Journal of Alloys and Compounds 509S (2011) S2–S7

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Diffusion and viscous flow in bulk glass forming alloys

A. Bartsch[a], V. Zöllmer[a], K. Rätzke[a], A. Meyer[b], F. Faupel[a,*]

[a] *Institut für Materialwissenschaft – Materialverbunde, Technische Fakultät, Christian-Albrechts Universität zu Kiel, Kaiserstr. 2, 24143 Kiel, Germany*
[b] *Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR), 51170 Köln, Germany*

ARTICLE INFO

Article history:
Received 19 September 2010
Received in revised form 1 November 2010
Accepted 17 November 2010
Available online 25 November 2010

Keywords:
Diffusion
Viscosity
Stokes–Einstein equation
Mode-coupling theory
Isotope effect
Radiotracer technique
Quasi-elastic neutron scattering

ABSTRACT

We review radiotracer diffusion and isotope measurements in bulk glass forming alloys from the glassy state to the equilibrium melt and compare diffusion and viscous flow. In the glassy as well as in the deeply supercooled state below the critical temperature T_c, where the mode coupling theory predicts a freezing-in of liquid-like motion, very small isotope effects indicate a highly collective hopping mechanism. Not only in the glassy state but also in the supercooled state below T_c the temperature dependence of diffusion is Arrhenius-like with an effective activation enthalpy. A clear decoupling takes place between the diffusivities of the individual components of the alloys and between time scales related to diffusive transport and viscous flow. While the component decoupling is small for the smaller components a vast decoupling of more than 4 orders of magnitude is observed in Pd–Cu–Ni–P alloys between the diffusivity of the large majority component Pd and of the smaller components at the glass transition temperature T_g. The diffusivities of all components merge close to the critical temperature T_c of mode coupling theory. Above T_c, the onset of liquid-like motion is directly evidenced by a gradual drop of the effective activation energy. This strongly supports the mode coupling scenario. The isotope effect measurements show atomic transport up to the equilibrium melt to be far away from the regime of uncorrelated binary collisions. For Pd, in contrast to the behavior of single component molecular glass formers, the Stokes–Einstein equation even holds in the entire temperature range below T_c over at least 14 orders of magnitude. Apparently, the majority component Pd forms a slow subsystem in which the other elements move fast. Rearrangement of the Pd atoms thus determines the viscous flow behavior. The decoupling of atomic mobility seems to arise from a complex interplay between chemical short order and atomic size effects that gets more pronounced on approaching the glass transition temperature. The ability of the bulk glass forming alloys to form a slow subsystem in the liquid state appears to be a key to the understanding of their excellent glass forming properties.

1. Introduction

Even though metallic glasses, also termed amorphous alloys, where first discovered 50 years ago they are currently among the most actively studied metallic materials with many novel, applicable properties [1–3]. Metallic glass forming alloys have also been the focus of research advancing our understanding of liquids and glasses in general [4,5].

The first metallic glasses, in order to prevent crystallization, were prepared by rapidly quenching (106 K/s) a melt of binary or ternary metal–metalloid or of early-late-transition metal alloys, resulting in very thin ($d \approx 50\,\mu$m) ribbons. Since then, continuous alloy developments [6,7] allow low cooling rates now exceeding 1 K/min and hence bulk samples with the smallest dimension of several cm can be prepared. Thus, deeply undercooled metallic melts are now accessible on experimental time scales, which make possible investigations around and above the caloric glass transition, where previous alloys immediately crystallized.

Since metallic glasses are metastable systems there exists a driving force to the crystalline equilibrium state. During the first heat treatment near the glass transition structural relaxation occurs [8–10]. Subsequently, the glass transition sets in, and finally the sample crystallizes. All these processes are mainly governed by diffusion. Diffusion and viscous flow are also crucial in melt processing as well as from the fundamental point of view, particularly with respect to the glass transition.

While for crystalline metals self-diffusion occurs via single jumps involving thermal vacancies [11], the situation for metallic glasses is much more complex. Early experiments were often interpreted in terms of a conventional, vacancy-like mechanism (for reviews see, e.g. [12,13]). Now, there is ample evidence form radiotracer experiments [14–16] and molecular dynamics simulations [17,18] that diffusion in the glassy state generally proceeds via highly collective thermally activated jumps involving many

---

[*] Corresponding author. Tel.: +49 431 880 6225; fax: +49 431 880 6229.
E-mail address: ff@tf.uni-kiel.de (F. Faupel).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.11.123

atoms [19]. Molecular dynamics simulations suggest a connection between the low-frequency excitations in glasses observed at low temperatures and collective long-range diffusion at elevated temperatures. Only for large atoms, vacancy-like defects seem to play a role [20] and may give rise to an opposite Kirkendall effect [21]. Vacancy-like defects may also enhance diffusion in as quenched metallic glasses prior to structural relaxation [9] although this effect is not seen in all systems [10]. Diffusion in the glassy state of metallic glass formers has recently been reviewed [19]. Here we will focus on diffusion and viscous flow above the caloric glass transition.

As mentioned above, for the so-called bulk glass forming alloys, the undercooled melt above the caloric glass transition temperature becomes accessible. This allows testing of recent theories of the glass transition and the dynamics of undercooled systems. Among these the most advanced theory describing the slowing down of liquid-like motion is the mode coupling theory (MCT) [22,23]. In this extension of the hydrodynamic theory of fluids a kinetic freezing of microscopic (liquid-like) viscous flow is predicted at a critical temperature T_c far above the caloric glass transition temperature T_g. Below this critical temperature only thermally activated hopping processes should be possible and are envisioned as highly collective medium assisted hopping in an augmented version of the mode coupling theory which includes the behavior below T_c [22,23].

