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Chemical diffusion in bulk glass-forming $Pd_{40}Cu_{30}Ni_{10}P_{20}$ melts

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Abstract

Interdiffusion and self-diffusion of bulk metallic glass-forming Pd–Cu–Ni–P alloys have been investigated above the liquidus temperature at 993 K by the long-capillary method. Good agreement between the calculated partial mixing enthalpies and observed uphill-diffusion was found. The flow direction of uphill-diffusing elements is towards regions with the highest negative heat of mixing.

Keywords: Bulk amorphous materials; Metallic glasses; Diffusion in liquids; Thermodynamics; Uphill-diffusion

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1. Introduction

During the past few years multicomponent Zr- and Pd-based alloys have been found, which show large glass forming abilities (GFA) during cooling below their melting temperatures [1,2]. For some Pd–Cu–Ni–P alloys critical cooling rates as low as 0.1 K/s are sufficient to avoid crystallization and to produce bulk metallic glass (BMG) castings up to some cm in diameter. The viscosity of the equilibrium melt of these alloys at melting temperature is at least one order of magnitude higher [3,4] than the viscosity of ordinary multicomponent metallic melts, such as liquid steel. This seems to be an important prerequisite of glass forming. Furthermore, $Pd_{40}Cu_{30}Ni_{10}P_{20}$ combines a deep eutectic with a liquidus temperature T_{liq} at only 843 K with a high glass transition temperature $T_g \approx 583$ K (both measured by differential scanning calorimetry (DSC) with 1 K/s heating rate), which altogether characterizes this alloy as an outstanding example of a system with extraordinary high GFA. The above mentioned findings for systems with good GFA can be described by empirical rules that are followed by all BMGs [5]. Indeed, in the case of $Pd_{40}Cu_{30}Ni_{10}P_{20}$, these rules are not fulfilled stringently [6] because not all element pairs of the alloys have large negative values of the mixing enthalpy ΔH^{mix} [7] as mostly observed for other BMGs.

$Pd_{40}Cu_{30}Ni_{10}P_{20}$ has been subject to several investigations of its diffusion behavior [8]. The measured temperature dependence of Ni-self-diffusion in Pd-based equilibrium melts was reported to comply with the mode-coupling theory of the liquid-to-glass transition [9], whereas at lower temperatures, below a critical temperature, an Arrhenius-law of the temperature dependence of diffusion was found [10]. Recently, we have investigated interdiffusion in liquid Pd-based alloys with the help of long-capillary experiments [11] in order to study the influence of thermodynamic forces on chemical diffusion. Although mostly attractive interactions between the elements were reported from calculations of the mixing enthalpy of the partial ternary systems [7], uphill-diffusion was observed, indicating a strong influence of thermodynamic forces due to chemical potential gradients.

In this work we report on systematic interdiffusion and self-diffusion measurements in $Pd_{40}Cu_{30}Ni_{10}P_{20}$ melts. The experiments were performed in order to investigate the influence of thermodynamic forces on diffusion in the equilibrium melt in more detail.

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2. Diffusion and thermodynamic

For binary solid solutions $A+B$ Darken showed [12] that

$$D_{AB} = N_A D_B + N_B D_A \tag{1}$$

and that

$$\begin{aligned} D_A &= M_A kT(1+\partial \ln \gamma_A / \partial \ln N_A) \\ D_B &= M_B kT(1+\partial \ln \gamma_B / \partial \ln N_B) \end{aligned} \tag{2}$$

with the interdiffusion coefficient D_{AB}, the intrinsic diffusion coefficients D_A and D_B, the mole fractions N_A and N_B, the mobilities M_A and M_B, the Boltzmann constant k, the absolute temperature T and the activity coefficients γ_A and γ_B. It should be noted that in Eq. (2) the term $1+\partial \ln \gamma / \partial \ln N$ is the same whether written for component A or B because of the Gibbs–Duhem relation. This term is basically the second derivative of the Gibbs free enthalpy $\partial^2 G/(\partial N_A \partial N_B)$ also named the thermodynamic factor Φ. In the case of a lack of proper values for the Gibbs free enthalpy, Φ can be replaced in a first approximation by regular solution parameters $\omega_{AB} \approx \Delta H^{\mathrm{mix}}/\ (N_A N_B)$.

