 495 K at 20 K/min and reheated at the same rate, and curves 2 and 3 in Fig. 4.33 were obtained. These show no indication of a further exotherm. The enthalpy released on this reheating is 1.40 kJ/mol (of the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ composition) in comparison with 0.89 kJ/mol given in Table 4.3 for the same heating rate without annealing. Vanishing of the exotherm may indicate that crystallites growing at different sites produced a solid containing extremely small grains and hence a large surface area, and annealing was insufficient for grain growth to reach completion. But the 1.40 kJ/mol of the heat evolved for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$

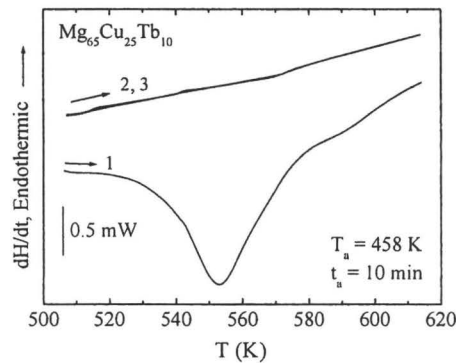


Fig. 4.33. The plots of dH/dt against T of $Mg_{65}Cu_{25}Tb_{10}$ glass that was annealed at 458 K for 10 min then heated at 20 K/min, as shown by curve 1. The scan did not show the first minimum but the second minimum persisted. The curves 2 and 3 were obtained by reheating the sample to 620 K. These showed no features.

composition from curve 1, seems too large for surface energy reduction by grain growth of particles. It is possible that a metastable phase had formed on annealing and it transformed to a stable phase on heating a process for which the heat evolved would seem acceptable. But we also realize that $Mg_{65}Cu_{25}Tb_{10}$ may not be a ternary eutectic composition in which case crystallization would be incongruent, leaving behind a melt that crystallizes at a slower rate. It seems that the latter occurrence is more probable. For $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and $Pr_{60}Cu_{20}Ni_{10}Al_{10}$, similar experiments were performed as in $Mg_{65}Cu_{25}Tb_{10}$ with T_a of 633 K and 468 K, respectively, for t_a of 10 min. The experiment results are shown in Fig. 4.34. As in $Mg_{65}Cu_{25}Tb_{10}$, it is possible that a metastable phase had formed on annealing and it transformed to a stable phase on heating a process for which the heat evolved. In addition, $Pd_{40}Ni_{10}Cu_{30}P_{20}$ and $Pr_{60}Cu_{20}Ni_{10}Al_{10}$ may not be a eutectic composition in which case crystallization would be incongruent, leaving behind a melt that crystallizes at a slower rate.

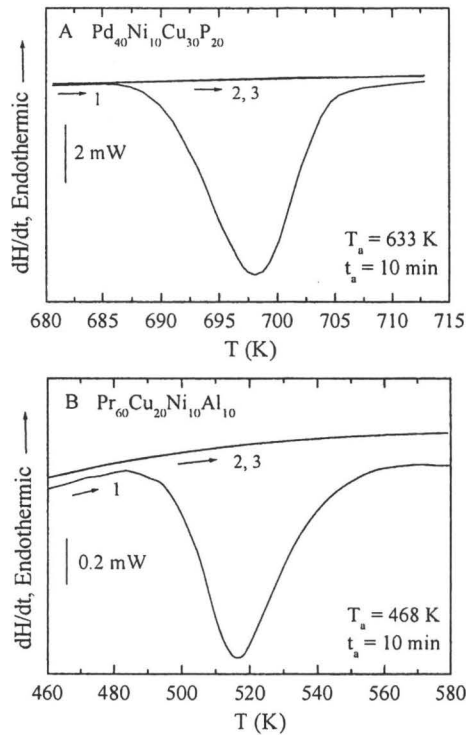


Fig. 4.34. The plots of dH/dt against T of: A. $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass that was annealed at 633 K for 10 min then heated at 20 K/min, as shown by curve 1, and B. $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glass that was annealed at 468 K for 10 min then heated at 20 K/min, as shown by curve 1. Both curves 1 did not show the first minima but the second minima persisted. The curves 2 and 3 were obtained by reheating the sample to 714 K for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and to 580 K for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. These showed no features.

4.5 Conclusions

Isothermal crystallization of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ ultraviscous melts obtained by heating their bulk metallic glass states shows one exothermic feature for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and two for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$. But their non-isothermal crystallization shows two exothermic features over a shorter total time. The total heat evolved on isothermal crystallization of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ melts varies with the crystallization temperature and that evolved on non-isothermal crystallization varies with the heating rate. The heat of crystallization in the isothermal experiment is less than the total heat of crystallization in non-isothermal experiment. The second exotherm is exceptionally broad when the heating rate is high. This shows that the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and

$\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ melts crystallize incongruently and the heat of crystallization per mole may not be determined by using the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ compositions. The remaining melt of a different composition has a higher viscosity and or slower overall rate of crystallization. There also may be exothermic effects of grain growth but the enthalpy change seems too large for its occurrence. Isothermal crystallization at different temperatures shows no such occurrence.

The crystallization of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses follows classical nucleation and growth kinetics. The resulting values of the exponent m of the Kolmogorov-Johnson-Mehl-Avrami equation, which is used to interpret the mechanisms of both isothermal and non-isothermal crystallizations, suggests that crystal growth of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass is interface-controlled with increasing nucleation rate. Mechanism of both isothermal and non-isothermal crystallization of the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses is also interface-controlled growth with decreasing nucleation rate. The higher activation energy of crystallization of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass relative to that of the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ glasses indicates that $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass has higher thermal stability against crystallization than the other two, and is therefore more useful in applications where crystallization is detrimental to the use of the bulk metallic glass. As crystallization approaches completion, the fraction crystallized is less than that deduced from the KJMA equation, and the rate of crystallization becomes slower. This indicates persistence of inter-granular ultraviscous melt.

As crystallization approaches completion, the fraction crystallized isothermally at the lowest temperature is slightly more than that calculated from the KJMA equation, and the rate of crystallization shows random deviation, but the rate of non-isothermal crystallization in the first step is slightly higher at high temperatures for the high heating rate. The broad and small second exothermic peak observed in non-isothermal experiments is likely to be due to slower crystallization of the melt that persists after incongruent crystallization of a melt (Thorpe et al 1988, Tsai et al 1989, Wang et al 2000b, Louzguine and Inoe 2001, Liu et al 2005, Legg et al 2007) or a solid-solid transformation.

CHAPTER 5

ELECTRICAL RESISTIVITY MEASUREMENT OF METALLIC GLASSES

5.1 Introduction

In this chapter, a study of electrical resistivity, ρ , of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ due to crystallization and due to structural relaxation is provided. Experiments were done in two manners: (i) on rate-heating the sample and (ii) and isothermal annealing. In (i), the sample was heated from room temperature through its crystallization range while its ρ was measured as a function of temperature and in (ii), the sample was held at a certain temperature while ρ was measured as a function of time.

As a review of earlier studies, we note that a change in ρ on structural relaxation was found for $\text{Au}_{77}\text{Ge}_{13.6}\text{Si}_{9.4}$ (Chen and Turnbull 1968), $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$ (Balanzat et al 1980, 1985), $\text{Pd}_{82}\text{Si}_{18}$ and $\text{Pd}_{76}\text{Si}_{18}\text{V}_6$ (Kelton and Spaepen 1982, 1984, 1985), $\text{Pd}_{82-x}\text{V}_x\text{Si}_{18}$ ($x = 0, 1$, and 2) (Hygate and Gibbs 1989), and $\text{Fe}_{40}\text{Ni}_{38}\text{Mo}_4\text{B}_{18}$ (Tiwari et al 2001) occurs. Tiwari et al (2001) have provided a detailed study. They found that structural relaxation on annealing of some metallic glass increases ρ . In diverse alloys composition, it has been also observed (Tiwari et al 2001) that the change in ρ at the onset of isothermal annealing does not follow diffusion rate kinetics. By using the observations of acoustic emissions and results from the Mossbauer experiment, Tiwari et

al (2001) suggested that viscous flow is the mechanism for structural relaxation during isothermal annealing, and further that short range ordering during this process is also a consequence of the viscous flow process. Haruyama et al (2001) had performed a structural relaxation study of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ metallic glass by measuring ρ . They annealed the sample at three annealing temperatures, T_a , for a certain times, t_a , and measured ρ after cooling to room temperature. They found that in the plots of ρ increased with t_a at one T_a and decreased with t_a at two T_a s. They discussed this finding in terms of structural relaxation processes involving the CSRO and TSRO of the glass. Jiang et al (2003) also measured ρ during structural relaxation of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ bulk metallic glass. They performed annealing only at 773 K for 2 h, and did not change the annealing parameters to obtain details. Change in ρ of a sample on cooling to room temperature may differ before and after structural relaxation. Therefore, it was necessary to perform *in situ* studies of ρ , as described here.

5.2 Experimental Methods

Samples of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses were used for this study. Thin samples of 1 mm x 1.5 mm x 4 mm used were cut from the same specimens as used for structural relaxation study described in Chapter 2. The resistivity was measured *in situ* by using a four-probe resistivity measurement method. The schematic diagram for experiment setup by using this method is shown in Fig. 5.1.

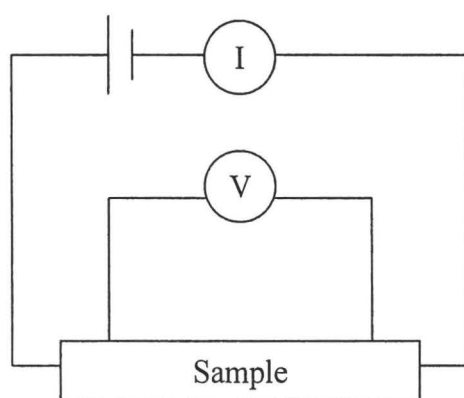


Fig. 5.1. Diagram of four-probe resistivity measurement method.

I alone designed an equipment and software for such measurements by automatic data acquisition. Three multimeters, Hewlett Packard model 3478A, were used for measuring the current, I , and the voltage, V , of the sample in the circuit, and the emf from thermocouple. The current was supplied by a power supply of L4D-090070R model manufactured by Cyber Acoustics. A constant current of 1 mA was used for measuring ρ . A tungsten-nickel wire of diameter, 0.5 mm was used to connect the sample with the multimeters for the voltage and current probe measurements. The temperature of the sample was measured by means of a K-type thermocouple. Because the sample size was relatively small, spot welding of the probe wires to it could cause partial crystallization. Therefore, a special sample holder was made, which is shown in photograph in Fig. 5.2. It was made of aluminum by casting and machining. It consisted of two parts, the top and the bottom discs. Alumina ceramic tubes were embedded in the top disc during casting thus firmly positioning the tubes. Electrical probe wires and thermocouple wires were led

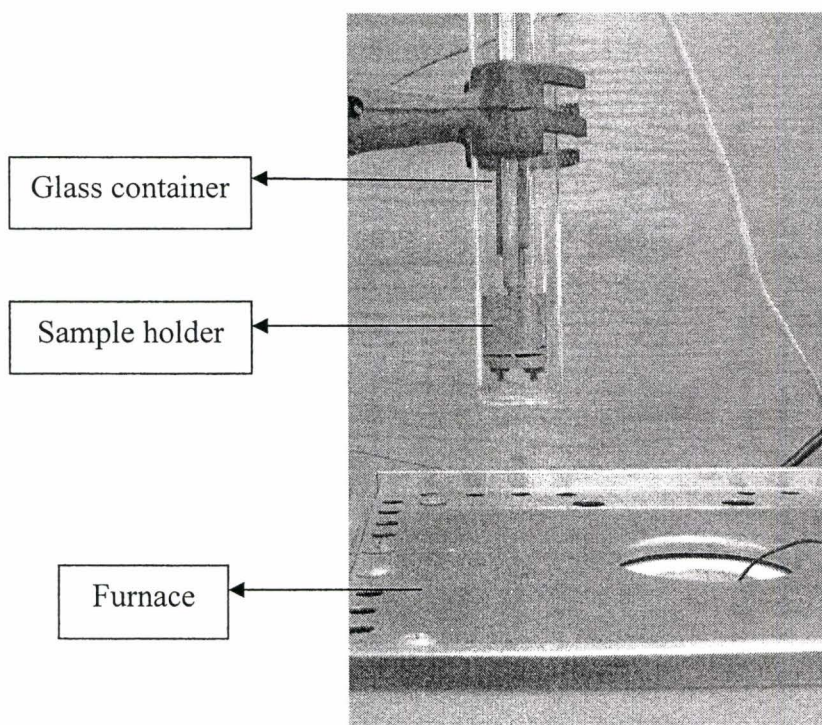


Fig. 5.2. Sample holder inside a glass container.

through these tubes. A piece of alumina ceramic was placed on the upper surface of the bottom aluminum disc during casting. The metallic glass sample was placed on this ceramic piece so that it remained electrically insulated from the aluminum disc. Two fastening bolts were inserted through the holes on the sides of the top and bottom aluminum discs and these were tightened to ensure that the sample was firmly held, and provided good electrical contacts between the sample and the probing wires as well as good physical contact between the sample and the thermocouple. The assembly was kept inside a glass cylinder which in turn was placed inside a Fisher 260F furnace. For avoiding surface oxidation of the samples and the probe wires, an argon gas atmosphere

was used in the glass cylinder. The temperature of the furnace was controlled by a Eurotherm 847 temperature controller.

Real time measurements of I and V were used to determine ρ by,

$$\rho = \frac{VA}{IL} \quad (5.1)$$

where A is the cross section of the sample and L is the distance between the voltage probes.

The temperature of the sample along with I and V were recorded automatically by a computer by using a software I developed in Visual Basic language. The computer was interfaced with the instruments by means of a GPIB card from National Instruments with IEEE 488.2 specifications. The instrument was calibrated by using pure copper sample and its known ρ . The voltage reading during the measurement of ρ included thermal emf generated by the probe wires junction with the copper electrical leads that formed a junction (thermal effect). This thermal emf was measured as a function of temperature by shorting the voltage probe wires without the sample, and it was subtracted from the measured voltage in the sample. Electrical resistance was measured with an accuracy of $\pm 10^{-6}$ ohm and the temperature to that of ± 3 K. The experimental setup is shown in the photograph in Fig. 5.3 and the screenshot of the software is shown in Fig. 5.4.

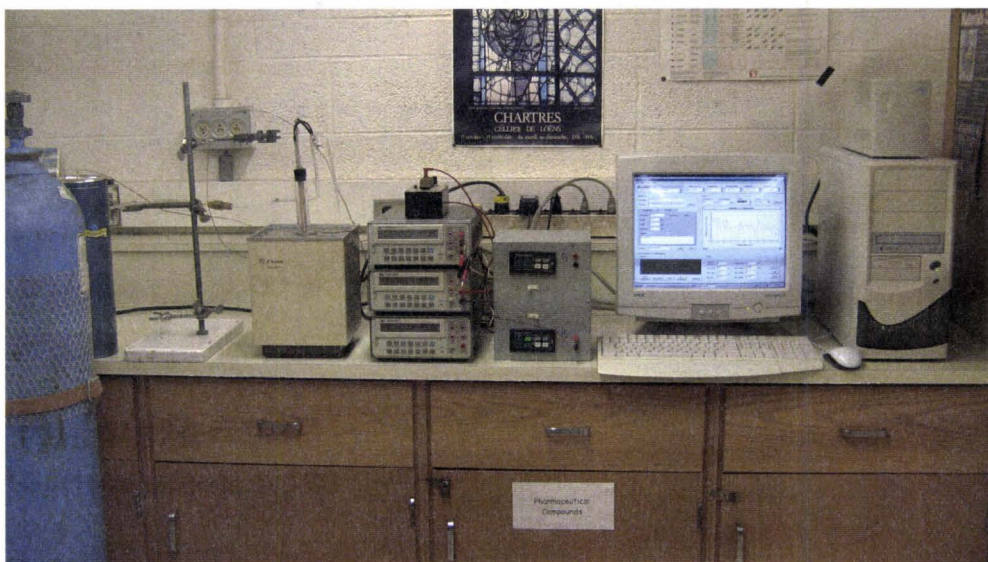


Fig. 5.3. The experimental setup for electrical resistivity measurements.