Bulk glass forming alloys, for the first time in metallic systems, allow diffusion experiments to be carried out from the glassy state up to the equilibrium melt. In conventional metallic melts, due to their low viscosity, diffusion experiments are normally affected by convection [24].

In simple liquids and melts, where diffusion and viscous flow take place by uncorrelated binary collisions, the Stokes–Einstein equation

$$D(T) = \frac{kT}{6\pi\, r\eta(T)} \tag{1}$$

generally holds. Here, D and η are diffusivity and viscosity, respectively, k is the Boltzmann constant, T the absolute temperature and r is the radius of the diffusing species [12]. In the supercooled state of metallic glass forming alloys a break down of the Stokes–Einstein equation has already been reported by Geyer et al. [25]. Recent molecular dynamics simulations on a binary Lennard–Jones mixture have shown the breakdown of the Stokes–Einstein relation at a temperature between the melting temperature and the critical temperature T_c [26]. The breakdown of the Stokes–Einstein relation was also observed in single component glass formers [27]. Now, most explanations are centered around the concept of dynamical heterogeneity, i.e. the existence of spatially correlated regions of relatively high or low mobility that persist for finite lifetime in the supercooled liquid, and that grow in size as the temperature decreases [28,29].

In the present review we report on our recent results of radiotracer diffusion experiments in bulk glass forming Pd-alloys from the glassy state to the equilibrium melt and compare them with viscosity data from the literature [30–32]. For the first time, a complete set of data for all components is available over the whole relevant temperature range. Special attention is devoted to the change in atomic dynamics around T_c where the decoupling behavior is now accessible for the individual components. In addition, a comparison of the equilibrium melt with the dynamics of simple liquids will be made.

2. Experimental methods

The glasses were prepared as published in, e.g. [33]. The caloric glass transition temperatures were determined by means of differential scanning calorimetry (DSC) at a heating rate of 20 K/min to 577 K. All samples were checked by X-ray diffraction for crystallinity before and after thermal treatment. Diffusion experiments were performed with the well established radiotracer technique, as described in, e.g. [34,35]. Tracers were either commercially available (^{32}P, ^{57}Co, ^{60}Co) or produced by irradiation of a suitable non-radioactive isotope in the research reactor of the Hahn–Meitner Institute in Berlin (^{103}Pd). After cutting the samples (diameter 10 mm, thickness 1 mm) and polishing the samples the tracer elements were flash-evaporated onto the sputter-cleaned surfaces. The samples were annealed on a heated copper plate or in specially designed graphite crucibles for temperatures and times deduced from the TTT diagram [36,37].

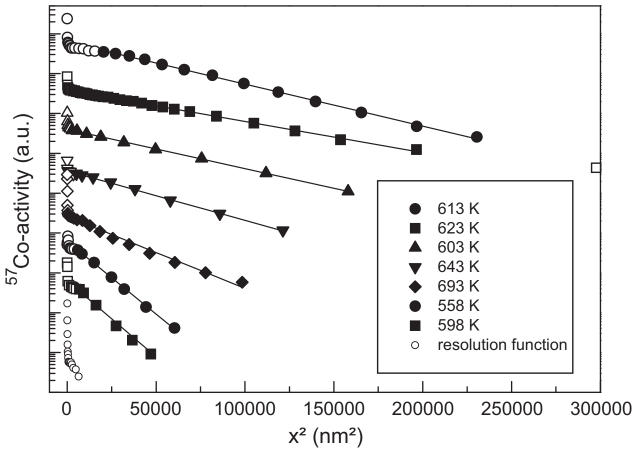

Fig. 1. ^{57}Co-penetration profiles in the glass forming alloy $Pd_{40}Cu_{30}Ni_{10}P_{20}$ at temperatures as given. Profiles were shifted on the *y*-axis for better comparison. Open symbols are affected by surface artifacts and were not taken into account in the evaluation. The resolution function of the microsectioning technique is shown, too (from [39]).

The serial sectioning has been performed either by the sputtering technique, employing an Ar-ion beam similar to the one described in [34] or for larger penetration depths, serial sectioning was performed by mechanical grinding using emery paper of different grain sizes. After serial sectioning the tracer concentration of the respective tracer was determined in each section by use of an intrinsic Ge-detector (^{57}Co, ^{60}Co, and ^{103}Pd). In the case of ^{32}P, a suitable method for the detection of the β-decay with the liquid scintillation counter taking into account the simultaneous usage of ^{57}Co had to be established.

The diffusivity was obtained from the thin film solution of Fickˇs second law.

$$c(x, t) = \frac{I_0}{\sqrt{\pi D t}} \cdot \exp\left(\frac{-x^2}{4Dt}\right) \tag{2}$$

Here, D denotes the diffusivity, t is the annealing time, x is the penetration depth and, I_0 is the initial layer thickness. Typical penetration profiles are shown in Figs. 1 and 2(a). Only closed symbols represent long-range diffusion and were taken into account for the determination of the diffusivities whereas data points shown as open symbols are affected by surface hold-up or sputtering artifacts, respectively. These effects are well-known from earlier work [39]. The resolution function of the sputtering technique is also shown in Figs. 1 and 2(a). To obtain this function, serial sectioning was performed on a non-annealed sample. The tail at large penetration depths originates from tracer atoms that were first distributed onto components other than the collector foil and then sputtered off again. The resolution function shows that effects on the evaluation of diffusivities and isotope effects are negligible within experimental errors.