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Solubility of helium in melts of the metallic glass system Pd–Ni–P and in related systems

JOACHIM DIETRICHS*, GÜNTHER H. FRISCHAT
Arbeitsgruppe Glas, Institut für Nichtmetallische Werkstoffe, Technische Universität Clausthal, FRG

Glass melts of the metallic alloy system $Pd_{10-70}Ni_{10-70}P_{14-26}$ were saturated with helium gas during the melt-spinning process. Some melts with platinum substituted for palladium; manganese, iron or cobalt for nickel; and boron for phosphorus could also be saturated. The helium could be extracted from the glasses and the amount of gas was quantitatively measured with a mass spectrometer. The helium solubilities, obtained between 750 and 1250° C, varied between about 2 and 45 (μl He per mol glass)(T/273). These solubilities turned out to be strongly composition-dependent. This fact is discussed in terms of different short-range order structure units which are directly related to the free volume available for the gas solution process.

1. Introduction

Metallic glasses are of increasing interest both from a scientific and a technological point of view. Many glass-forming systems have been determined and different interesting and promising properties have been reported. There have also been many attempts to elucidate the structure of metallic glasses by diffraction methods, and different structure models have been set up. However, precise knowledge in this field is still restricted [1, 2].

An indirect method to obtain structural information on glasses and glass melts can be seen in the possibility to dissolve gases in them. If one takes an inert gas (e.g. helium), this is incorporated into the atomic interstices of the structure in small amounts. Since the interaction between glass and gas is weak, the gas solution does not change the structure and properties of the glass. The gas solubility (saturation concentration) depends on the number and size of structural interstices (free volume) and the size of the gas atoms or molecules. As has been shown for oxide [3, 4] and for chalcogenide [5] glasses and glass melts, the amount of gases which may be dissolved is sensitively dependent on structural changes, e.g. changes in composition, thermal history, microstructure, etc. No such investigation has been done so far for metallic alloy glass systems. Some results are available for hydrogen solution; however, this gas is dissolved in a different way and is, therefore, not comparable with helium [6].

2. Experimental procedure

2.1. Glasses

The system Pd–Ni–P was chosen because of its broad glass-forming region both with respect to metal and metalloid contents [7, 8]. Table I details the compositions of the glasses investigated and also some property data. For some compositions platinum was substituted for palladium; manganese, iron and cobalt for nickel; and boron for phosphorus. The master alloys were prepared in rotating sealed silica glass ampoules from the components palladium (purity 99.9%), platinum (99.9%), nickel (99.8%), manganese (99.8%), iron (99.8%), cobalt (99.5%), black phosphorus (99.5%) and boron (99.99%). Before use the black phosphorus had to be purified and dried. The mixtures were heated for 12 h at 750° C and for 6 h at 900° C. The ampoules were then quenched at 15 K sec^{-1} in order to obtain a fine-grained material. The metallic glasses were prepared in a 1 bar (100 kPa) helium atmosphere by a melt-spinning method (Kristallobor SFB 126, Göttingen-Clausthal). For this process 2 g of the pre-alloy was placed in a silica glass crucible having an orifice 0.4 to 0.5 mm in diameter at the bottom. After inductive heating was completed (the temperature of the melt was varied between 950 and 1250° C) the melt was ejected by helium gas pressure on a rotating copper wheel (6000 r.p.m.) and quenched as a foil, typically 1 to 1.5 mm wide and 20 μm thick. Further details of the preparation and properties are given elsewhere [9–11].

2.2. Gas saturation

In a first attempt it was tried to saturate the solid metallic glasses by annealing them below T_g in a helium atmosphere. However, this method failed because after 14 days of annealing at 279° C no helium was detectable in the glasses. From this a diffusion coefficient for helium of $< 7.6 \times 10^{-16}\,cm^2\,sec^{-1}$ can be estimated.

The saturation of the metallic glass melt had to be accomplished during the melt-spinning process in the time between extrusion from the orifice in the SiO_2 glass crucible and the final solidification on the copper

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*Present address: Nederlandse Philipsbedrijven BV, TY-1, NL-5600 MD Eindhoven, The Netherlands.