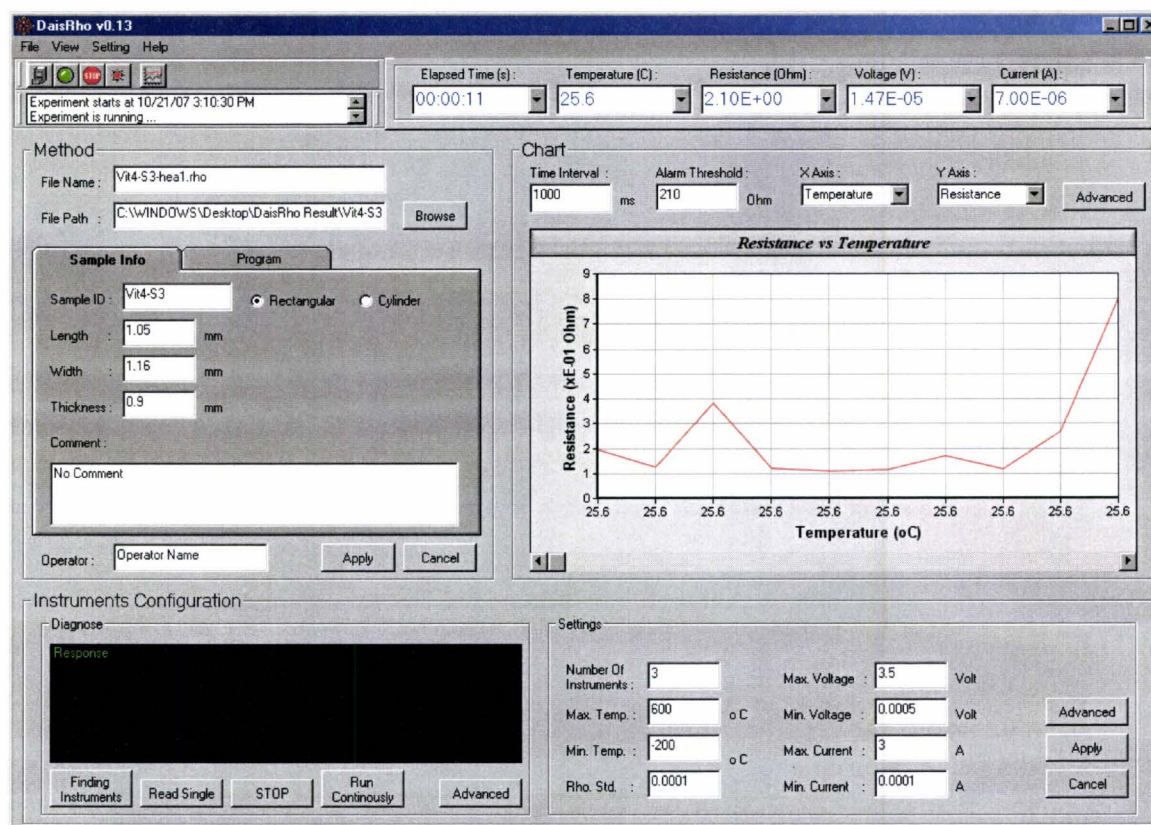


Fig. 5.4. A screenshot of the software for automatic data acquisition of resistivity measurements.

The general experimental procedure was as follows. For rate-heating experiments, an as-cast sample was heated at 10 K/min from room temperature through the glass transition temperature to a temperature T_h (in the ultraviscous melt state) and then cooled at 10 K/min rate to room temperature. This removed any ageing effects on its ρ during storage of the sample. It was then reheated at 10 K/min through its irreversible crystallization range. Its ρ was measured during the heating and cooling as a function of temperature. For isothermal annealing experiments, an as-cast sample was heated at 100 K/min from room temperature through the glass transition temperature to a temperature T_h and then cooled at 100 K/min to the annealing temperature T_a . It was then held at T_a while the resistivity was measured as a function of time. Here also the first heating eliminated the effect of structural relaxation during storage of the sample. The T_g s of the two metallic glasses and T_a and T_h used for the study are listed in Table 5.1.

Table 5.1. Annealing temperatures for isothermal annealing method of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses.

Metallic Glass	T_g (K) $q_h = 20\text{K/min}$	T_h (K)	T_a (K)
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	569	600	523, 533, 543, 553, 563
$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$	622	630	563, 573, 583, 593, 603

5.3 Results and Discussion

5.3.1 The Irreversible Effects of Rate-Heating

For the rate-heating experiments, an as-cast sample of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass was first heated at a rate of 10 K/min from 300 K through its T_g range to 600 K in its

ultraviscous state and then cooled at the same rate to 300 K. The sample thereafter was reheated at a heating rate of 10 K/min to 720 K. The measured value of ρ is plotted against T in Fig. 5.5A. It is apparent that as the temperature is increased ρ decreases initially slowly and then after a certain temperature, it decreases rapidly. The onset of the decrease is at T_g . There is an abrupt decrease to a much lower value in a temperature range of 17 K. This is attributed to crystallization of the sample at T_x . In the plot in Fig. 5.5A, the T_g and T_x values are 570.3 K and 665.3 K, respectively.

Similarly for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, an as-cast sample was heated at a rate of 10 K/min from 300 K through its T_g range to 630 K in the ultraviscous state, and then cooled at the same rate to 300 K. The sample thereafter was reheated at a rate of 10 K/min to 768 K. The measured value of ρ is plotted against T in Fig. 5.6A. It is apparent that the plot is qualitatively similar to that for the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass. As the temperature is increased ρ decreases initially slowly and then after a certain temperature, it decreases rapidly. The onset of the decrease is at T_g . There is an abrupt decrease to a much lower value in a temperature range of 67 K. This is attributed to crystallization of the sample at T_x . In the plot in Fig. 5.6A, the T_g and T_x values are 590.2 K and 657.5 K, respectively.

Figs. 5.5B and 5.6B show the relative change in ρ , i.e., $[(\rho - \rho_{300\text{ K}})/\rho_{300\text{ K}}]$ as a function of temperature during heating where $\rho_{300\text{ K}}$ is the value of ρ at 300 K. It is evident that the decrease in ρ from 300 K to T_g for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass is larger than

for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass. The decrease in ρ from 300 K to crystallization region is 20.1 % for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and 10.6 % for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass.

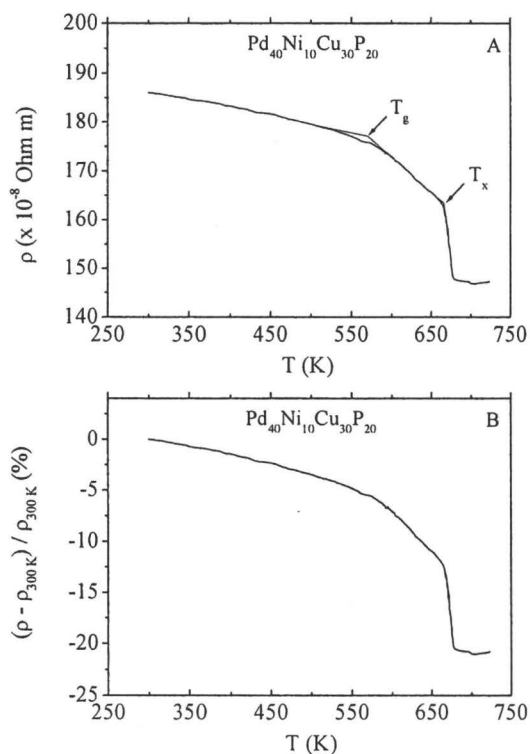


Fig. 5.5. A. Resistivity plot against temperature during heating at 10 K/min from 300 K to crystallization region for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$. B. The corresponding relative change in resistivity.

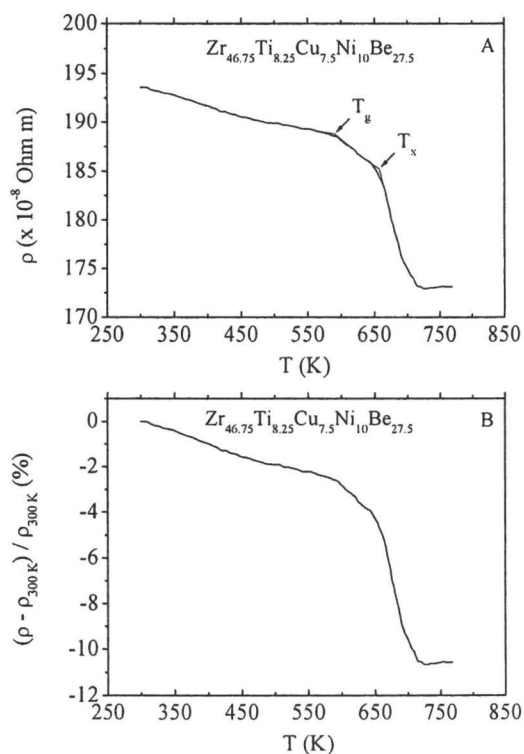


Fig. 5.6. A. Resistivity plot against temperature during heating at 10 K/min from 300 K to crystallization region for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$. B. The corresponding relative change in resistivity.

5.3.2 Effects of Isothermal Annealing

For isothermal annealing experiments, an as-cast sample of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass was heated at a heating rate of 100 K/min from 300 K through its T_g to 600 K in the ultraviscous state then cooled at the same rate to T_a of 523 K and its ρ at this temperature was measured with time. The experiment was repeated with new samples but at different

T_a s of 533 K, 543 K, 553 K, and 563 K as listed in Table 5.1. Fig. 5.7A shows the plots of ρ as a function of t_a for annealing at these T_a s. It is evident that ρ of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass decreases with increase in t_a .

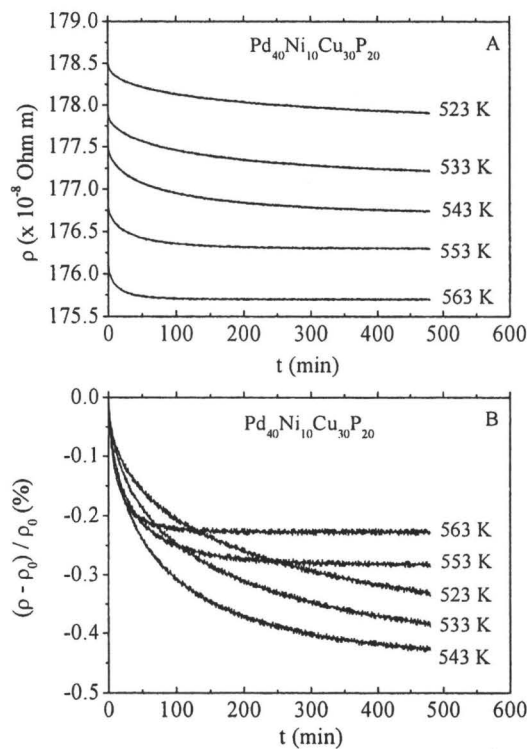


Fig. 5.7. A. Resistivity plots against time during annealing at 523 K, 533 K, 543 K, 553 K, and 563 K for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$. B. The corresponding plots of relative change in resistivity.

As for the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass, ρ of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass was similarly studied. Its as-cast sample was heated at a rate of 100 K/min from 300 K through its T_g to 630 K in the ultraviscous state and then cooled at the same rate to T_a of 563 K and its ρ at this temperature was measured with time. The resistivity of the sample was measured as a function of time. The experiment was repeated with new samples but at different T_a s of 573 K, 583 K, 593 K, and 603 K, as listed in Table 5.1. Fig. 5.8A shows the plots of ρ as a function of t_a at these T_a s. As for the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass, ρ of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass decreases with increase in t_a . Figs. 5.7B and 5.8B

show the relative change of the resistivity, $[(\rho - \rho_0)/\rho_0]$ as a function of time during annealing where ρ_0 is the initial resistivity at $t_a = 0$.

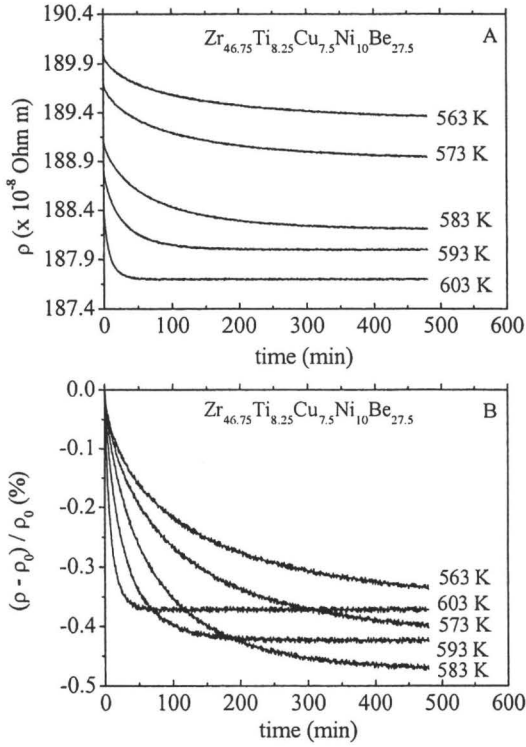


Fig. 5.8. A. Resistivity plots against time during annealing at 563 K, 573 K, 583 K, 593 K, and 603 K for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$. B. The corresponding plots of relative change in resistivity.

The kinetics of the structural relaxation of the two glasses during annealing were analyzed by using the stretched-exponential relaxation function,

$$\phi(t) = \exp \left[- \left(\frac{t_a}{\tau} \right)^\beta \right] \quad (5.2)$$

where ϕ is a normalized relaxation function,

$$\phi = \frac{\rho(t_a) - \rho(t_a \rightarrow \infty)}{\rho(t_a = 0) - \rho(t_a \rightarrow \infty)} \quad (5.3)$$

In Eq. (5.2), τ is the characteristic relaxation time, and β is the stretched relaxation parameter. Its value is between 0 and 1. For fitting Eq. (5.2), it was combined with Eq.

(5.3) and transformed to, $\ln[-\ln(\phi)] = \beta \ln(t_a) - \beta \ln(\tau)$. The measured value of $\ln[-\ln(\phi)]$ was plotted against $\beta \ln(t_a) - \beta \ln(\tau)$. Thus values of β and τ were determined. Fig. 5.9A shows the fitting for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ for T_a of 543 K which yields $\beta = 0.60$ and $\tau = 80.1$ min. Fig. 5.10A shows the fitting for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass for T_a of 583 K, which yields $\beta = 0.75$ and $\tau = 66.9$ min. The values of β and τ for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses for all annealing temperatures from the fitting are shown in Table 5.2. Figs. 5.9B and 5.10B show the fitting result for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses.

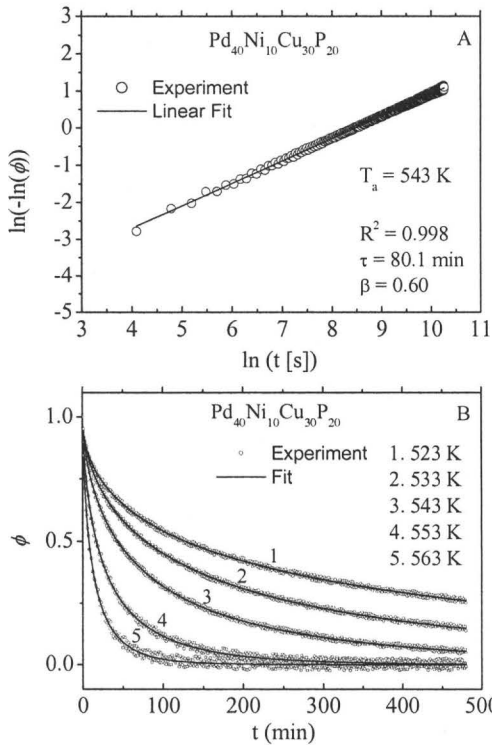


Fig. 5.9. A. Fitting of the stretched exponential function to the annealing data for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ for T_a of 543 K. B. Fitting of the stretched exponential function to the annealing data for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ for T_a of 523 K, 533 K, 543 K, 553 K, and 563 K plotted as relaxation function ϕ against time.

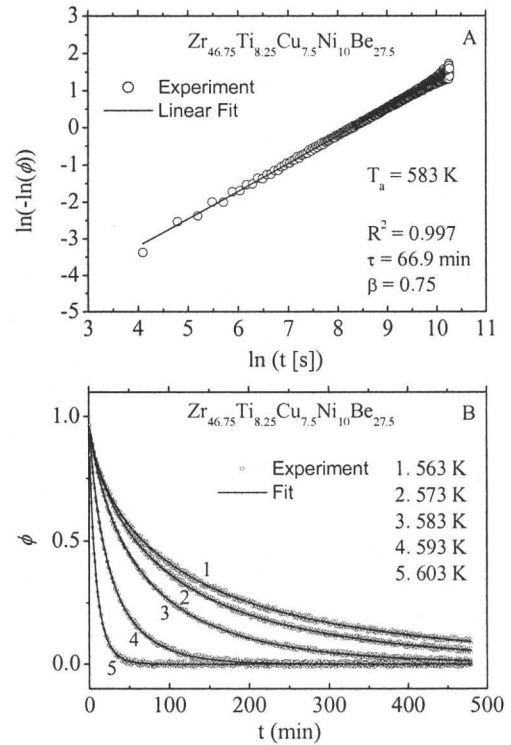


Fig. 5.10. A. Fitting of the stretched exponential function to the annealing data for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ for T_a of 583 K. B. Fitting of the stretched exponential function to the annealing data for $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ for T_a of 563 K, 573 K, 583 K, 593 K, and 603 K plotted as relaxation function ϕ against time.