When dealing with ideal or sufficiently dilute alloys, Φ is unity and in the case of self-diffusion we get

$$D_A^* = M_A kT \text{ and } D_B^* = M_B kT \tag{3}$$

with the self-diffusion coefficients D_A^* and D_B^* in the alloy. It is evident that the self-diffusion coefficients have the same compositional dependence as the respective mobilities. Then Eq. (1) can be rewritten as

$$D_{AB} = (N_A D_B^* + N_B D_A^*)\Phi \tag{4}$$

where Φ represents a force generated by gradients of the chemical potentials in the alloy. The above considerations are always restricted to single-phase systems, in which possible volume changes of mixing, lateral dimension changes and free volume generation (e.g. vacancies in the case of a lattice) can be neglected. Indeed, the existence of a rather strict local equilibrium for all chemical species is assumed. The chosen concentration intervals (see Table 1) for the interdiffusion couples are therefore just large enough to allow a sufficient resolution of the concentration measurement method. Thus, the diffusion coefficients are also assumed to be concentration independent. For the extension of the Darken analysis and equation to n-component systems, see the book by Kirkaldy and Young [13].

3. Experimental procedures and results

The long-capillary technique has been used to measure interdiffusion and self-diffusion in the liquid quaternary system. The sample production, the diffusion couple preparation and the experimental set-up are described elsewhere [4].

3.1. Interdiffusion

In order to define the lowest possible diffusion temperature in the molten state, solidus and liquidus temperature T_{sol} and T_{liq}, respectively, of the used alloys were determined by DSC (Perkin–Elmer Pyris 1) with heating rates of about 1 K/s (similar to those in the diffusion experiments). T_{sol} and T_{liq} are given in Table 1. Hereupon, the interdiffusion was measured at 993 K, which is slightly above the highest measured liquidus temperature.

Six independent chemical diffusion experiments were performed with the help of one-dimensional diffusion couples of the average composition $Pd_{40}Cu_{30}Ni_{10}P_{20}$. A diffusion couple consists of two thin rods of 1.5 mm diameter and 15 mm length each, oriented one above the other, joined at their abutting face and having an initial concentration difference of 10% of the respective elements.

Because of the lack of precise density data for the alloys at diffusion temperature and in order to estimate the influence of buoyancy-driven convection, two experiments per diffusion couple were always performed with respective inverse stacking. This allows the determination empirically of the mechanically stable configuration for each diffusion couple, where the specific lighter liquid is placed on top of the specific heavier liquid, inside the vertical diffusion capillary. This procedure minimizes buoyancy-driven convection [14,15] due to solutal stabilization of the liquid column during the experiment.

The chemical concentration profiles of all elements (Fig. 1) were measured by means of energy-dispersive X-ray spectrometry EDS (JEOL SEM 6400 with Link detector). For this purpose the diffusion samples were embedded into a resin and ground to half of their diameter. Each

Table 1

Solidus and liquidus temperatures of the investigated Pd-based alloys. Columns 1–6 contain the alloys of the six diffusion couples. The last column gives the values for the concentration of the self-diffusion samples

	$Pd_{40}Cu_{30}Ni_{15}P_{15}$	$Pd_{40}Cu_{30}Ni_{5}P_{25}$	$Pd_{40}Cu_{35}Ni_{10}P_{15}$	$Pd_{40}Cu_{25}Ni_{10}P_{25}$	$Pd_{45}Cu_{25}Ni_{10}P_{20}$	$Pd_{35}Cu_{35}Ni_{10}P_{20}$	$Pd_{45}Cu_{30}Ni_{5}P_{20}$	$Pd_{35}Cu_{30}Ni_{15}P_{20}$	$Pd_{45}Cu_{30}Ni_{10}P_{15}$	$Pd_{35}Cu_{30}Ni_{10}P_{25}$	$Pd_{40}Cu_{35}Ni_{5}P_{20}$	$Pd_{40}Cu_{25}Ni_{15}P_{20}$	$Pd_{40}Cu_{30}Ni_{10}P_{20}$
T_{sol} [K]	859	837	808	847	808	778	808	782	808	731	807	808	803
T_{liq} [K]	985	898	936	898	879	681	858	945	968	951	861	928	843