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TABLE I Compositions and properties of metallic glasses prepared [10]

Melt No.	Composition (mol %)	ϱ (g cm^{-3})	T_g (°C)
1	$Pd_{43}Ni_{43}P_{14}$	9.40	327
2	$Pd_{41.5}Ni_{41.5}P_{17}$	9.21	327
3	$Pd_{40}Ni_{40}P_{20}$	8.90	329
4	$Pd_{38.5}Ni_{38.5}P_{23}$	–	353
5	$Pd_{37}Ni_{37}P_{26}$	8.63	392
6	$Pd_{10}Ni_{70}P_{20}$	8.48	325
7	$Pd_{25}Ni_{55}P_{20}$	8.73	335
8	$Pd_{55}Ni_{25}P_{20}$	9.46	330
9	$Pd_{70}Ni_{10}P_{20}$	10.0	346
10	$Pd_{40}Mn_{40}P_{20}$	7.95	340
11	$Pd_{40}Fe_{40}P_{20}$	8.80	349
12	$Pd_{40}Co_{40}P_{20}$	9.40	404
13	$Pt_{40}Ni_{40}P_{20}$	13.6	266
14	$Pd_{40}Ni_{40}B_{20}$	9.79	375

TABLE II Helium solubilities, S, in (μl He per mol glass) (T/273) for the metallic glass melts investigated

Melt No.	Temperature (°C)			
	750	950	1100	1250
1		5.2	12.0	18.8
2		5.0	8.7	15.0
3	1.95	4.0	7.6	16.6
4		3.4	7.2	11.1
5		2.0	4.8	9.6
6		3.1	8.5	12.7
7		4.3	9.9	19.4
8		6.2	15.4	22.8
9		9.8	18.2	33.7
10			12.2	
11			16.3	
12			30.5	
13			34.8	
14			45.4	

wheel. Because of the short period of time this seems to be impossible. However, as was shown elsewhere [11], eddy diffusion instead of atomic diffusion leads to a degree of saturation > 99% of the melt.

2.3. Gas analysis

The helium content of the glass samples was removed by a hot extraction method and analysed quantitatively in a quadrupole mass spectrometer [9, 11]. For the analysis about 1 to 1.5 g of the metallic glass, saturated with helium, was placed in a platinum extraction vessel. This was then evacuated to 5×10^{-6} mbar (0.5 mPa) and heated to 950° C. The helium was extracted from the melt and passed through the mass spectrometer. Before and after each measurement a calibration was done. The quantities of helium analysed in this way were as low as 20 nl helium per gram of glass.

3. Results

3.1. Solubility data

Solubility coefficients may be defined in different ways [3, 4]. The Bunsen solubility coefficient is defined as

$$S_{Bu} = \frac{\text{cm}^3 \text{ (s.t.p.) gas}}{\text{cm}^3 \text{ solvent at } p,\, T} \qquad (1)$$

With increasing temperature the number of gas atoms or molecules decreases. This is taken into account by the Ostwald solubility coefficient

$$S_{Os} = S_{Bu}\frac{T}{273} \qquad (2)$$

In this work a solubility coefficient S, which gives the volume of gas atoms or molecules per mole of the glass is defined, with the unit (litres of gas per mol glass) (T/273). This coefficient is convenient for structural discussion.

Table II contains all the solubilities obtained for the melt compositions investigated as a function of temperature between 750 and 1250° C. The individual errors of the solubility values are about ±20%.

The temperature dependence of this solubility coefficient is given by

$$S = A \exp(-\Delta H/RT) \qquad (3)$$

where A is the pre-exponential constant, ΔH is the enthalpy of solution, R is the gas constant and T is the absolute temperature. Figs 1 and 2 show $\log S = f(1/T)$ for the composition lines $(Pd_xNi_{1-x})_{80}P_{20}$ and $(Pd_{50}Ni_{50})_{1-y}P_y$. Table III gathers together the data for A and ΔH according to Equation 3, the entropy of solution Δs and the Gibbs free energy ΔG at T_g. The solubility at T_g, S_{T_g}, can be estimated to be of the order of 10 (nl He per mol glass) (T/273). This value is directly related to the free volume of the glasses and represents structural information. The enthalpy of solution was obtained from the slopes of the plots of $\log S = f(1/T)$ and the entropy of solution from the slopes of the plots of $\log S = f(\log T)$ [12].