Table 5.2. Fitting of the stretched exponential function for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses during annealing.

Metallic Glass	T_a (K)	τ (min)	β
$\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$	523	266.2 ± 0.2	0.50 ± 0.01
	533	150.4 ± 0.2	0.56 ± 0.01
	543	80.1 ± 0.2	0.60 ± 0.01
	553	30.0 ± 0.2	0.64 ± 0.01
	563	13.3 ± 0.2	0.66 ± 0.01
$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$	563	120.2 ± 0.2	0.63 ± 0.01
	573	99.9 ± 0.2	0.68 ± 0.01
	583	66.9 ± 0.2	0.75 ± 0.01
	593	26.8 ± 0.2	0.79 ± 0.01
	603	8.0 ± 0.2	0.82 ± 0.01

5.3.3 The Temperature Coefficient of Resistivity

Figs. 5.5 and 5.6 show that during heating from room temperature to crystallization temperature for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, ρ decreases as the temperature increases. In terms of the Temperature Coefficient of Resistivity (TCR), defined as $\frac{1}{\rho} \frac{d\rho}{dT}$, these two glasses have negative TCR. This phenomenon is commonly observed for metallic glasses with ρ higher than $\sim 150 \times 10^{-8}$ ohm m, have negative TCR, as discussed by Mooij (1973).

For crystalline metals, TCR is positive. For metallic glasses, it has been found to be both positive and negative. For example, positive TCR has been observed by

Haruyama et al (2002) during heating Pd₄₃Ni₃₇P₂₀ bulk metallic glass and negative TCR has been observed by Haruyama et al (2004) during heating Pd₄₃Cu₂₇Ni₁₀P₂₀ bulk metallic glass. During isothermal annealing, the electrical resistivity may increase or decrease monotonically. In either case, the change would be characteristic of the effect of electron scattering resulting from the structural change by the diffusion process or lack of it.

Ziman (1961) had proposed a diffraction model for resistivity in liquid metals. In this model, the scattering of electrons was treated as plane waves. These were viewed to be arising from coherent scattering from the atomic potentials, leading to a diffraction process from assembly of atoms. It has been found that Ziman's model can explain most of the electrical behavior of simple liquid metals, in particular, both its positive or negative sign of TCR and the prediction of the resistivity value. Since metallic glasses are in a structurally frozen state of a liquid, we attempt to qualitatively explain the negative TCR of Pd₄₀Ni₁₀Cu₃₀P₂₀ and Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni₁₀Be_{27.5} by using his model.

According to Ziman's model, ρ of a disordered state may be expressed as,

$$\rho = \frac{12\pi}{e^2 v_F \hbar} \int_0^1 |V_{kk'}(K)|^2 S(K) \left(\frac{K}{2k_F} \right)^3 d\left(\frac{K}{2k_F} \right) \quad (5.4)$$

where, e is electron charge (1.9×10^{-19} Coulomb), v_F is velocity of electron at Fermi level (m/s), $\hbar = h / 2\pi$, h is a Planck constant (6.63×10^{-34} J s), $V_{kk'}(K)$ is matrix element, $S(K)$ is structure factor, $K = \left| \vec{k}' - \vec{k} \right|$ is scattering vector (rad/m), $\vec{k}$ is incident electron wave vector (rad/m) and $\vec{k}'$ is scattered electron wave vector (rad/m). Structure factor is

formulated as $S(K) = \frac{1}{N} \left| \sum_j \exp(i \vec{K} \cdot \vec{r}_j) \right|^2$, where N is the total number of atoms and $\vec{r}$

is the distance of ion j to an atom chosen as the origin. Eq. (5.4) is valid under the following assumptions, that (i) the state contains free-electrons, (ii) there is elastic scattering, (ii) there is no multiple scattering, and (iv) the ion cores do not overlap.

In Eq. (5.4), high value of K , the K^3 factor would give a large contribution to the integral, which is near the upper limit of K around $2k_F$. Therefore, it is important to determine the values of $2k_F$ and the pseudopotential in this region. When the temperature changes, $S(K)$ is the only term that changes significantly. Therefore, one can investigate the change in ρ with change in $S(K)$. Fig. 5.11 illustrates the effect of change in T on $S(K)$ of a liquid which in turn determines how ρ would change.

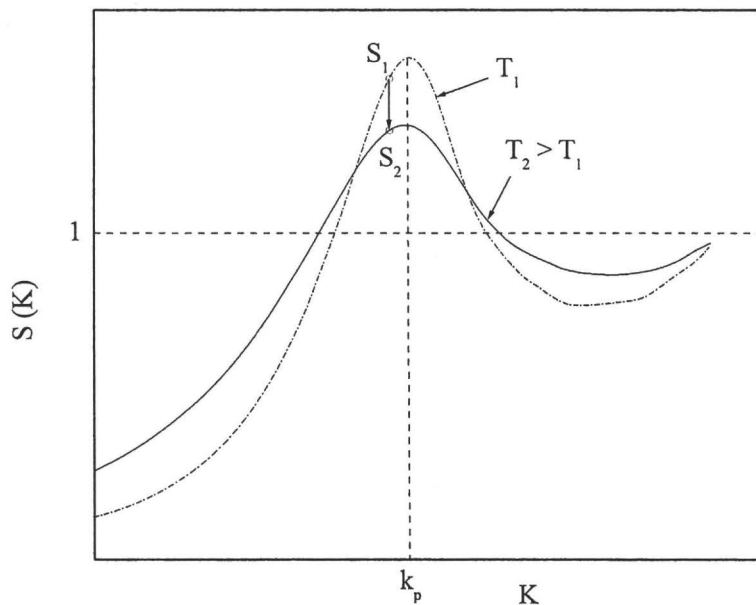


Fig. 5.11. Illustration of the effect of temperature on structure factor $S(K)$ of a liquid.

Consider the temperature increases from T_1 to T_2 , the liquid becomes more disordered, so it tends to become more gas-like. $S(K)$ will tend towards unity, i.e the curve will broaden and the peak decreases. For most monovalent liquid metals, $2k_F$ is smaller than the first peak of $S(K)$, which is equal to k_p in Fig. 5.11, with the corresponding $S(K)$ value near or below 1. For most divalent and higher valency liquid metals, $2k_F$ is very close to the first peak of $S(K)$. For most divalent and higher valency liquid metals, as illustrated in Fig. 5.11, $2k_F$ corresponds to point S_1 at T_1 and to point S_2 at T_2 . As noted, an increase in T decreases the value of $S(K)$, and therefore, ρ decreases according to Eq. (5.4) and TCR is negative.

For $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses, since changing the temperature does not change their structure factors, the structure factor for these glasses is not the same as the structure factor $S(K)$ derived from diffraction experiment for liquids. A modified structure factor for metallic glasses, $S^{MG}(K)$, was proposed by Nagel (1977),

$$S^{MG}(K) \cong 1 + [S_E(K) - 1]e^{-2W(T)} \quad (5.5)$$

where S_E is the X-ray structure factor at $T = 0$ K, being the equilibrium function and $W(T)$ is the Debye-Waller factor. $W(T)$ is written as,

$$W(T) = \frac{3\hbar^2 k^2 T^2}{2Mk_B \theta_D^3} \int_0^{\theta_D/2} \left(\frac{1}{e^z - 1} + \frac{1}{2} \right) z dz \quad (5.6)$$

where M is the atomic mass, θ_D is the Debye temperature, and $Z = \frac{\hbar f}{k_B T}$, f is the vibration frequency of the atoms and k_B is the Boltzmann constant. The TCR, then, can be written as,

$$\text{TCR} \cong 2 \left(\frac{1 - S^{MG}(2k_F)}{S^{MG}(2k_F)} \right) \frac{\partial W(T)}{\partial(T)} \quad (5.7)$$

The value of $\partial W(T)/\partial T$ is always positive. Assuming that the value of $2k_F$ is very close to k_p , i.e $S^{MG}(K) > 1$ in Eq. (5.7) for the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glasses, the sign of their TCRs is negative.

5.4 Conclusions

A study of electrical resistivity of metallic glasses shows that,

1. The resistivity of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glasses decreases during heating from room temperature to crystallization temperature.
2. The decrease in resistivity with time during structural relaxation follows the stretched exponential function.
3. The decrease in electrical resistivity can be described well in terms of the diffraction model suggested by Ziman and Nagel.

CHAPTER 6

DIFFUSION IN METALLIC GLASSES

6.1 Introduction

Diffusion in metallic glasses and ultraviscous melts determines both their structural relaxation and crystallization kinetics. It has been studied extensively since the discovery of multicomponent bulk metallic glasses by Inoue (1990) and Peker and Johnson (1993) in bulk metallic glasses and ultraviscous melt (Geyer et al 1995, Budtke et al 1997, Ehmler et al 1998, Nakazima et al 1999, Zumkley et al 2001). It also determines phase separation and crystallization at elevated temperatures (Spaepen 1981, Haasen 1986, Cahn 1991). Altogether these properties are used to determine their thermal stability, which is crucial to their production and use.

Diffusion measurements in metallic glasses have been performed by radiotracer method. The technique requires mechanical sectioning of a sample, as used by Schuehmacher and Guiraldenq (1983) and sputter sectioning, which was used by Gupta et al (1975). Other methods used for the diffusion in metallic glasses are : (i) secondary ion mass spectrometry (SIMS), which Tyagi et al (1990, 1991) used to study self-diffusion in Ni-containing alloys by using ^{63}Ni isotope as tracer, (ii) Auger electron spectroscopy (AES), which was used in combination with sputter profiling by Stelter and Lazarus (1987) to measure Au and Ag diffusion in amorphous Cu-Zr, (iii) Rutherford backscattering spectrometry, which was used by Chen et al (1978) to study Au diffusion

in Pd-Cu-Si metallic glasses, and (iv) small-angle x-ray scattering, which was used by Rosenblum et al (1980) and Greer et al (1982).

The mechanism of diffusion in metallic glasses is still unresolved. Two main mechanisms of diffusion in metallic glasses have been proposed. Firstly, a kink in the Arrhenius plots of the diffusion coefficient at the glass transition temperature has been attributed to a transition from single-atom jumps in the glassy state to viscous flow in the ultraviscous state (Greer 1999, Tang et al 1999). Secondly, the diffusion in both glassy and ultraviscous states of metal alloys is a highly collective hopping process (Buchenau et al 1986, Ehmler et al 1998, Meyer et al 1998, Robler and Teichler 2000).

Diffusion of substitutional atoms in crystalline solid is attributed to the mechanism of vacancy transfer from site to site in its lattice. This was shown by Kirkendall and Smisglas (1947), and their finding is known as Kirkendall effect. In these experiments, inert markers are placed at the interface between an alloy and a metal that form a diffusion couple. During annealing at a temperature where diffusion occurs at a measurable rate, the markers move towards the alloy region. For example, when molybdenum is used as a marker between copper and brass, molybdenum atoms are found to move towards the brass. This was explained by assuming that the zinc diffuses more rapidly than the copper, and thus diffuses out of the (brass) alloy down its concentration gradient. Such a process is impossible if the diffusion is by direct exchange of atoms or by ring mechanism (Jeffries 1924, Zener 1950).

Diffusion studies in metallic glasses have been performed only for one interstitial or substitution atom in its structure, by Rosenblum et al (1980) and Greer et al (1982). In

their experiments, they used compositionally modulated amorphous multilayer specimens. They measured the intensity decay of the small-angle x-ray peak corresponding to the interlayer separation so that the interdiffusion coefficients which pertain to diffusion in a chemically inhomogeneous material were able to be determined.

Diffusion across the interface between crystalline phase and amorphous phase of bulk metallic glass, which leads to diffusion-bonding between two samples, is of importance for design engineering of such glasses, but such studies have not yet been performed. This chapter presents efforts in investigations of the mechanism of diffusion across such an interface. The interface is formed between $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass and a crystalline metal.

6.2 Experimental Methods

In the method used here the diffusion couple consisting of a metallic glass and crystalline metal was isothermally annealed for a certain time. After definite time intervals, imaging of the sample was done by optical and electron microscopy. The composition of the diffusing zone was determined by using Energy Dispersive X-Ray Spectroscopy (EDX).

$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass was used to form a diffusion couple with crystalline Sn and with Zn, in two separate studies. In preparing the samples, the sides of the sample that configured the diffusion couples were cut from the as-cast specimens. The surface for the coupling interface were ground and polished. Annealing was performed in a vacuum furnace. After annealing, the surface of the diffusion couple

across the interface was ground and polished and imaged by using both an optical microscope and Philips SEM 515 Scanning Electron Microscopy (SEM). Elemental profiling was measured by EDX which was integrated in the SEM. The experiment conditions used are listed in Table 6.1.

Table 6.1. Conditions for studying Kirkendall effect for diffusion couples.

Condition	Side 1	Side 2	T_a (K)	t (h)
1	$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ glass	crystalline Sn	490	48
2	$Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$ glass	crystalline Zn	600	48

We needed to ensure the reliability of the equipment used for annealing the diffusion couples. Therefore, a diffusion couple of pure tin (99.99 %) and pure crystalline copper (99.9 %) were first made and studied. Both Cu and Sn half couple size was approximately $4 \times 4 \times 2 \text{ mm}^3$. After polishing the surfaces of two sides by using 0.1 micron diamond, the two sides were put together with the polished surfaces intact and compression-held by a sample holder that was made as a yoke by using two plates with two bolts. This configuration is illustrated in the insert of Fig. 6.1. The sample holder with the sample was placed in a pyrex glass tube and annealed in a furnace at 490 K for 48 h in vacuum (10^{-5} Pa). After the annealing, the diffusion couple was polished by using 0.1 micron diamond.

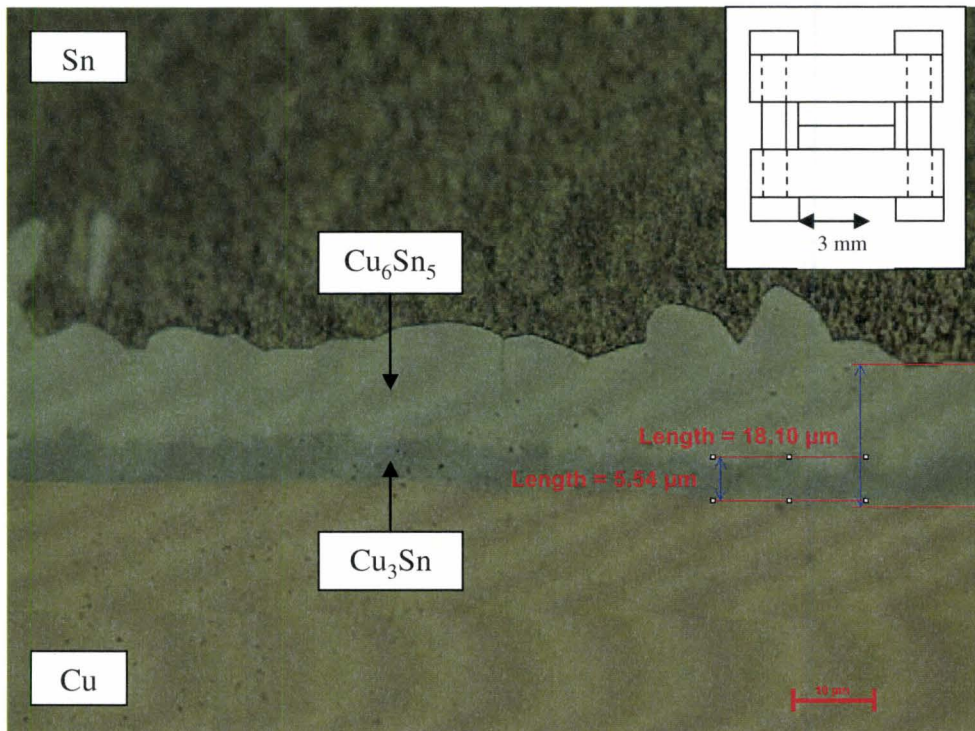


Fig. 6.1. Optical micrograph of diffusion couple of copper and tin after annealing at 490 K for 48 h. The insert shows the sample holder diagram.

6.3 Results and Discussion

Optical micrograph of the annealed sample is shown in Fig. 6.1. It is evident that diffusion occurred across the copper-tin interface. The intermetallic compounds of Cu_6Sn_5 and Cu_3Sn were formed as the result of diffusion. The compounds were determined by elemental concentration measurement by using EDX. This experiment ascertained that the method devised here for the annealing of diffusion couple is reliable.

