Dynamic Arrest in Multicomponent Glass-Forming Alloys

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(Received 23 November 2009; revised manuscript received 22 April 2010; published 13 May 2010)

We report radiotracer diffusivities in a $Pd_{43}Cu_{27}Ni_{10}P_{20}$ melt, presenting for the first time a complete set of data for all components over the whole relevant temperature range. While a vast decoupling of more than 4 orders of magnitude is observed between the diffusivity of 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. For Pd, the Stokes-Einstein relation holds in the whole range investigated encompassing more than 14 orders of magnitude suggesting the formation of a slow subsystem as a key to glass formation in systems with dynamic asymmetry.

DOI: 10.1103/PhysRevLett.104.195901 PACS numbers: 66.30.−h, 66.20.−d

Recently, glass transition has again strongly attracted materials scientists as well as physicists [1–4]. Particularly, metallic glasses are currently among the most actively studied metallic materials. Apart from their many novel applicable properties [3,5,6] metallic glasses have also been in the focus of research advancing our understanding of liquids and of glasses in general [7–9]. The most interesting alloys are from the family of the bulk metallic glass formers [10–13]. Unlike conventional metallic glasses, bulk metallic glasses exhibit exceptional stability in the undercooled liquid state with respect to crystallization. They have thus enabled studies of atomic diffusion, viscous flow, and the glass transition previously not possible in metallic systems [3,7,9,14,15]. In this connection, Pd-Ni-Cu-P alloys were used as the model system [14,16–20].

The slowing down of the atomic dynamics when approaching the glass transition from the high temperature side is now generally described in terms of the mode coupling theory (MCT) [21]. According to the theory, upon supercooling a liquid, the trapping of atoms in cages made up by their nearest neighbors finally leads to a freezing in of liquidlike atomic motion at a critical temperature T_c well above the caloric glass transition temperature. Below T_c, diffusion is envisioned as a medium assisted highly collective hopping process [22]. MCT gives a consistent description of the dynamics that governs the mass transport in liquid Pd-Ni-Cu-P alloys. In an analysis of quasielastic neutron scattering results, MCT scaling laws extrapolate to a critical temperature T_c at about 20% below the liquidus temperature [16,17]. T_c is well above the caloric glass transition temperature obtained at 20 K/ min (see below).

Concerning diffusion, only some small components were studied in Pd-based alloys [14,18] and other metallic glass formers [7] and were found to show little decoupling in the supercooled liquid state. No diffusivities were available for the much more interesting large component which is required as a constituent of good metallic glass formers and is expected to play the crucial role in glass formation as well as in viscous flow.

Here, we report radiotracer diffusivities in a multicomponent $Pd_{43}Cu_{27}Ni_{10}P_{20}$ melt. In particular, using the radiotracer ^{103}Pd, we succeeded in measuring the diffusivity of the large component in the Pd alloy at hand together with the tracer diffusivities of other elements. The diffusion characteristics of all constituents are fully known for a metallic glass former in the supercooled liquid state. We thus obtained new insight into decoupling of diffusion of the different species, here referred to as component decoupling. Our results are also interesting within the general concept of dynamic asymmetry [23] and its relation to size disparity [24]. Taking viscosities from the literature, we also studied viscous decoupling between viscosity and the diffusivities. We point out that both phenomena have to be clearly discriminated. The viscous decoupling could be regarded as just a consequence of the effect of the broadening of the distribution of mobilities and the different ways transport and relaxation sample that distribution; i.e., viscous decoupling (because it involves two qualitatively different physical quantities) may be considered as reflecting something rather general about the statistics of dynamics. In contrast, the component decoupling must have an explicit structural origin and reveals information on the relation between composition and atomic dynamics. While we observe a vast decoupling of more than 4 orders of magnitude between the diffusivity of Pd and of the smaller components at the glass transition temperature T_g, the diffusivities of all components merge on a single temperature dependence close to the critical temperature T_c of mode coupling theory [25]. For Pd, in contrast to the behavior of single-component molecular glass formers [26,27], the Stokes-Einstein relation holds in the whole range investigated encompassing more than 14 orders of magnitude suggesting the formation of a slow subsystem as a key to glass formation in systems with dynamic asymmetry.