3.2. Dependence on composition

Figs 3 and 4 show S as functions of palladium concentration in the system $(Pd_xNi_{1-x})_{80}P_{20}$ and of phosphorus concentration in the system

TABLE III Characteristic data for helium solubilities in the metallic glass melts

Melt No.	$A \times 10^6 \left(\frac{\text{nl He} \times T}{\text{mol glass} \times 273}\right)$	ΔH (kJ mol^{-1})	Δs (J mol^{-1} K^{-1})	$(\Delta G)_{T_g}$ (kJ mol^{-1})
1	3.81	66.8	48.9	37.2
2	1.30	56.7	41.5	31.8
3	0.93	53.4	43.8	27.0
4	1.28	59.9	43.5	32.7
5	5.06	79.5	58.1	40.9
6	4.56	73.5	53.4	41.6
7	8.59	77.2	56.3	43.0
8	5.53	68.6	49.8	38.6
9	5.06	63.8	46.7	43.9

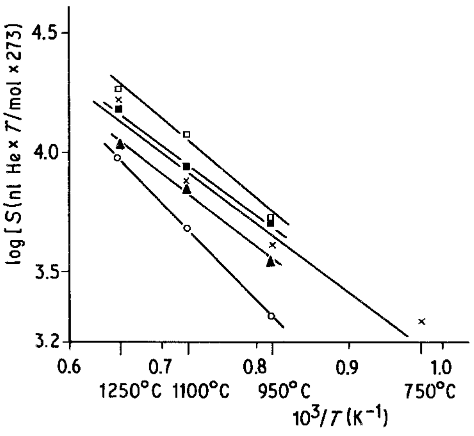

Figure 1 Temperature dependence of the helium solubility coefficient in glass melts of the system $(Pd_{50}Ni_{50})_{1-y}P_y$. (□) Melt 1, (■) Melt 2, (x) Melt 3, (▲) Melt 4, (○) Melt 5.

$(Pd_{50}Ni_{50})_{1-y}P_y$ at constant temperatures. Fig. 5 shows a comparison of the solubility data at 1100° C for the compositions Pd_{40}(Mn, Fe, Co, Ni)$_{40}P_{20}$, $Pt_{40}Ni_{40}P_{20}$ and $Pd_{40}Ni_{40}B_{20}$. In all cases an obvious dependence on concentration can be found. Moreover, it is interesting to compare the helium solubilities in the metallic alloy glass melts with those in Na_2O–CaO–SiO_2 [13] and Se–Ge–As [5] glass melts, respectively. As can be seen from Fig. 6 the *S* data for the metallic glass melts are by far the lowest ones.

4. Discussion

Although the solubilities were obtained for the liquid state it is believed that these data also present a basis for a structural discussion related to the supercooled liquid and the glassy state. Radial distribution functions display no essential differences between the liquid and the glassy states.

Glasses or glass melts may dissolve gas particles only if they contain structural voids or interstices large enough to be able to take up these particles. The total free volume of a glass or melt, however, generally has two parts of free volume, the distributed free volume with small interstices and the free volume with interstices of the size of the metal atoms. If these interstices are larger than the respective gas particles, a part of them may be activated for gas solution under given conditions.

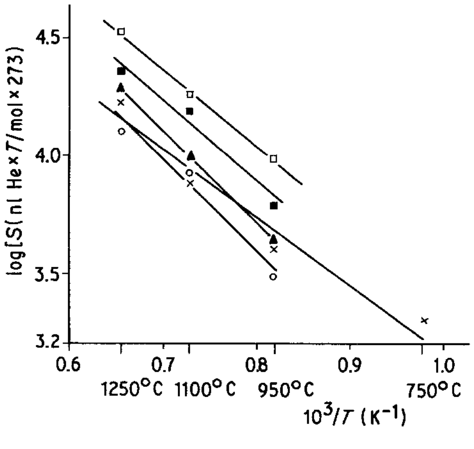

Figure 2 Temperature dependence of the helium solubility coefficient in glass melts of the system $(Pd_xNi_{1-x})_{80}P_{20}$. (□) Melt 9, (■) Melt 8, (x) Melt 3, (▲) Melt 7, (○) Melt 6.