Fig. 6.2 shows optical micrograph of diffusion couple made with the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass and crystalline Sn after annealing at 490 K for 48 h. Fig. 6.3 shows the optical micrograph of diffusion couple made with the

$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass and crystalline Zn after annealing at 600 K for 48 h. For both diffusion couples, the interface of glass and crystals can be clearly observed eventhough the diffusion zone is not obvious.

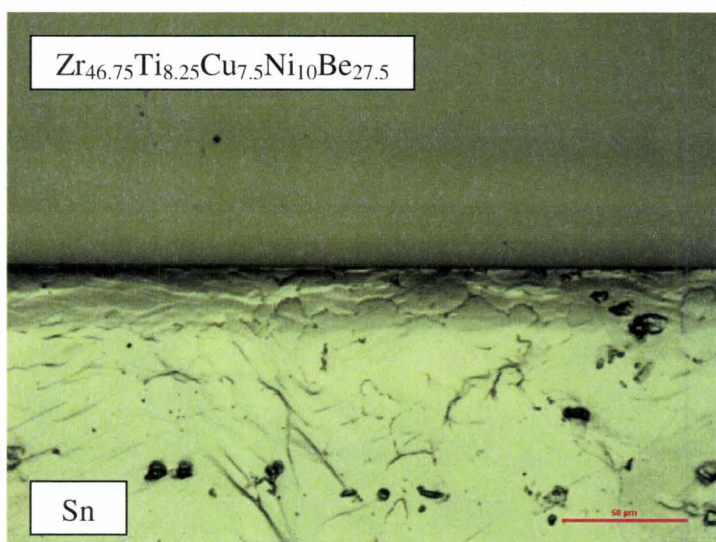


Fig. 6.2. Optical micrograph of diffusion couple of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass and crystalline Sn after annealing at 490 K for 48 h.



Fig. 6.3. Optical micrograph of diffusion couple of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass and crystalline Zn after annealing at 600 K for 48 h.

Concentrations of the element Sn after annealing the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass–crystalline Sn diffusion couple are shown in Fig. 6.4. The corresponding plots for Zr, Cu, Ni and Ti are shown in Figs. 6.5, 6.6A, 6.6B, and 6.7, respectively. Concentration of the element Zn after annealing of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ glass–crystalline Zn diffusion couple are shown in Fig. 6.8. The corresponding plots for Zr, Cu, Ni and Ti are shown in Figs. 6.9, 6.10A, 6.10B, and 6.11, respectively.

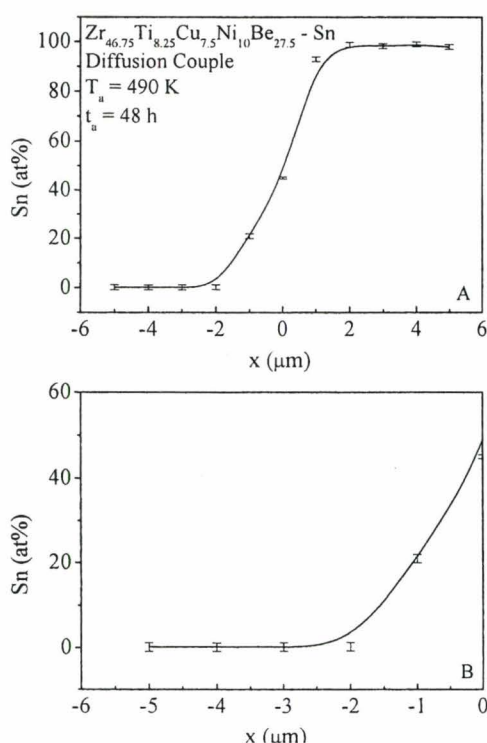


Fig. 6.4. A. Sn concentration in the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Sn diffusion couple annealed at 490 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Sn. The negative sign of x refers to the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side and the positive sign refers to Sn side. B. The data in plot (A) for the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side showing the depth to which Sn has diffused.

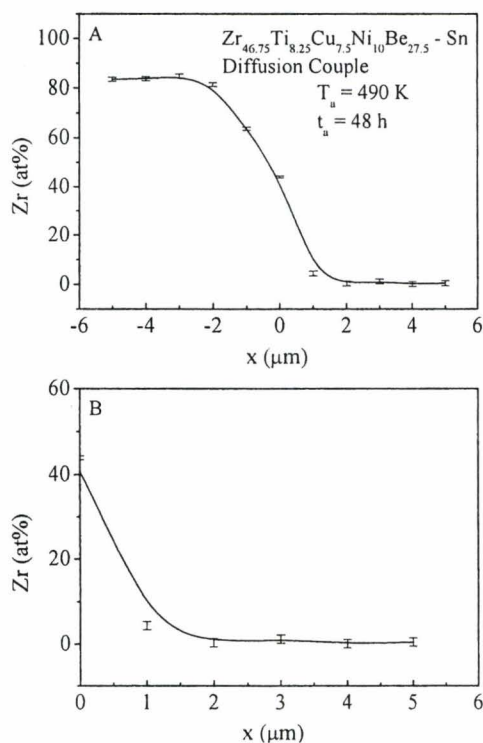


Fig. 6.5. A. Zr concentration in the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Sn diffusion couple annealed at 490 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Sn. The negative sign of x refers to the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side and the positive sign refers to Sn side. B. The data in plot (A) for the Sn side showing the depth to which Zr has diffused.

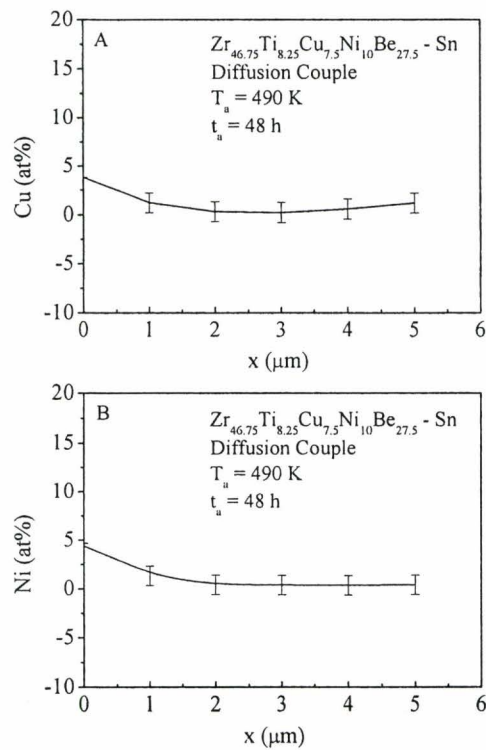


Fig. 6.6. A. Cu concentration in Sn side of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5} - \text{Sn}$ diffusion couple annealed at 490 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Sn. B. The corresponding plot for Ni.

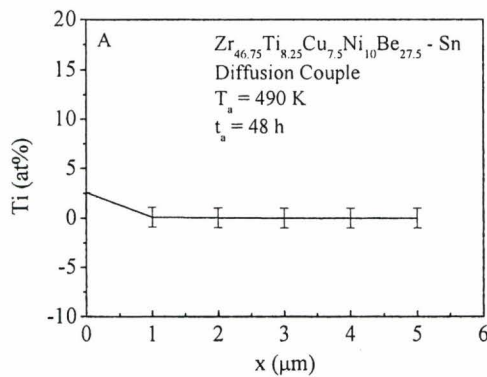


Fig. 6.7. Ti concentration in Sn side of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5} - \text{Sn}$ diffusion couple annealed at 490 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Sn.

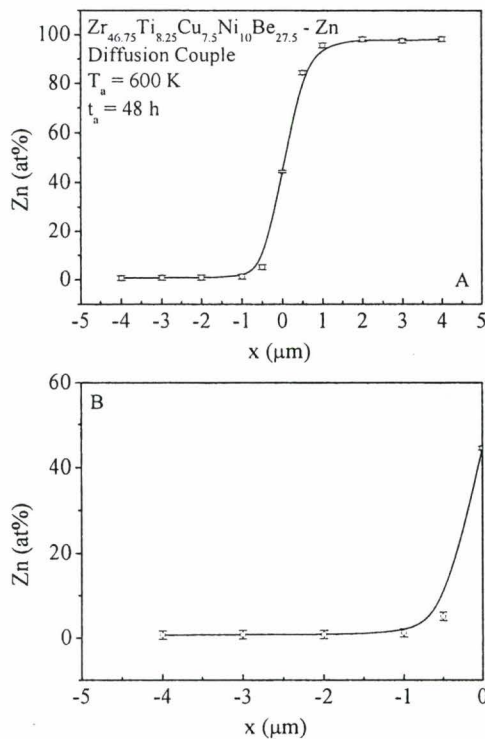


Fig. 6.8. A. Zn concentration in the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Zn diffusion couple annealed at 600 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Zn. The negative sign of x refers to the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side and the positive sign refers to Zn side. B). Plot of (A) with $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side only.

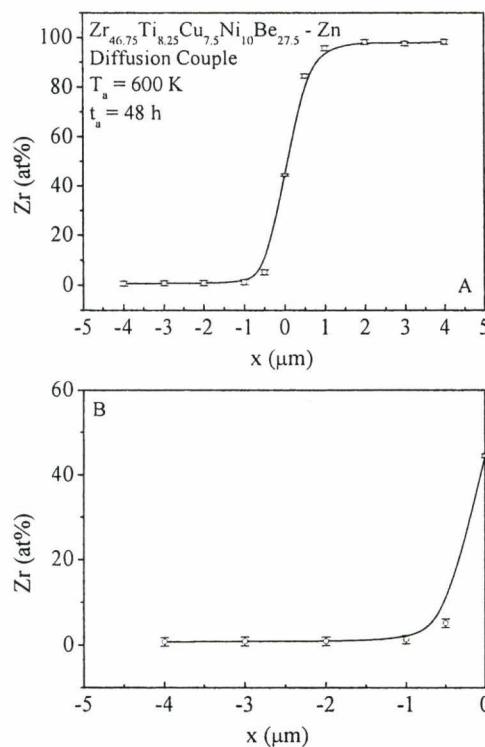


Fig. 6.9. A. Zr concentration in the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Zn diffusion couple annealed at 600 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Zn. The negative sign of x refers to the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ side and the positive sign refers to Zn side. B. Plot of (A) with Zn side only.

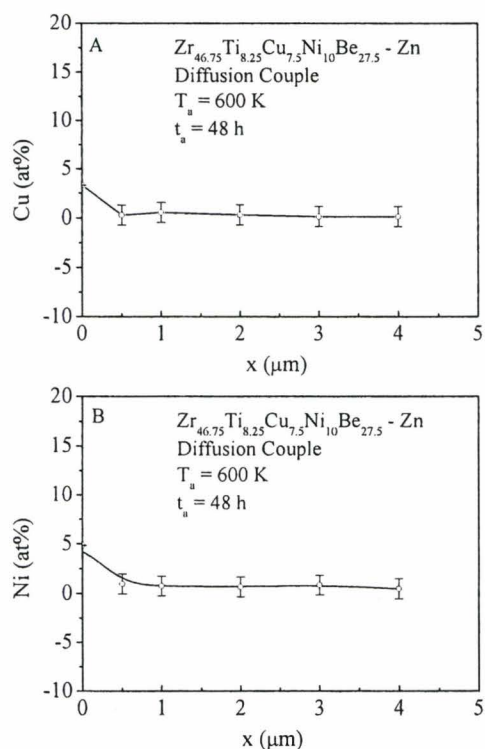


Fig. 6.10. A. Cu concentration in Zn side of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Zn diffusion couple annealed at 600 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Zn. B. The corresponding plot for Ni.

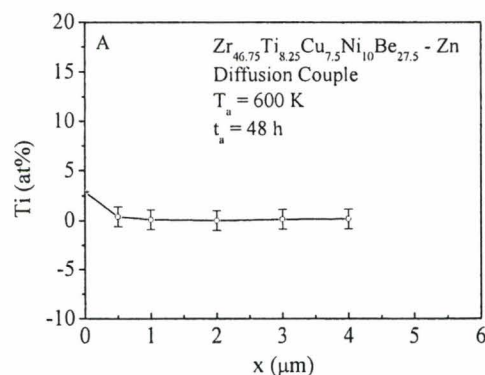


Fig. 6.11. Ti concentration in Zn side of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ - Zn diffusion couple annealed at 600 K for 48 h as a function of distance, x , from the interface of $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ and Zn.

We expected that after annealing the diffusion zone of both diffusion couples, the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ – Sn and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ – Zn would be more than 10 μm , which has been usually observed in diffusion couple of crystals, as in Fig. 6.1 where the diffusion zone of Sn–Cu couple is more than 20 μm . But in Figs. 6.4 – 6.11, and considering the error bars for concentration measurement by EDX, there is no diffusion beyond 2 μm from the interface. Nevertheless, the concentration of elements within 2 μm from the interface is significant despite the measurement error from the interaction volume of incident electron and sample, which is calculated as 1 μm by using Monte Carlo simulation algorithm provided with the data analysis software of EDX. It is evident that in metallic glasses the diffusion is too slow to allow a larger concentration profile and it is conceivable that at higher temperatures, the concentration profile may extend to a longer zone. But at high temperatures, the metallic glasses crystallized. It is also possible that other surface characterization techniques, such as Electron Energy Lost Spectroscopy (EELS) and Auger Electron Spectroscopy (AES) may be useful for a more accurate characterization of the 2 μm zone than EDX. This was not done here.

6.4 Conclusions

Inter-diffusion of atoms across a metallic glass–pure crystalline metal interface is limited, but occurrence of Kirkendall effect is still demonstrable. The extent of inter-diffusion is still sufficient for diffusion bonding of the metallic glass with pure metals. Elements of Sn, Zn, Zr, Cu, Ni, and Ti in both $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ – Sn and

$\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ – Zn diffusion couples during annealing diffuse at most to a distance of 2 μm . The mechanism of diffusion is complicated by the co-operative nature of diffusion in a glass as well as by the multiplicity of the atomic sizes, rather than the simple vacancy-type diffusion in a crystal lattice.

CHAPTER 7

FICTIVE TEMPERATURE, STRUCTURAL RELAXATION, AND REALITY OF RESIDUAL ENTROPY

7.1 Introduction

As described in Chapter 2, glass formation on cooling a liquid is characterized by two features: (i) properties measured in the glass-formation temperature range depend upon the observation time, and (ii) structure of the glass formed spontaneously relaxes with time toward the equilibrium state of lower enthalpy, H , and lower volume. When a glass is heated, its structure relaxes at a faster rate, and its apparent (measured) specific heat C_p decreases initially. When the temperature is sufficiently high its value is regained by a broad peak-like overshoot in the C_p against T plot. The temperature at which the structure of a liquid kinetically freezes on cooling is known as the fictive temperature, T_f (Tool 1946, Moynihan et al 1976a, 1976b, Scherer 1986). It is estimated from the enthalpy change, i.e., by using the area confined by the C_p against T plot measured during cooling a liquid through the vitrification range at a fixed cooling rate q_c . The glass-softening temperature T_g is defined as the temperature at which the structural relaxation time of a glass on heating at 20 K/min rate reaches 100 s. When q_c is higher than this rate, T_f of the glass formed is higher than its T_g , and when q_c is low, T_f of the glass formed is lower.

Quenching of a liquid ($q_c > 10^5$ K/min) produces a glass of T_f much higher than T_g . When such a glass is heated at a fixed rate, the heat released on its structural relaxation appears as a rapid decrease in its measured C_p by a large amount. On further heating a relatively small overshoot appears in C_p before the state of equilibrium melt is reached (Moynihan et al 1976a, 1976b, Scherer 1986, Gutzow and Schmelzer 1995, Nemilov 1995, Donth 2003). When C_p data during the cooling are not available, T_f has been determined by analyzing the area under the C_p against T plot obtained by heating a glass at a fixed rate, q_h . Such studies are currently used to define how T_f decreases with time and in doing so, T_f at a given instant is taken as the temperature on the supercooled liquid curve at which the extrapolated H of glass would be equal to that of the supercooled liquid (Moynihan 1976b, Scherer 1986). Thus, T_f becomes a useful measure of thermal history of a glass. On structural relaxation at a fixed T , C_p of a glass decreases monotonically with time according to a stretched exponential equation (Tombari et al 2002, 2008). The decrease contains the relaxation of several components, the main one being configurational (Tombari et al 2002, 2008).

Residual entropy, S_{res} , of a glass, i.e., its entropy at zero Kelvin, is estimated by using relations of reversible thermodynamics. Gutzow and Schmelzer (1995) have listed the S_{res} data of a large number of glasses. But these values appear to be in contrast with the precepts of statistical thermodynamics, according to which, $S_{conf} = k_B \ln \Omega$, where k_B is the Boltzmann constant and Ω the number of configurations of equal energy. Since the structure of a non-crystalline solid is fixed, $\Omega = 1$, and thus its S_{conf} should be equal to zero. Therefore, it would appear that a glass, like a perfect crystal, should obey the third

law, i.e., its entropy should be zero at 0 K, irrespective of the method by it has been produced and whatever its thermal history. Since S_{res} is equal to the frozen-in configurational entropy, which decreases on structural relaxation, its value decreases as a glass structurally relaxes. This suggests that there is a conflict between the finite S_{res} obtained from classical thermodynamics and the zero value for S_{res} obtained from statistical thermodynamics.