The $Pd_{43}Cu_{27}Ni_{10}P_{20}$ glass-forming alloy was prepared and characterized as reported previously [17]. The caloric glass transition temperature T_g of 582 K (at 20 K/min) and the quasieutectic melting temperature T_m of 802 K were determined by means of differential scanning calorimetry. Microscopic dynamics in the equilibrium liquid were studied by inelastic neutron scattering and were shown to be in accordance with the predictions of the mode coupling theory. The temperature dependence of the structural relaxation times as well as the temperature dependence of amplitude and time scale of a localized cage motion (fast beta relaxation) extrapolates consistently to a T_c at 710 K [17]. For the diffusion measurements, we employed the radiotracer technique in conjunction with serial sectioning and used an elaborate encapsulation technique in a graphite container. Details are described in [28]. The following isotopes were used: ^{103}Pd, ^{32}P, ^{51}Cr, and ^{57}Co. Co is well known to probe the self-diffusion behavior of Ni[7] [28]. ^{103}Pd as well as ^{51}Cr were obtained from neutron irradiation of enriched ^{102}Pd with an admixture of ^{50}Cr. Serial sectioning was performed by ion-beam sputtering or mechanical grinding, depending on the penetration depth and annealing temperature. The diffusion profiles will be published elsewhere. The covalent radii of 131, 126, and 106 pm were taken for Pd, Co, and, P, respectively, to calculate viscosities from the tracer diffusivities by means of Eq. (1).

Figure 1 summarizes our data on ^{103}Pd tracer diffusion together with radiotracer diffusivities of ^{32}P, ^{57}Co, ^{51}Cr, and ^{62}Ni. The latter [29] and part of the ^{32}P data [18] were taken from the literature. Figure 1 also depicts the results from quasielastic neutron scattering, mentioned above, which essentially represent diffusivities of Cu and Ni. One notes a similar diffusion behavior of all components in the equilibrium melt and down to the range near T_c as expected for liquidlike diffusion. As for the fast elements, very little decoupling is also seen below T_c. In contrast, Pd shows a very strong decoupling, which reaches several orders of magnitude between the slow and the faster components near T_g, and sets in close to T_c. Significant decoupling of the component diffusivities has not been demonstrated before in such multicomponent systems nor was it shown to start close to T_c which was determined independently from quasielastic neutron scattering. Decoupling is a signature of solidlike hopping over barriers, which—unlike in crystals—is envisioned as a highly collective process [15]. The barriers are expected to freeze in at T_c and to decay quickly somewhat above T_c, which is as much as 128 K above the caloric glass transitions temperature T_g (at 20 K/min) in the present metallic glass former.

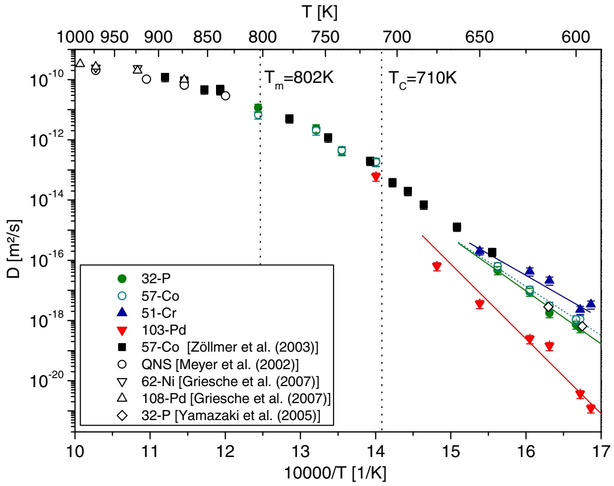

FIG. 1 (color online). Arrhenius plot for diffusion in liquid $Pd_{43}Cu_{27}Ni_{10}P_{20}$ alloys. Shown are diffusivities of the radiotracers ^{103}Pd, ^{32}P, ^{57}Co, and ^{51}Cr. Dashed lines display quasieutectic melting temperature T_m and critical temperature T_c of the mode coupling theory, determined from quasielastic neutron scattering. T_c is well above the caloric glass transition temperature T_g of 582 K (at 20 K/min). ^{32}P- (green solid circles) and ^{57}Co-data (blue open circles) for $T < 650$ K are from Ref. [18]. ^{57}Co data, shown as solid squares, are from [29]. The QNS data represent Ni and Cu diffusion.