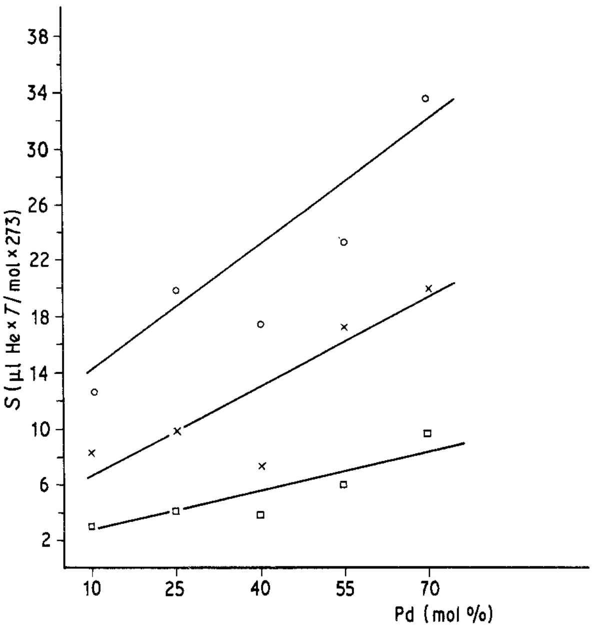

Figure 3 Dependence of the helium solubility coefficient on palladium concentration in glass melts of the system $(Pd_xNi_{1-x})_{80}P_{20}$. (□) 950, (x) 1100, (○) 1250° C.

As has been shown elsewhere [10] the molar volumes of the glasses in the system Pd–Ni–P exceed those of the respective crystals by up to 5%. Solution should therefore be expected if the free volume does not consist of distributed free volume only.

The data in Table II and Figs 1 and 2 show that the helium solubility can readily be measured by the method used. Fig. 6 demonstrates the low solubility values compared to silicate and chalcongenide glass melts; however, Figs 3 to 5 also show that the solubility is clearly composition-dependent. How can this fact be explained?

The metallic alloy glasses and melts may be composed of the following structure units:

Pd–Ni–P:	Pd_3P	Ni_3P	Pd–Ni	Ni_2P
Pt–Ni–P:	$Pt_{20}P_7$	Ni_3P	Pt–Ni	
Pd–Mn–P:	Pd_3P	Mn_3P	Pd–Mn	
Pd–Fe–P:	Pd_3P	Fe_3P	Pd–Fe	
Pd–Co–P:	Pd_3P	Co_2P	Pd–Co	
Pd–Ni–B:	Pd_3B	Ni_3B	Pd–Ni	

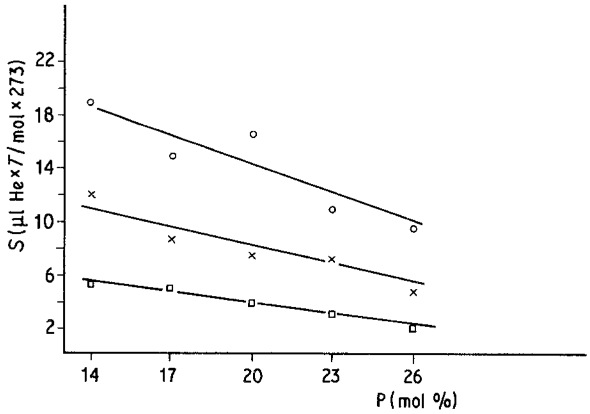

Figure 4 Dependence of the helium solubility coefficient on phosphorus concentraction in glass melts of the system $(Pd_{50}Ni_{50})_{1-y}P_y$. (□) 950, (x) 1100, (○) 1250° C.

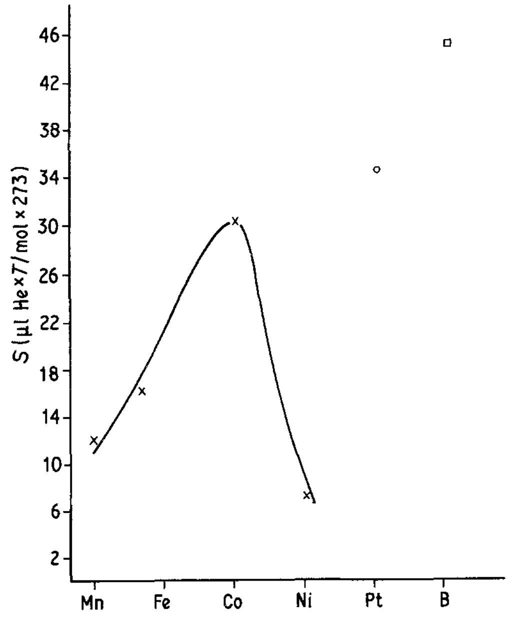

Figure 5 Dependence of the helium solubility coefficient on concentration for different glass melts at $T = 1100°C$. (×) $Pd_{40}(Mn, Fe, Co, Ni)_{40}P_{20}$; (○) $Pt_{40}Ni_{40}P_{20}$; (□) $Pd_{40}Ni_{40}B_{20}$.