Attempts to rationalize this conflict have been considered since the 1920s, and several recent papers (Kivelson and Reiss 1999, Goldstein 2008, Schmelzer and Gutzow 2009, Nemilov 2009) briefly describe its history. In discussing the mutually exclusive statistical and classical thermodynamics views, Kivelson and Reiss (1999) focused on the possible loss of S_{conf} when a liquid vitrifies on cooling and concluded that S_{res} is unreal. Goldstein (2008) critically discussed their views and concluded that arguments for the unreality of S_{res} are untenable in terms of both the second law of thermodynamics and known experiments and S_{res} is real. Since Goldstein, several authors (Schmelzer and Gutzow 2009, Johari 2010a, 2010b) have discussed the configurational entropy, S_{conf} , of a liquid and glass, by reviewing the evolution of the third law (Schmelzer and Gutzow 2009, Nemilov 2009) discussing theoretical aspects of the entropy of a non-equilibrium state (Schmelzer and Gutzow 2009) and describing experiments on the solubility and other properties of a glass (Goldstein 2008, Schmelzer and Gutzow 2009, Johari 2010a), all concluding against the view that S_{conf} vanishes on vitrification. Reiss (2009) appealed that S_{res} violates the causality principle, and suggested that the impression of S_{res} stems from inclusion of a *path-irreversible* segment in the thermodynamic cycle of the liquid

and glass. Thus S_{res} is an artifact from use of the C_p data in this segment (Reiss 2009). He neither provided experimental evidence in support of his arguments, nor suggested methods for testing it.

Goldstein (2008) and Johari (2010a) have recently discussed experiments that may be used to resolve it. In an earlier paper, Johari (2010a) also described (thermodynamically) analogous kinetic freezing of defect diffusion in a crystal lattice and suggested that thermodynamic arguments (Kivelson and Reiss 1999, Reiss 2009) against the reality of S_{res} of glasses would apply equally well to crystals containing lattice defects. By using the spontaneous enthalpy decrease in a calorimetric experiment, and the known enthalpy of formation of vacancy, one can calculate the decrease in the (fractional) vacancy population, x and use it to estimate the decrease in S_{conf} from the relation $S_{conf} = -R [x \ln x + (1-x) \ln(1-x)]$, where R is the gas constant. This may be compared against the change determined from the $C_p d \ln T$ integral. Alternatively, one may measure the emf of a cell made from two electrodes containing different vacancy populations, as was suggested for glasses of different thermal history (Johari 2010b), to ascertain whether such crystals have S_{res} or not (Johari 2010a).

Since the C_p measured during the rate-heating of a glass includes the effects of spontaneous enthalpy loss from structural relaxation, the quantity determined from the $C_p d \ln T$ integral is not the entropy change. This is evident from Clausius inequality, $dS > dq_{irrev}/T$, where dq_{irrev} is the irreversible heat transfer at temperature T . Nevertheless, it provides the upper and lower limits of the entropy, the Clausius limits, when data are available for both the cooling and the heating paths. For maintaining a distinction

between the real entropy change and the quantity determined from the $C_p \ln T$ integral on the cooling and heating paths through the glass-liquid transformation temperature range, we refer the quantity determined from the integral as $\Delta\sigma$ instead of ΔS , and T_f determined from it as T_f^σ . The usual T_f determined from the $C_p dT$ integral is denoted as T_f^H . In principle, T_f^σ would not be equal to T_f^H , and a slight difference between the two is also expected on geometric considerations of the two integrals. Therefore, if one finds T_f^σ to be closely similar to T_f^H it would show that the time-dependence of the thermodynamic path between glass and liquid is insufficient to produce a significant difference between the Clausius limits, i.e. the upper and lower limits of the entropy change, from the real entropy change, and S_{res} would be real. But if they are found to be very different then S_{res} would be unreal. Since we have described an analysis for the entropy relaxation of a glass in Chapter 2, we need to substantiate this analysis by showing that the configurational and residual entropy of a glass is real. Here we do so by determining T_f^σ and T_f^H for several metallic glasses studied here and other glasses that had been obtained by quenching of a melt and spray-drying of liquid droplets, both of which show a large enthalpy decrease on heating, and examine if T_f^H and T_f^σ determined from the C_p data obtained here by simulations from the non-exponential, non-linear relaxation model for glass-liquid relaxation differ substantially.

We also performed new calorimetric studies on $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ melts and glass in order to use a direct approach for ascertaining whether S_{res} could be an artefact of using $\Delta\sigma$. In this study a sample was cooled at a certain rate to

form a glass and the glass was heated at the same rate. By using the (time-dependent) $C_p - T$ data on the cooling and heating paths, we determine the Clausius limits. These experiments also show that S_{res} can not be zero. Since the experimental technique and procedure are the same as given in Chapter 2, it is excluded. Two papers on these findings have been published (Aji and Johari 2010, Johari and Aji 2010).

7.2 Results

The quantity dH/dt measured by DSC experiments was divided by the heating rate ($q_h = dT/dt$) and thus converted to dH/dT . This quantity is proportional to the C_p of the sample, but for accuracy we use our original plots. When data on C_p are available in the literature we use those data. Fig. 7.1A shows the plot of dH/dT against T for bulk $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass heated at 20 K/min (curve 1) and a rescan of the same sample by first cooling the melt at 20 K/min to 440 K and then heating the glass at 20 K/min (curve 2). Fig. 7.2A shows the corresponding plots of dH/dT against T for a sample of bulk $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass. Here curve 1 (aged) refers to the as-cast sample that had been stored at ambient temperature for an unknown period, and curve 2 is the rescan after cooling its ultraviscous melt to 320 K at 20 K/min and then heating the glass at 20 K/min.

We also used the data from the literature for other metallic glasses. Fig. 7.3A shows the plot of dH/dT against T for quenched and aged $\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$ glass that had been heated at 20 K/min (curve 1) and a rescan of the same sample by first cooling the melt at

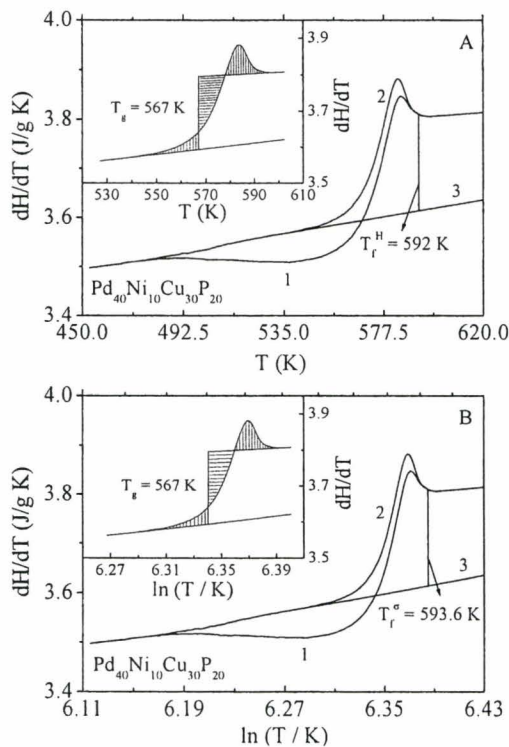


Fig. 7.1. A. The plot of C_p of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass (curve 1) and a 20 K/min cooled sample (curve 2) both obtained on heating at 20 K/min. Curve 3 is the extrapolated line from $T < T_g$. B. The corresponding plots of C_p against $\ln(T)$.

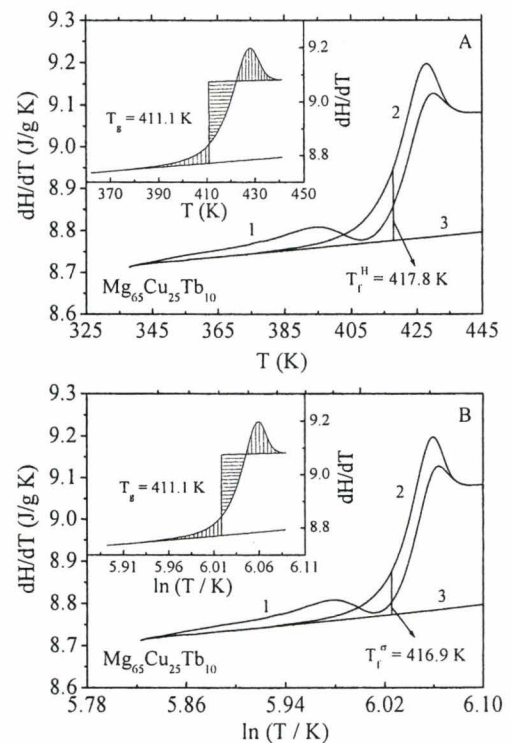


Fig. 7.2. A. The plot of C_p of $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass that was stored at ambient conditions (curve 1) and a 20 K/min cooled sample (curve 2) both obtained on heating at 20 K/min. Curve 3 is the extrapolated line from $T < T_g$. B. The corresponding plots of C_p against $\ln(T)$.

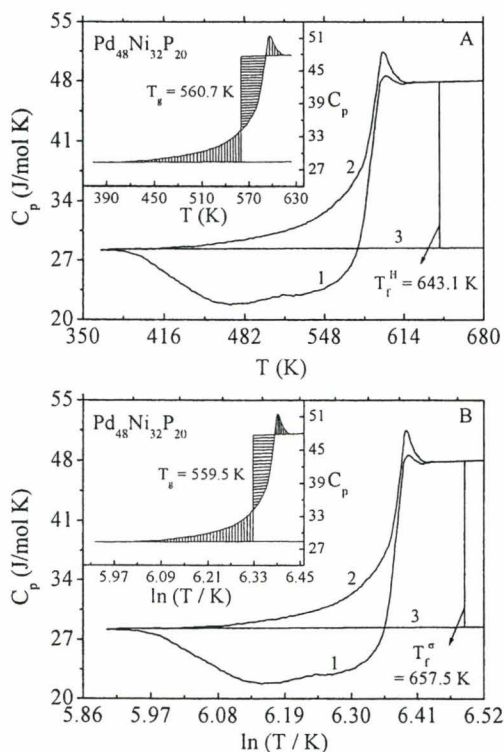


Fig. 7.3. A. The plot of C_p against T of quenched sample of $\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$ glass heated at 20 K/min (curve 1), and of the sample vitrified by cooling the melt at 20 K/min that was heated at 20 K/min (curve 2). Curve 3 is the extrapolated line from $T < T_g$. B. The corresponding plots of C_p against $\ln(T)$. The inserts are the plots of C_p used for determining T_g by matching the area shown by vertical lines with the area shown by horizontal lines. The top tick marks of Fig. (B) indicate the T values. Data are taken from Chen (1982).

20 K/min to 320 K and then heating the glass at 20 K/min (curve 2). The data were read from Fig. 6 in Chen's paper (1982). Fig. 7.4A shows the corresponding plots of dH/dT against T for a sample of bulk $(\text{Pd}_{0.86}\text{Ni}_{0.14})_{83.5}\text{Si}_{16.5}$ glass for which the data were read from Fig. 2a published by Chen and Inoue (1984). Here curve 1 (quenched-aged) is for the sample that had been stored at ambient temperature for an unknown period, and curve 2 is the rescan after cooling its ultraviscous melt to 320 K at 20 K/min to vitrify it and then heating the glass at 20 K/min.

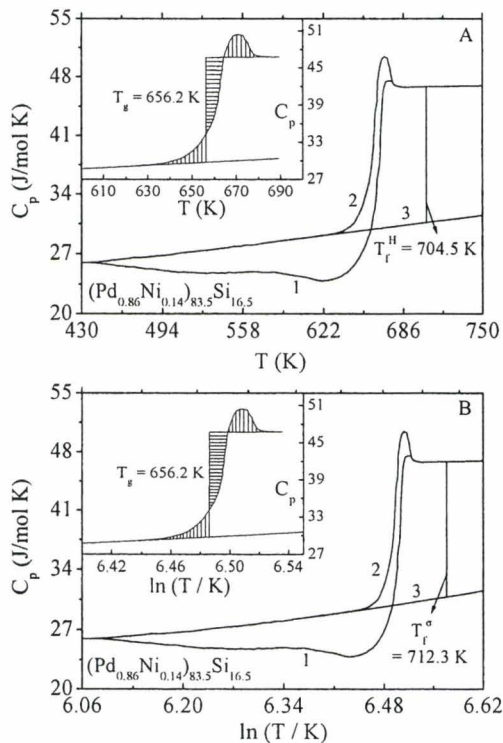


Fig. 7.4. A. The plot of C_p against T of quenched sample of $(\text{Pd}_{0.86}\text{Ni}_{0.14})_{83.5}\text{Si}_{16.5}$ glass heated at 20 K/min (curve 1), and of the sample vitrified by cooling the melt at 20 K/min that was heated at 20 K/min (curve 2). Curve 3 is the extrapolated line from $T < T_g$. B. The corresponding plots of C_p against $\ln(T)$. The inserts are the plots of C_p used for determining T_g by matching the area shown by vertical lines with the area shown by horizontal lines. T_g determined from the $C_p dT$ integral is the same as from the $C_p d\ln T$ integral. The area matching yields $T_f^H = 704.5$ K, and $T_f^\sigma = 712.3$ K, as indicated. The top tick marks of Fig. (B) indicate the T values. Data are taken from Chen and Inoue (1984).

To investigate validity of our analysis for the glassy state in general, data for several inorganic and organic glasses were taken from the literature. Fig. 7.5A shows the plot of C_p against T for a sample of basalt glass fibers (composition, 49.3 SiO_2 , 15.6 Al_2O_3 , 1.8 TiO_2 , 11.7 FeO , 10.4 CaO , 6.6 MgO , 3.9 Na_2O , and 0.7 K_2O in wt %) read

from the figure published by Yue (2004). Here curve 1 (quenched) refers to the sample made by quenching and curve 2 is the rescan of the sample cooled at 20 K/min and then heated at 20 K/min. Also shown in Fig. 7.5A is the plot of C_p for a sample of basalt fibers that had been aged for 3 h at 683 K, cooled back to room temperature and rescanned in DSC.

Huang and Gupta (1992) had earlier studied NBS-710 glass (composition, 70.5 SiO₂, 8.7 Na₂O, 7.7 K₂O, 11.6 CaO, 1.1 Sb₂O₃, 0.2 SO₃ in wt %) as glass fibers of several diameters. We use their C_p data for the quenched sample F3 (diameter 12 μ m), taken from their Fig. 5, and the C_p data for the same sample but rescanned at 20 K/min after cooling at 20 K/min, as described in their Fig. 6. These are plotted as curves 1 and 2 in Fig. 7.6A.

Fig. 7.7A shows the corresponding plots for a sample of basalt glass fibers (composition, 49.3 SiO₂, 15.6 Al₂O₃, 1.8 TiO₂, 11.7 FeO, 10.4 CaO, 6.6 MgO, 3.9 Na₂O, and 0.7 K₂O in wt %) read from Fig. 1 published by Yue et al (2002). Here curve 1 (quenched) refers to the sample made by quenching and curve 2 is the rescan of the sample cooled at 20 K/min and then heated at 20 K/min. Fig. 7.8A shows the plot of C_p of spray-dried propylene glycol from Fig. 1 in Angell et al's study (2003). Curve 1 is for a spray-dried sample heated at 20 K/min and curve 2 for the sample that had been vitrified by cooling at 20 K/min and then heated at the same rate. Curve 3 is the extrapolated line from $T < T_g$. Fig. 7.8B shows the corresponding plots of C_p against $\ln(T)$.