Figure 2 shows viscosity data for the present metallic glass former, taken from the literature [19,20], together with our new diffusion data from Fig. 1, converted according to the Stokes-Einstein (SE) relation:

$$D = \frac{k_B T}{6\pi\eta r}. \tag{1}$$

In Eq. (1), D is the diffusion coefficient, η is the viscosity, k_B the Boltzmann constant, and r the particle radius. The SE relation is well obeyed in normal liquids not too close to

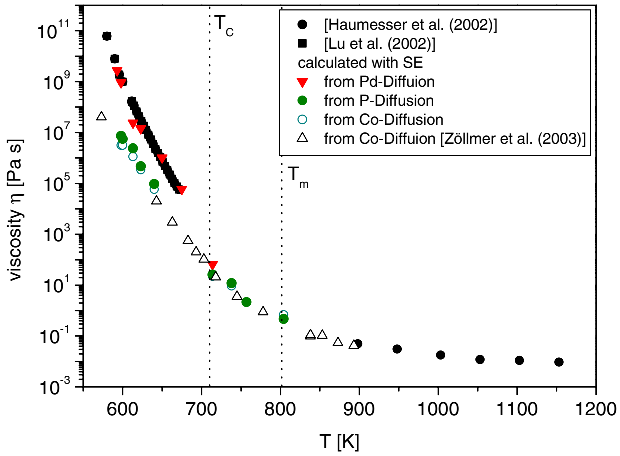

FIG. 2 (color online). Comparison of diffusion and viscosity. For the elements Pd, Co, and P, "diffusion-viscosities" were calculated via the Stokes-Einstein relation from the tracer diffusivities displayed in Fig. 1 and plotted together with measured viscosities from the literature (T_m, and T_c as in Fig. 1).

the glass transition temperature. In Fig. 2, one sees that the SE equation holds in the equilibrium melt and down to near T_c where the Stokes-Einstein relation as a hole starts to break down. The disparity reaches 4 orders of magnitude in the supercooled liquid state near the caloric glass transition in accord with the decoupling observed in Fig. 1 for the diffusivities.

This breakdown of the SE relation upon supercooling a liquid or melt is well known now [9,30] and is interpreted by many as a direct piece of evidence for dynamical heterogeneities in glassy liquids [31,32]. In these terms, the decoupling comes about because diffusion is dominated by the fastest particles whereas structural relaxation and viscous flow are dominated by the slowest regions.

A remarkable observation, however, is that despite this strong decoupling, the SE equation holds very well over at least 14 orders of magnitude for the slowest component palladium which is also the majority component and has the largest atomic size. This is even more remarkable in view of the breakdown of the SE equation in single-component systems and the above mentioned connection between the breakdown of the SE relation and dynamic heterogeneities [32]. Apparently, Pd forms a slow subsystem in the supercooled melt inside which the smaller elements carry out fast diffusion while viscous flow requires rearrangement of the Pd subsystem. This behavior resembles the situation in network glass formers [33] or gel glasses [34]. However, formation of a rigid covalent network is not expected for metallic glass formers. Obviously, a complex interplay between atomic size effects and chemical short range order leads to a decoupling of atomic mobilities that gets more pronounced on approaching the glass transition.

Recent molecular dynamics simulations in hard sphere liquids with size disparity [24,35,36] indeed suggest that subsystems of low mobility can form in materials without directed bonds. Apparently, not even chemical short range order is required, and only size effects are sufficient. In these terms bulk glass-forming alloys are a subclass of the aforementioned systems with dynamic asymmetry [23]. The asymmetry arises from size disparity and chemical short range order, where the latter certainly plays a crucial role in bulk glass-forming alloys [9]. This also explains the contrasting behavior to the single-component molecular glass formers referred to above [26,27]. Their glass-forming ability is neither due to size disparity nor to chemical short range order but results from a complex and highly asymmetric structure.

In summary, using the radiotracer technique, we measured all individual diffusivities, including the large Pd component, in a well-characterized multicomponent glass-forming $Pd_{43}Cu_{27}Ni_{10}P_{20}$ melt upon supercooling. The fast elements show a very strong decoupling from Pd diffusion, which reaches 4 orders of magnitude near T_g, and sets in close to the critical temperature of T_c of the mode coupling theory which was determined independently from quasielastic neutron scattering and is well above the caloric glass transition temperature T_g (determined at 20 K/ min). Despite this strong component decoupling, the Stokes-Einstein relation turned out to hold very well over at least 14 orders of magnitude for the slow Pd component suggesting the formation of a slow subsystem that has to rearrange for structural relaxation and viscous flow. The building up of a slow subsystem, which does not require directed bonding, appears to be the crucial factor in glass formation in systems with dynamic asymmetry.

The authors thank Thomas Voigtmann (DLR Köln), Peter Harrowell (University of Sydney), and Takeshi Egami (University of Tennessee) for fruitful discussions. Financial support by the German Science Foundation (DFG) under Projects No. Ra 796/3, No. Ra 796/4, and No. Me 1958/2 is gratefully acknowledged. We would also like to thank Gregor Bukalis from HMI Berlin for irradiation of the Pd tracers.

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