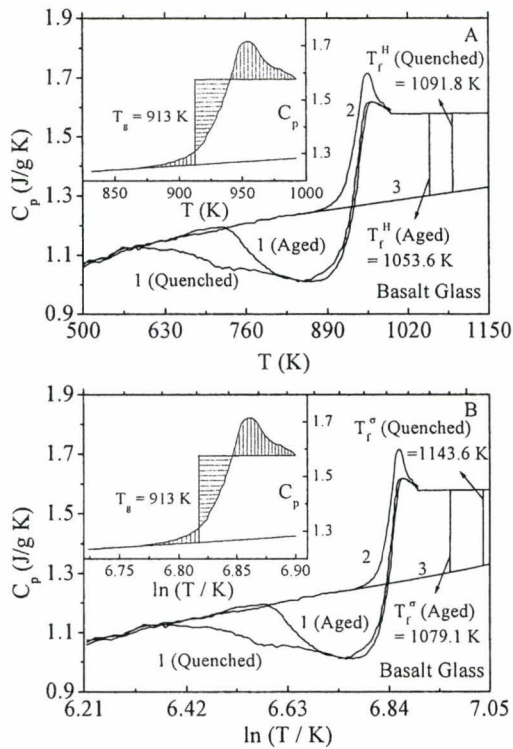


Fig. 7.5. A. The plot of C_p of quenched fibers sample of basalt glass (curve 1-quenched) and a 20 K/min cooled sample (curve 2) both obtained on heating at 20 K/min. Also shown are the data for a sample of basalt fibers that had been aged for 3 h at 683 K, cooled back to room temperature and rescanned (curve 2-aged). B. The corresponding plots of C_p against $\ln(T)$. The top tick marks of Fig. (B) indicate the T values on the axis of Fig. (A). Data are taken from Yue (2004).

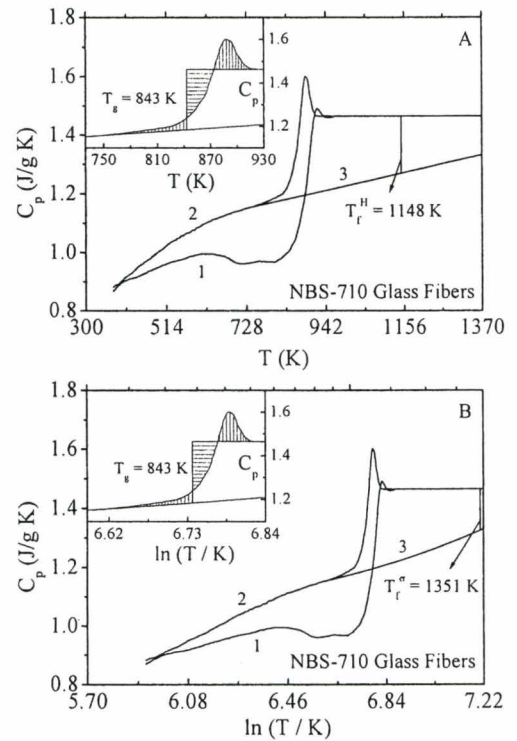


Fig. 7.6. A. The plot of C_p of quenched fibers sample of NBS-710 glass (sample F3 with diameter 12 μm from Huang and Gupta (1992) and for the same sample but rescanned after cooling at 20 K/min from their Fig. 6). B. The corresponding plots of C_p against $\ln(T)$. The top tick marks of Fig. (B) indicate the T values on the axis of Fig. (A).

In Figs. 7.1 – 7.8 the inserts show the plots of C_p used for determining T_g s from the $C_p dT$ and from the $C_p d\ln T$ integrals by matching the area shown by vertical lines with the area shown by horizontal lines.

New experiments performed on two metallic glasses yielded the quantity dH/dT . Its plot against T for cooling the $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ melt at 20 K/min is shown by curve 1 in

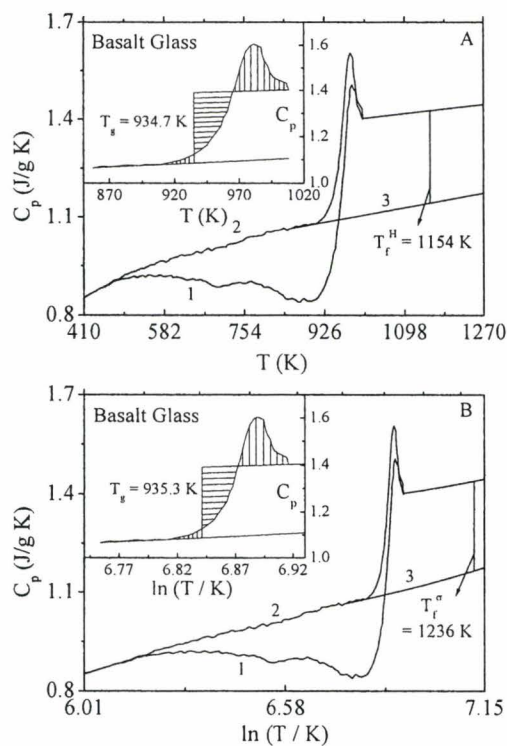


Fig. 7.7. A. The plot of C_p against T of quenched fibers sample of basalt glass at 20 K/min (curve 1), and of the sample vitrified by cooling the melt at 20 K/min that was heated at 20 K/min (curve 2). Curve 3 is the extrapolated line from $T < T_g$. B. The corresponding plots of C_p against $\ln(T)$. The top tick marks of Fig. (B) indicate the T values. Data are taken from Yue et al (2002).

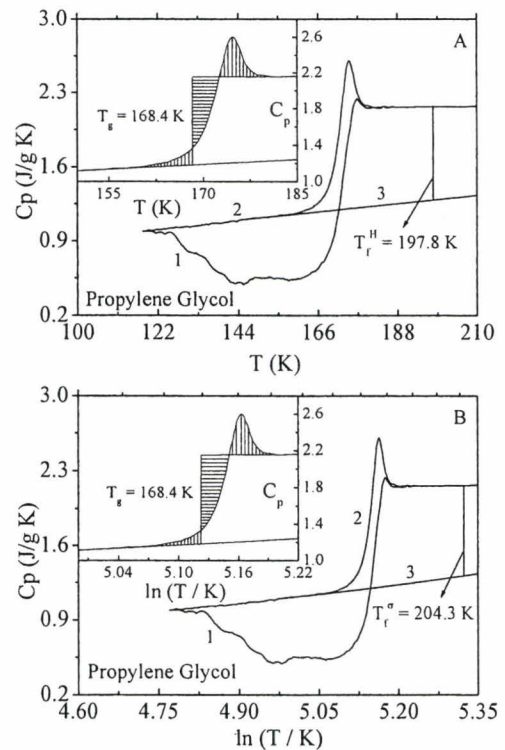


Fig. 7.8 A. The plot of C_p against T of spray dried propylene glycol heated at 20 K/min (curve 1), and of the sample vitrified by cooling the melt at 20 K/min that was heated at 20 K/min (curve 2). B. The corresponding plots of C_p against $\ln(T)$. The top tick marks of Fig. (B) indicate the T values. Data are taken from (Angell et al 2003).

Fig. 7.9A and that on heating the glass to the melt at 20 K/min is shown by curve 2. The corresponding plots of dH/dT against $\ln(T)$ are shown in Fig. 7.9B.

Lastly, the plot of dH/dT for cooling of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ melt at 20 K/min is shown by curve 1 in Fig. 7.10A, where the plot for heating the glass at 20 K/min is shown by curve 2. The corresponding plots of dH/dT against $\ln(T)$ are shown in Fig. 7.10B.

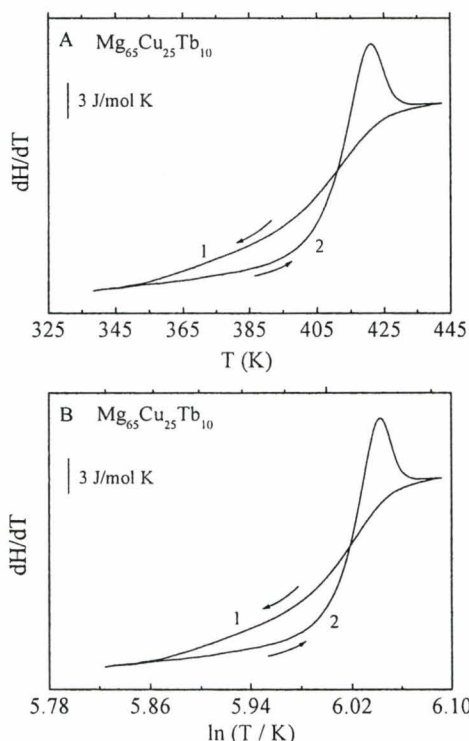


Fig. 7.9. A. The plot of dH/dT against T on cooling $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ melt to the glassy state (curve 1) and then on heating the glass to the melt state (curve 2), both at 20 K/min. B. The corresponding plot of dH/dT against $\ln T$. The temperatures limits for the integration are 338.5 K and 442.4 K. The top tick marks of Fig. (B) indicate the T values on the axis of Fig. (A).

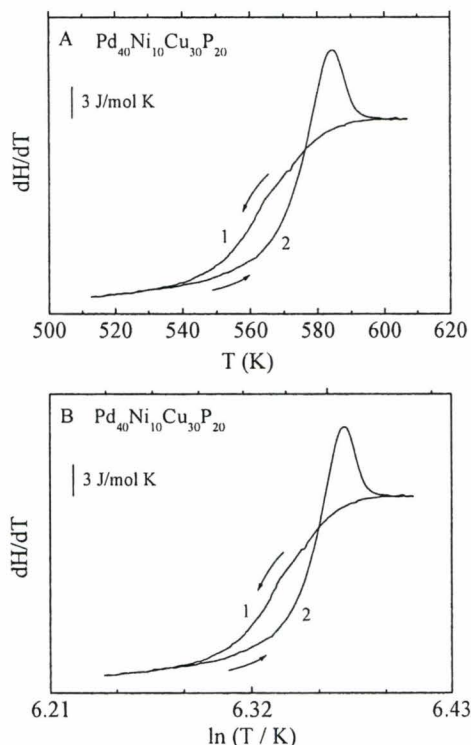


Fig. 7.10. A. The plot of dH/dT against T on cooling $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ melt to the glassy state (curve 1) and then on heating the glass to the melt state (curve 2) both at 20 K/min. B. The corresponding plot of dH/dT against $\ln T$. The temperatures limits for the integration are 512.7 K and 606.9 K. The top tick marks of Fig. (B) indicate the T values on the axis of Fig. (A).

7.2.1 Fictive Temperature from Enthalpy and Entropy Integrals

In the literature, both T_g and T_f have been determined from the plot of C_p against T , or from a DSC scan. Moynihan et al (1976a) had described a method that uses the C_p or dH/dT data obtained by heating at 10 K/min rate a glass that was formed on cooling the melt at the same rate. As Moynihan et al (1976a) had noted, the method had been suggested by Guttman (1974) for determining T_g . Its procedure was based (Moynihan et al 1976a, Guttman 1974) on the physical continuity of a thermodynamic function in

both time and T . The rate of change of a function with T is extrapolated from two temperatures in this method, one temperature below and one above the sigmoid shape part of the scan. This shows a step-like change at T_f' when the condition,

$$\int_{T^*}^{T_f'} (C_{p,liq} - C_{p,glass})dT = \int_{T^*}^{T'} (C_{p,meas} - C_{p,glass})dT \quad (7.1)$$

is fulfilled. Here, $C_{p,liq}$ is specific heat of the liquid, $C_{p,glass}$ that of the glassy state and T^* is any temperature above the transition region when the state is a liquid, T' is the temperature well below the glass transition region, and $C_{p,meas}$ is the measured C_p on heating from the glassy to liquid state. For use in the integral, $C_{p,glass}$ at $T > T_g$ is obtained from a curve drawn as an extension of the curve for $C_{p,glass}$ from $T < T_g$ to higher temperatures. This extension is either done by linear extrapolation from $C_{p,glass}$ or done by fitting the $C_{p,glass}$ data to a polynomial equation. The longer the extension, the greater is the error in the estimate of $C_{p,glass}$ at $T > T_g$. Moynihan et al (1976a) estimated T_f' of a glass for both cases, when $q_h = q_c = 10$ K/min, and when $q_h = 10$ K/min and $q_c = 80$ K/min. In both cases, T_g was taken to be equal to T_f' . (T_g itself is determined either by drawing a tangent to the maximum slope point and determining its intersection with the extended curve from the glassy state or by the midpoint temperature of the sigmoid-shape curve.) In the current practice of using $q_c = q_h = 20$ K/min, it is assumed that the calorimetric relaxation time at the T_g obtained from the DSC scan is 100 s. But it is also known that this method does not yield the same calorimetric relaxation time for liquids of different distribution of relaxation times and/or temperature-dependence of the relaxation time (Pacheto et al 1994, Johari and Aji 2008).

We first determine T'_f in Eq. (7.1), which is in the range of sigmoid-shape increase. When T'_f satisfies the conditions of Eq. (7.1), $T_g^H = T'_f$. We write Eq. (7.1) in terms of the corresponding $\Delta\sigma$ by replacing dT by $d\ln T$,

$$\int_{T^*}^{T'_f} (C_{p,liq} - C_{p,glass}) d\ln T = \int_{T^*}^{T'_f} (C_{p,meas} - C_{p,glass}) d\ln T \quad (7.2)$$

Similarly when the conditions of Eq. (7.2) are satisfied, $T_g^\sigma = T'_f$

Eqs. (7.1) and (7.2) are useful also when $q_h > q_c$, or when the glass has been annealed. But when $q_c \gg q_h$, i.e., when a glass is formed by quenching, Eqs. (7.1) and (7.2) can still be used, but they require extrapolation from a very low temperature. Yue et al (2002) described a procedure for estimating T_f . Here we modified their procedure, the $C_p dT$ integral for the enthalpy release is matched with the $C_p dT$ integral for the enthalpy gain by using T_g^H determined by the break-point in the DSC heating scan for 20 K/min rate of a glass formed by cooling the melt at 20 K/min rate. Thus, to determine T_f for such glasses, one uses two DSC scans. One is obtained by heating the plot for a quenched glass referred here as scan-1, and the other by heating the same glass formed by cooling at 20 K/min, referred here as scan-2. T_f^H is determined by area-matching according to the relation,

$$\int_{T_{ref}}^{T_{eq}} (C_{p,2} - C_{p,1}) dT = \int_{T_g}^{T_f^H} (C_{p,liq} - C_{p,glass}) dT \quad (7.3)$$

where $C_{p,1}$ is the data from scan-1, $C_{p,2}$ that from scan-2, T_{ref} is the temperature at which scan-1 begins to deviate from scan-2 at $T < T_g^H$, T_{eq} is a temperature in the equilibrium liquid state, and $C_{p,liq}$ and $C_{p,glass}$ are as defined earlier. As mentioned earlier here, $C_{p,glass}$

at $T > T_g$ is extrapolated either linearly or by fitting a curved line to the measured data obtained at $T < T_g$. The resulting error in T_f^H is higher the longer is the extrapolation of C_p to the liquid state.

To estimate T_f^σ , we replace dT in Eq. (7.3), by $d \ln T$,

$$\int_{T_{ref}}^{T_{eq}} (C_{p,2} - C_{p,1}) d \ln T = \int_{T_g}^{T_f^\sigma} (C_{p,liq} - C_{p,glass}) d \ln T \quad (7.4)$$

and find the value of T_f^σ that satisfies the conditions of Eq. (7.4).

It is understood that values of T_f^H and T_f^σ can be estimated only with reference to either T_g^H or T_g^σ , which in turn are determined for low values of both q_c and q_h . When $C_p - T$ data are not available, the heat flow rate (in W/mol) measured directly from a DSC scan may be divided by q_h to obtain (dH/dT) which may be used in place of C_p .

To illustrate the method used, we determine T_g^H in Eq. (7.1) by using the C_p data for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass. The data for the glass that had been formed by cooling its melt at 20 K/min, i.e., from curve 2 in the main frame of Fig. 1A is replotted in the insert in Fig. 1A. First we chose a T in the range of sigmoid-shape increase in C_p and determined the areas of the shaded regions as shown in the insert. When the temperature chosen was such that the area shaded by horizontal lines was equal to the sum of the two areas shaded by vertical lines (to satisfy the conditions of Eq. (7.1)), that temperature is equal to T_g^H . This temperature is 567 K. The same C_p data are plotted against $\ln(T)$ in the insert in Fig. 1B. The same area matching but by using $\Delta\sigma$ yields $T_g^\sigma = 567$ K. We conclude that the T_g thus estimated, T_g^H and T_g^σ have the same values.

We now determine T_f^H of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass heated at 20 K/min rate. In the main frames of Fig. 1A and B, curve 1 is the plot of C_p from the first scan, and curve 2 from the rescan, and curve 3 is an extrapolation from the glassy state which is used as a baseline to determine the difference, $(C_{p,liq} - C_{p,glass})$, needed for determining T_f^H from Eq. (7.3). Values of T_g^H estimated from curve 2 are indicated in both figures, and its value 567 K is the same as before. Analysis yields T_f^H as 592 K. By using the corresponding plots in Fig. 1B, we determine T_f^σ of the $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ glass as 593.6 K.

The corresponding plots of $C_p - T$ data for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ glass are shown in Fig. 7.2A and B, those for $\text{Pd}_{48}\text{Ni}_{32}\text{P}_{20}$ glass are shown in Fig. 7.3A and B and those for $(\text{Pd}_{0.86}\text{Ni}_{0.14})_{83.5}\text{Si}_{16.5}$ glass are shown in Fig. 7.4A and B. The plots of C_p against T and against $\ln(T)$ for an inorganic glass fibers of basalt composition glass in both the quenched and aged states are shown in Fig. 7.5A and B. The corresponding plots of C_p of quenched fibers sample of NBS-710 glass are shown in Fig. 7.6A and 7.6B and for quenched basalt glass are shown in Fig. 7.7A and B. For the spray dried and normal cooled glass of propylene glycol the corresponding plots are shown in Fig. 7.8A and B.

The T_g values determined from the enthalpy and entropy integrals, T_g^H or T_g^σ , and the values of T_f^H , and T_f^σ , the ratio T_f^σ/T_f^H along with the values of A_H and A_σ and the ratio A_H/A_σ for all these glasses are also listed in Tables 7.1 and 7.2. The ratio A_H/A_σ increases as T_g increases, and it also increases on ageing of the basalt composition glass.

We estimate a combined error of about 5 % in the $C_p - T$ and in the dH/dT measurements, in our reading of the published $C_p - T$ data and in determining the path integrals. While geometrical considerations indicate that T_f^H would differ slightly from T_f^σ , the difference is within the combined errors.

Table 7.1. The T_g s and T_f s of several glasses as determined from the $C_p dT$ integrals and from the $C_p \ln T$ integrals, the ratio of the two T_f s, the integrals used in determining T_f s and their ratio, A_H/A_σ .

Material	T_g^H (K)	T_g^σ (K)	T_f^H (K)	T_f^σ (K)	A_H (J/g)	A_σ (mJg ⁻¹ K ⁻¹)	T_f^σ / T_f^H	A_H/A_σ (K)
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	567	567	592.0	593.6	4.54	8.3	1.00	547
Mg ₆₅ Cu ₂₅ Tb ₁₀	411.1	411.1	417.8	416.9	0.77	1.5	1.00	513
Pd ₄₈ Ni ₃₂ P ₂₀	560.7	559.5	643.1	657.5	1341.9	2.66	1.02	504.5
(Pd _{0.86} Ni _{0.14}) _{83.5} Si _{16.5}	656.2	656.2	704.5	712.3	767.2	1.30	1.01	590.2
Basalt glass fiber (quenched) ⁽¹⁾	912.7 ^(a)	913.1	1090.8	1143.6	51.68	64	1.05	807.5
	916.5 ^(b)	916.8	1101.0	1173.9	51.68	64	1.06	807.5
	903.4 ^(c)	904.2	1079.0	1117.7	51.68	64	1.04	807.5
Basalt glass fiber (aged) ⁽²⁾	912.6 ^(a)	913	1053.6	1079.1	41.14	48.3	1.03	852
	921.1 ^(b)	921.3	1078.2	1140.1	41.14	48.3	1.06	852
	903.0 ^(c)	903.8	1047.0	1067.7	41.14	48.3	1.02	852
NBS-710 fiber (quenched) ⁽³⁾	843 ^(a)	843	1148	1351	71.38	99.9	1.18	714.5
	844 ^(b)	844	1160	1463	71.38	99.9	1.26	714.5
	842 ^(c)	842	1139	1303	71.38	99.9	1.14	714.5

⁽¹⁾ Values obtained when the assumed dC_p/dT for the ultraviscous liquid is taken as:

(a) zero, (b) $-4.33 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $7.46 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$.

⁽²⁾ Values obtained when the assumed dC_p/dT for the ultraviscous liquid is taken as:

(a) zero, (b) $-9.25 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $7.75 \times 10^{-4} \text{ Jg}^{-1} \text{ K}^{-2}$.

⁽³⁾ Values obtained when the assumed dC_p/dT for the ultraviscous liquid is taken as:

(a) zero, (b) $-8.32 \times 10^{-5} \text{ Jg}^{-1} \text{ K}^{-2}$, and (c) $9.95 \times 10^{-5} \text{ Jg}^{-1} \text{ K}^{-2}$.

Table 7.2. The T_g s and T_f s of several glasses as determined from the $C_p dT$ integrals and from the $C_p d \ln T$ integrals, the ratio of the two T_f s, the integrals used in determining T_f s and their ratio, A_H/A_σ .

Material	T_g^H (K)	T_g^σ (K)	T_f^H (K)	T_f^σ (K)	A_H (Jmol ⁻¹)	A_σ (Jmol ⁻¹ K ⁻¹)	T_f^σ / T_f^H	A_H/A_σ (K)
Basalt Glass	934.7	935.3	1154	1236	4038.41	5.08	1.07	794.9
Propylene glycol (spray-dried)	168.4	168.4	197.8	204.3	2020.19	13.13	1.03	153.9
TNM-simulation ($q_c = 6 \times 10^6$ K/min, $q_h = 20$ K/min)	408	408	463	465	49.64	0.1342	1.00	369.9
TNM-simulation ($q_c = 60$ K/min, $q_h = 20$ K/min)	408	408	416	417	3.04	0.0117	1.00	259.8

Finally, we obtained the plots of normalized C_p by simulation and using the Tool-Narayanaswamy-Moynihan formalism as described in Chapter 2. The simulation was performed to obtain the plots of normalized C_p against T . We used, $\ln A = -88.4$, $x = 0.4$, $\beta = 0.55$, $\Delta h^* = 318$ kJ/mol in all cases. For the slow cooling rate, we chose, $q_c = 60$ K/min and for heating $q_h = 20$ K/min. For fast cooling, $q_c = 6$ MK/min and the same q_h of 20 K/min. From the plots obtained, we determined T_g^H and T_g^σ , T_f^H and T_f^σ , and the values of A_H and A_σ , as described above. These values and the ratios T_f^σ / T_f^H and A_H/A_σ are also listed in Table 7.2. The simulated plots of normalized C_p are not shown.

7.2.2 Enthalpy and Entropy Integrals on Cooling and Heating Paths

To investigate whether or not the amount of entropy change on cooling a liquid to glass is the same as that on heating a glass to liquid, we integrate the respective cooling

plots for the metallic glasses given in Figs. 7.9 and 7.10, between two temperatures, one in the glassy state, T_{glass} , and other in the liquid state, T_{liq} , as follows,

$$\Delta H_{cool} = c \int_{T_{liq}}^{T_{glass}} \left(\frac{dH}{dT} \right)_q dT; \quad \Delta H_{heat} = c \int_{T_{glass}}^{T_{liq}} \left(\frac{dH}{dT} \right)_q dT \quad (7.5)$$

$$\Delta \sigma_{cool} \geq c \int_{T_{liq}}^{T_{glass}} \left(\frac{dH}{dT} \right)_q d \ln(T); \quad \Delta \sigma_{heat} \leq c \int_{T_{glass}}^{T_{liq}} \left(\frac{dH}{dT} \right)_q d \ln(T) \quad (7.6)$$

where c is a material-dependent calibration constant, i.e., $C_p = c(dH/dT)_q$, $\Delta H_{cool} = (H_{liquid} - H_{glass})$ on cooling, $\Delta H_{heat} = (H_{glass} - H_{liquid})$ on heating, $\Delta \sigma_{cool}$ is higher than the real entropy change on cooling and $\Delta \sigma_{heat}$ is lower than the real entropy change on heating.

The plots in Figs. 7.9 and 7.10 are terminated at T_{glass} and T_{liq} where the data obtained on the cooling path appear to merge with those obtained for the heating path. For $Mg_{65}Cu_{25}Tb_{10}$ glass and liquid, the data are shown in Fig. 7.9A and B, $T_{glass} = 338.5$ K and $T_{liq} = 442.4$ K and the integrals were done with respect to the baseline with the value at $(dH/dT)_q$ at T_{glass} . The values of ΔH_{cool} , ΔH_{heat} , $\Delta \sigma_{cool}$ and $\Delta \sigma_{heat}$ are listed in Table 7.3. Here the ratios $x_H = (\Delta H_{cool} - \Delta H_{heat}) / \Delta H_{cool}$ and $x_\sigma = (\Delta \sigma_{cool} - \Delta \sigma_{heat}) / \Delta \sigma_{cool}$ are also listed. The corresponding plots for the $Pd_{40}Ni_{10}Cu_{30}P_{20}$ glass and melt are shown in Figs. 10A and B, and the values of the parameters are listed in Table 7.3.

We also simulated the plots of normalized $C_p - T$ plots for heating and for cooling by using the Tool-Narayanaswamy-Moynihan equation for $q_c = q_h = 20$ K/min in one case and for $q_c = q_h = 1$ K/min in the second case and by using the same parameters as given in

Section 7.2.1. These plots were analyzed in the same manner as the plots of $(dH/dT)_q$ for the metallic glasses and the various parameters obtained are listed also in Table 7.3.

Table 7.3. The cooling and heating rates q , the temperature limits of integration T_{glass} and T_{liq} , the $\Delta H/c$ and $\Delta\sigma/c$ measured for cooling and for heating and the percentage differences, x_H between ΔH_{cool} and ΔH_{heat} and x_σ between $\Delta\sigma_{cool}$ and $\Delta\sigma_{heat}$.

Material	q (K/min)	T_{glass} (K)	T_{liq} (K)	$\Delta H_{cool}/c$ (Jmol ⁻¹)	$\Delta H_{heat}/c$ (Jmol ⁻¹)	x_H %	$\Delta\sigma_{cool}/c$ (Jmol ⁻¹)	$\Delta\sigma_{heat}/c$ (Jmol ⁻¹ K ⁻¹)	x_σ %
Mg ₆₅ Cu ₂₅ Tb ₁₀	20	338.5	442.4	2445	2419	1.5	8.39	8.25	1.7
Pd ₄₀ Ni ₁₀ Cu ₃₀ P ₂₀	20	512.7	606.9	806.8	793.5	1.6	1.39	1.36	2.0
TNM-simulation*	20	312	454	46.25	46.16	0.2	0.109	0.107	1.9
TNM-simulation*	1	305	438.5	43.14	43.06	0.2	0.105	0.103	1.9
B ₂ O ₃ *	N/A	405.2	556.1	3230	3027	6.3	6.31	5.82	7.8

* C_p integral values, i.e. $c = 1$.

7.3 Discussion

7.3.1 The Fictive Temperatures

It is generally understood that the rate at which a liquid is cooled to form a glass determines its enthalpy as well as its frozen-in entropy. The rate at which a glass is heated determines the extent of its enthalpy loss by structural relaxation that shows up as a decrease in C_p on initial heating. This decrease appears as a broad minimum before an endothermic overshoot indicating the enthalpy recovery before $C_{p,liq}$ is reached. This contrast the Reiss's view (2009) of the configurational entropy loss based on the Boltzmann equation in which the rate at which a liquid is cooled to form a glass only determines the enthalpy. The entropy of a glass is zero and remains so until the

equilibrium or liquid state is reached even when structural relaxation of a glass decreases the enthalpy. Since the measured C_p is time-dependent, Kivelson and Reiss (1999) and Reiss (2009) have argued that it cannot be used to obtain the entropy because $dS > (dq_{\text{irrev}}/dT)$. In thermodynamic studies in the glass-liquid transformation temperature range, one finds a spontaneous decrease in both C_p and enthalpy at any instant on both the cooling path and the heating path of a temperature cycle. But here we find that T_f^σ obtained is closely similar to T_f^H . Also, in all cases, T_g^H is equal to T_g^σ for all cases.

It is recognized that, (i) strictly speaking, there is a *path-irreversible* segment between the liquid and glass states, and (ii) liquid-like structural fluctuations do not occur in a (rigid) glass. Regarding (i), the above-given finding show that consequences of the path-irreversible segment are too small to make T_f^σ differ significantly from T_f^H . This would suggest that for such purposed, calorimetric measurements meet the classical thermodynamics criteria for path-reversibility. Regarding (ii), one cannot deny Reiss (2009) that S_{res} violates the causality principle when Boltzmann equation is used, but a resolution of this violation would not be found in the difference of C_p values on the cooling and heating path in the glass-liquid transformation temperature range.

From the normalized $C_p - T$ data obtained by simulations in a TNM model, we obtain T_f^σ slightly higher than T_f^H , and the difference is more when the cooling rate is high, but it is not substantial and probably reflects the fact that geometrical considerations alone would not yield the same values of T_f^σ and T_f^H for an ideal set of data.

7.3.2 Effect of Path Irreversibility on the Enthalpy and Entropy

We now discuss the magnitudes of ΔH_{cool} and ΔH_{heat} values given in Table 7.3. Conservation of energy requires that ΔH_{cool} be equal to ΔH_{heat} . This would be the case if T_{glass} was near 0 K or at a temperature such that structural relaxation effect were vanishingly small. Our experiments yield ΔH_{cool} about 1 % higher than ΔH_{heat} . This may be not be due to a possible enthalpy loss on structural relaxation during the time period between the end of the cooling at T_{glass} and beginning of the heating from T_{glass} . Briefly, if the loss were small the decrease in the slope of the $H - T$ plot would be extremely small and would not appear in the measured C_p (or in $dH/dT)_q$ in the usual study, and ΔH_{heat} obtained from Eq. (7.1) would be higher than ΔH_{cool} by an amount equal to this loss. But we find the opposite. The manner of resolving the cooling and heating scans also causes an error. To elaborate, cooling and heating curves are obtained in a continuous cycle in which the heat flow signal changes from positive to negative in a DSC experiment and the two curves are separated by vertically displacing one curve and inverting it. The 1 % higher value of ΔH_{cool} would contain this error. The $\Delta \sigma_{cool}$ determined from Eq. (7.6) is about 2 % higher than $\Delta \sigma_{heat}$. This is partly attributable to this error plus the cumulative errors in the $(dH/dT)_q$ measurements, in the uncertainty of determining T_{glass} at which the cooling and heating curves meet, and in the integration procedure which also cause ΔH_{cool} and ΔH_{heat} to differ.

The corresponding values obtained by analyzing the data for C_p simulated from the Tool-Narayanaswamy-Moynihan model are also listed in Table 7.3. For the cooling

and heating paths for $q = 20$ K/min, x_H differs by 0.2 %, and x_σ by 1.8 %, and for $q = 1$ K/min, x_H differs by 0.2 %, and x_σ by 1.9 %. It is between 1.7 % for x_σ found for the measured data for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ and 2.0 % for $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$.

$C_p d\ln T$ integral can not be used for determining the entropy change in the glass-liquid transformation range because of the Clausius inequality, $dS > (dq_{\text{irrev}}/T)$. Also, the (time-dependent) C_p measured on the heating path through the glass-liquid range differs from the C_p measured on the cooling path, and classical thermodynamics is not used for systems whose properties change with time. Nevertheless, the Clausius inequality helps to ascertain the lower and upper limits of the actual entropy from C_p data when measurements are made on both the cooling and heating paths. These are known as Clausius limits for the entropy. The Clausius limits give the upper and lower bound values of the entropy change, and the entropy at T_{liq} is the same. A higher change in $\Delta\sigma$ would correspond to the lower entropy at T_{glass} and a lower change in $\Delta\sigma$ to a higher entropy at T_{glass} . Thus $\Delta\sigma$ of a glass determined from the cooling path would be lower than the real entropy and that determined from the heating path would be higher. Bestul and Chang (1965) determined the entropy change from the $C_p d\ln T$ integrals over the temperature range of glass formation for B_2O_3 by using the C_p data from Thomas and Parks (1931) measured for both cooling and heating at different and unknown rates. When the sample is cooled, the measured entropy change is upper bound to the true entropy change, and when it is heated, the measured entropy change is the lower bound to the true entropy change, the two bracketing the true entropy change. Since C_p measured on the cooling path from T_{glass} to near 0 K would retrace the C_p measured on the heating

path for $q_c = q_h$, this means that the difference observed between $\Delta\sigma_{cool}$ and $\Delta\sigma_{heat}$ will persist in the value of S_{res} . The difference was 0.58 ± 0.2 J/(mol K) and they concluded (Bestul and Chang 1965) that the magnitude of this difference was at least an order of magnitude less than the lower and upper limits of S_{res} , and $10.0 \leq S_{res} \leq 10.6 \pm 4.2$ J/(mol K) for B_2O_3 . This demonstrated that S_{res} differs from 0 in the case of B_2O_3 glass. In terms of the percentage, this difference is 6 % of S_{res} . This means that true S_{res} cannot be more than 6 % of the value determined from the entropy change on the cooling path and can not be less than 6 % of the entropy change on the heating path. That is the irreversible (enthalpy) relaxation lead to no more than 6 % difference between the true S_{res} and the value determined from the $C_p d\ln T$ integrals in the glass-liquid range.

Goldstein (1976, 2008) also analyzed the errors in determining the entropy of a structurally relaxing glass from $C_p - T$ data obtained by using both the adiabatic calorimetry and DSC techniques. He did so by using several activation energies within the approximation of single-relaxation time and by using different q_c and q_h . For $q_c = q_h$ ($= 0.001$ K/s), in his Table III, the minimum error in the entropy difference divided by the change in C_p is 1.2 %, and maximum error is ~ 4.8 %. He concluded that the error was negligibly small when adiabatic calorimetry was used, but it was a few percent when DSC was used. The error increased when q_c was higher than q_h and decreased when q_c and q_h were low. The 2 % difference between $\Delta\sigma_{cool}$ and $\Delta\sigma_{heat}$ noted in Table 7.3 is consistent with this estimate. In a more recent and closely related study, Fotheringham et al (2009) have provided a comprehensive discussion of the subject by using data on two commercial optical glasses. They compared both the lower limit of S_{res} resulting from the

use of Clausius limits and the upper limit given by S_{conf} of an equilibrium liquid with the same T_f and found that the difference between S_{res} and the Clausius limit is very small and negligible, in agreement with the earlier analyses. There is little doubt that the $C_p d\ln T$ integral would not yield the entropy change. It only yields the upper bound value of the actual entropy change, ΔS , on the cooling path and lower bound value on the heating path (Goldstein 1976, 2008, Bestul and Chang 1965). The difference between the two extremes is usually orders of magnitude less than the lower bound value of the actual entropy. Unfortunately, this aspect has not been generally recognized and Gupta (2009) regarded it as a measure of ΔS . To avoid confusion with ΔS , we consistently use here the term $\Delta\sigma$ for estimates of the $C_p d\ln T$ integral in the liquid-glass transformation range.

We also determined the $C_p dT$ integral and $\Delta\sigma$ (the $C_p d\ln T$ integral) for B_2O_3 glass from the Thomas and Parks' $C_p - T$ data (Thomas and Parks 1931). As shown in Table 7.3, in the glass – liquid range, for $T_{glass} = 405.2$ K and $T_{liq} = 556.1$ K, we find $\Delta H_{cool} = 3230$ J/mol and $\Delta H_{heat} = 3027$ J/mol, a difference of 6.3 % and $\Delta\sigma_{cool} = 6.31$ J/(mol K) and $\Delta\sigma_{heat} = 5.82$ J/(mol K), a difference of 7.8 % . Here also ΔH_{cool} differs from ΔH_{heat} due to experimental and analytical errors and these contribute to some of the difference between $\Delta\sigma_{cool}$ and $\Delta\sigma_{heat}$.

Bestul and Chang (1965) estimated S_{res} of B_2O_3 , because they could obtain an approximate value of the enthalpy of melting of its crystals state, but values for S_{res} of $Mg_{65}Cu_{25}Tb_{10}$ and $Pd_{40}Ni_{10}Cu_{30}P_{20}$ glass can not be estimated here, and the constant c used in Eqs. (7.5) and (7.6) to convert $(dH/dT)_q$ to C_p is not available for determining the

upper and lower bound values of S_{res} . But one expects that S_{res} would be close to the entropies of mixing, which is 7.12 J/(mol K) for $Mg_{65}Cu_{25}Tb_{10}$ and 10.16 J/(mol K) for $Pd_{40}Ni_{10}Cu_{30}P_{20}$. The real S_{res} of the two glasses can differ by about 2 % from the values measured on the heating or on the cooling path. But this amount is not enough to suggest that S_{res} would be reduced to zero if the limits of the Clausius inequality relative to the real entropy value are taken into account. Therefore, we deduce that the effect of time-dependence and enthalpy release on the measured C_p (or $dH/dT)_q$ has little effect on $\Delta\sigma$ for $q_c = q_h$.

The data in Table 7.1 show that except for the NBS-710 (quenched) glass fibers the T_f^σ / T_f^H ratio is close to 1 within the combined errors of 5 %. Now, if use of $\Delta\sigma$ were incorrect, one would not find the ratio T_f^σ / T_f^H equal to 1 for any of the glasses. This shows that the upper and lower limits of the entropy determined from use of $\Delta\sigma$ on the cooling and heating paths may be too close to make T_f^σ differ from T_f^H of these glasses within the combined errors. As mentioned earlier here, Goldstein (1976) had estimated the error in the entropy change from the use of C_p data for an irreversible process of glass relaxation. For adiabatic calorimetry measurements, he found that the error was negligible relative to the estimates of S_{res} and the measured entropies of glass and liquid. The errors were significant when C_p data were obtained from DSC, and also the errors were least when q_c was the same as q_h . Our finding that T_f^σ is the same as T_f^H within the combined errors may appear to support his estimates. We also stress that such calculations do not indicate reversibility of the path, only that consequence of such

calculation in terms of the upper and lower limits of the actual entropy is not large enough to make a significant difference between T_f^H and T_f^σ .

As noted earlier here, after analyzing his $C_p - T$ data for quenched samples of NBS-710 glass fibers, plotted here in Fig. 7.6, Gupta (2009) determined the T_f^σ and T_f^H values. He found that for these fibers $T_f^\sigma \gg T_f^H$. For bulk glass of the same composition as the fibers the difference between T_f^σ and T_f^H was negligible (Gupta 2009). Since $\Delta\sigma$ (Gupta had used the term entropy) has been used for calculating T_f^σ , one would expect that, as for the quenched NBS-710 fibers, T_f^σ would be much higher than T_f^H for all glasses, and the method of production or thermal history would have no consequence for this difference. But the data in Table 7.1 do not indicate it. Since our finding of $T_f^\sigma \gg T_f^H$ for NBS-710 glass fiber agrees with Gupta's finding (Gupta 2009), and not for others, we inquire why there is such a large difference between its T_f^σ and T_f^H .

We first consider whether the large difference may be caused by an incorrect extrapolation of $C_{p,liq}$. For this purpose we first examine the $C_{p,liq}$ data extrapolation of quenched and aged basalt glass fibers taken from Yue (2004) (plotted here in Fig. 7.5) for which T_f^σ / T_f^H is 1.05 or less. Here $C_{p,liq}$ was measured only up to T of 993 K. For determining T_f^H and T_f^σ , $C_{p,liq}$ has to be extrapolated to a higher T by using either a straight line or a curved line. In the simplest case, it may be a straight-line either parallel to the axis, or inclined to the axis. An extrapolation with a negative slope of $C_{p,liq}$ against

T plot would increase the ratio T_f^σ / T_f^H and that with a positive slope would decrease it towards 1. This is shown by calculations labeled (b) and (c) in Table 7.1. When a reasonable extrapolation with a positive slope was used, the estimated T_f^σ / T_f^H ratio for the quenched and partially annealed basalt composition glass decreased to 1.04 and 1.02, respectively. When such an analysis was done for the quenched NBS-710 fiber as described in the notes at the bottom of Table 7.1, the estimated T_f^σ / T_f^H ratio decreased from 1.18 to 1.14.

We also investigated the effect of change in the extrapolated plot of $C_{p,glass}$ and found that when its positive slope is decreased and thus the (extrapolated) difference between $C_{p,liq}$ and $C_{p,glass}$ is increased, the ratio T_f^σ / T_f^H decreases toward 1. It became closer to 1 for the annealed basalt composition glass fibers, but no reasonable extrapolation of $C_{p,glass}$ against T could bring the ratio closer than 1.13 for the quenched NBS-710 glass fibers. We conclude that extrapolation of $C_{p,liq}$ and $C_{p,glass}$ to high temperatures lead to erroneous values of both T_f^σ and T_f^H . Only $C_{p,liq}$ data used as a guide for extrapolation to higher temperatures would yield a correct value of T_f^σ and T_f^H . Extrapolation of $C_{p,glass}$ to higher T also has a similar effect on T_f^σ and T_f^H . Therefore, we need to investigate if there are additional reasons for the high T_f^σ / T_f^H value for the NBS-710 glass fibers, as follows.

Silicate glass fibers are made by centrifugal-blowing, centrifugal-multiroll and die-blowing or by simply surface blowing processes. The 3 - 13 μm diameter fibers

formed are in a highly strained state, and thus have energy stored from their deformation during their production. Their high surface area to weight ratio makes them more susceptible to chemical attack and they occasionally trap air between them. When a cluster of these fibers is heated in DSC measurements, the stored energy is released as heat and the apparent C_p decreases, gaseous impurities adsorbed on the surface and those within the fiber are released. As fibers approach the state of ultraviscous melt on heating they coalesce and their surface energy rapidly decreases. None of these extraneous energy-losing processes are reversed on heating, or show a gain in the energy or enthalpy as an overshoot in C_p before the liquid state is reached. In summary, strained fibers lose more energy than they gain during heating to the original melt state. Since T_f is determined by matching the exothermic with endothermic areas, i.e., the enthalpy (or entropy) lost against the enthalpy (or entropy) gained, and the endothermic area contains no gain of the extraneous energy, neither T_f^H nor T_g^H are accurately measured by the area matching of such fibers. This is not the case for bulk glasses, annealed glasses, fibers that have been already heated to their melt state or for the (ductile) metallic glasses.

7.4 Conclusions

We conclude that:

1. Fictive temperature determined from the entropy change by using a large and broad, time-dependent irreversible segment of C_p in the thermodynamic path between a glass and liquid is the same as that determined from the enthalpy change. Thus S_{res} of glass

may not be an impression resulting from use of this irreversible segment. The two fictive temperatures differ, (i) when the $C_{p,liq}$ and $C_{p,glass}$ data are extrapolated to high temperatures without the help of data in the liquid state, and (ii) when the samples have a high strain energy and/or large surface area. Therefore, fictive temperature of such glasses is not reliably determined.

2. The change in $\Delta\sigma$ between liquid and glass on the cooling path is 2 % more than that on the heating path through the glass–liquid transformation range, which represents the Clausius limits for the change in the apparent entropy relative to the change in the real entropy. This appears to meet the classical thermodynamic requirement for reversibility as suggested by Goldstein (1976). The lower Clausius limit is not sufficient to decrease the residual entropy to zero. This also shows that S_{res} of glass is not an impression resulting from use of an irreversible segment on the cooling or heating paths.
3. The continuous decrease in the entropy from liquid to glass is much less than the decrease in the configurational entropy, which would be at least the entropy of mixing of the metal alloys. It seems that a resolution for the dichotomy between the statistical entropy and calorimetric entropy of glass would not be resolved by an appeal to the time-dependent $C_p - T$ path in the glass–liquid transformation temperature range.

CHAPTER 8

SUMMARY

After describing general aspects of the glassy state, its phenomenology and development of technology of bulk metallic glasses in Chapter 1, the purpose of research, methods of investigations, findings, and conclusions described in the preceding chapters are summarized as follows:

The formalism and mechanism for change in the properties of bulk metallic glasses: (i) $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, (ii) $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, (iii) $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, and (iv) $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$, as a result of structural relaxation during ageing was investigated by studying the enthalpy release with time at different temperatures by using differential scanning calorimetry in isothermal and non-isothermal modes. Two types of changes are found, (i) an irreversible change that appears as an endotherm when a sample stored for some time at ambient conditions is heated and a reversible change that occurs on annealing and physical ageing a bulk metallic glass. The change in properties with time during storage and during use of these glasses follows stretched exponential kinetics, with the characteristic parameter in the range 0.4 – 0.8, and the characteristic relaxation time follows an Arrhenius type temperature dependence with an energy of 300 to 420 kJ/mol for the various glasses. It is concluded that change in the properties that are analogous to change in the structure and thermodynamics, can be modeled by using a non-exponential non-linear structural relaxation, and information on such changes over

longer periods of time and at different temperatures can be obtained. It is shown that consideration of the entropy in the glass-ultraviscous melt range yield the same quantitative features as of the enthalpy, irrespective of the irreversibility associated with the time-dependence of the thermodynamic path between a glass and its melt, i.e. the effects of irreversibility on the entropy determination of such processes is negligible within experimental errors. These aspects are described in Chapter 2. One paper based upon part of this study has appeared in *Thermochimica Acta*, 503 - 504 (2010) 121 - 131 and two others on the related problem of distribution of relaxation times in the *Journal of Chemical Physics*, 129 (2008) 056101 and on the kinetic unfreezing of a binary alloy in the *Journal of Chemical Physics*, 133 (2010) 056101.

The effect of a complex thermal history as would be found in the use of devices made from bulk metallic glasses and its general use as a material was also studied for $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$ bulk metallic glass by using calorimetry, as described in Chapter 3. It is shown that this glass, in which there is only translational diffusion (of atoms) occurs, show the so-called memory effect, like polymers, silicates and molecular glasses. Its mechanism involves the broad distribution of times and partial recovery of thermodynamic properties of different parts of the relaxation time distribution under different thermal cycling conditions. It is explained in terms of sub-enthalpies of the regions in the structure of a glass that have their own relaxation time and spontaneously relax at different rates at the same temperatures. This is described in Chapter 3, and part of the study has been published in *Journal of Non-Crystalline Solids*, 353 (2007) 3796 - 3811.

In order to investigate how crystallization of such glasses may occur on heating and change its properties, crystallization kinetics studies of ultraviscous melts obtained by heating of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$, $\text{Mg}_{65}\text{Cu}_{25}\text{Tb}_{10}$, and $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ bulk metallic glasses were performed and calorimetry was used for the purpose as in the study described in Chapters 2 and 3. Both isothermal and non-isothermal crystallizations occur in two steps, which were investigated. Furthermore, the possibility of spinodal decompositions was investigated. Kinetics of the main crystallization feature follows the Kolmogorov-Johnson-Mehl-Avrami equation that is based on the Poisson distribution of nucleation sites, and the kinetic parameters are found to vary amongst different bulk metallic glasses. The activation energies determined from their rate constant data are much less than those observed for polymers and other glasses and this is attributed to lack of rotational diffusion of atoms in the metallic glasses. It is suggested that their stability against crystallization at lower temperature and in the glassy state may be modeled by using the parameters given. The study is described in Chapter 4, and a small part of it has been published in *Thermochimica Acta* 510 (2010) 144 - 153.

Electrical properties of bulk metallic glasses also change with time. To investigate its mechanism and to describe its formalism, electrical resistivity of $\text{Pd}_{40}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{20}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glasses was studied isothermally in real time at different temperatures and non-isothermally on heating. For this purpose an equipment was designed and interfaced with computer. On heating, the results showed (i) a slow and gradual decrease in resistivity on structural relaxation, (ii) a faster change on glass-liquid transition, and (iii) an abrupt decrease on crystallization, hence all three regions could be

distinguished. Decrease in the resistivity on structural relaxation occurs according to stretched exponential kinetics with a characteristic time and temperature dependent distribution parameter. It is found that decrease in resistivity on structural relaxation and change in the temperature coefficient of resistivity occur approximately according to the Ziman model that uses structure factor as a resistivity determining quantity. The study is described in Chapter 5. It is planned to publish this study as a brief paper.

Diffusion in metallic glasses differs from that in crystals. To investigate the atomic diffusion across a junction interface with Sn and Zn metals, junction couples of the $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$ bulk metallic glass with the two crystalline metals were made and the concentration of Sn and of Zn into the metal glass was studied by Energy Dispersive X-Ray Spectroscopy (EDX) after annealing the samples for different periods at several temperatures. A device for the purpose was constructed. Thus the occurrence of Kirkendall effect was demonstrated for bulk metal glasses, and it is suggested that the effect may be useful for diffusion bonding of metallic glasses with other metals. The study is described in Chapter 6, and it is intended to be published as a brief paper.

There is a long-standing problem regarding the residual entropy of glasses: According to the Boltzmann equation, a glass has no configurations available to its structure and therefore its configurational as well as residual entropy should be zero, a view that led to the recent conclusion that residual entropy of a glass is an artefact of using the heat capacity integral for entropy along a time-dependent, apparently irreversible path. In Chapter 7, an analysis of the fictive temperature and glass-liquid transition temperature of several glasses is described by using the specific heat-

temperature data taken from the literature and also from the calorimetric measurements of a quantity proportional to the specific heat studied here. These are compared against the data obtained from a non-exponential, non-linear structural relaxation model. The results show that errors in entropy determination from a time-dependent path in the glass-liquid temperature range is too small to affect the residual entropy determination within experimental errors, and the residual entropy of glass is finite. Two papers on the subject have been published in the *Journal of Physical Chemistry B* 144 (2010) 9578 - 9585 and *Philosophical Magazine* 90 (2010) 4377 - 4392.

In all, seven papers based on part this thesis have been published. Several papers on the remaining studies are planned for publication in the near future.

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APPENDIX

Error Analysis

A. DSC Errors

Temperature Scan : ± 0.2 K

Heat Flow Signal : ± 2 % (mW)

Onset Temperature : ± 0.2 K

B. Resistivity Measurement Errors

Temperature Scan : ± 3 K

Resistance : $\pm 10^{-6}$ ohm

C. EDX Errors

Element Concentration : ± 0.2 % (concentration in fraction)

Distance Measurement : ± 0.2 μm

D. Annealing experiments for diffusion couple

Temperature Reading : ± 3 K