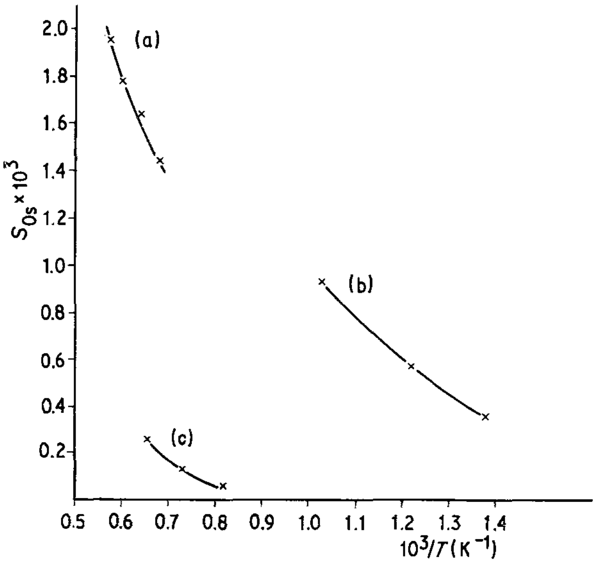

Figure 6 Comparison of the helium solubility (expressed in terms of a unitless Ostwald solubility coefficient) for (a) a silicate glass melt [13] with 15.8 mol % Na_2O, 10.1 mol % CaO, 74.1 mol % SiO_2; (b) a chalcogenide glass melt [5] $Se_{60}Ge_{30}As_{10}$; and (c) a metallic alloy glass melt $Pd_{25}Ni_{55}P_{20}$.

According to the overall composition, different portions of these units are present and determine the properties of the glass under consideration. The dimension of the unit cells are given in Table IV [14–21].

From the distance between the metal and the metalloid in the crystal lattice, the radius of the phosphorus atom is calculated as 0.095 nm. This small radius compared to that of 0.128 nm of the free phosphorus atom is due to the partial ionization of the atom [22, 23]. The unit cells show that the largest voids in Ni_3P and in Pd_3P are close to the size of the phosphorus atoms at the edge of the unit cell. However, the diameter of the voids of 0.13 nm for Ni_3P and of 0.14 nm for Pd_3P are smaller than the diameter of the helium atom. This is the reason why no helium can be dissolved in the crystalline alloys.

Let us first consider the glasses of the composition line $(Pd_xNi_{1-x})_{80}P_{20}$. With increasing palladium content the portion of Pd_3P structure units increases, with a free volume larger than that of Ni_3P. The molar volume also increases in the same direction [10] and the same is true for the helium solubility (Fig. 3). There is evidence that for the composition $Pd_{40}Ni_{40}P_{20}$ some excess volume is present; however, this does not influence the solubility, though it may influence the distributed free volume [24].

The glass composition line $(Pd_{50}Ni_{50})_{1-y}P_y$ is a little more complicated. If a phosphorus atom is removed from the unit cell the respective void grows, and the probability that helium may be incorporated in this hole increases. Hence the solubility increases (Fig. 4). However, there is a further reason. The lower the phosphorus content, the lower the portion of the metal which can form the phosphide. These metal atoms may then be deposited in between the phosphide structure units, thus leading to a more disordered short-range structure. Into these holes helium atoms may be incorporated. On the other hand this system also has a maximum excess volume at $Pd_{40}Ni_{40}P_{20}$ [10] and the RDF function shows a maximum distance between the atoms near 24 mol % P. Again this additional volume may increase the distributed free volume. This system may be considered as an example which demonstrates the mutual interrelations which influence the solubility of rare gases in metallic glasses.

Fe_3P and Mn_3P have a larger free volume than Ni_3P. Hence the solubility increases from $Pd_{40}Ni_{40}P_{20}$ via $Pd_{40}Mn_{40}P_{20}$ to $Pd_{40}Fe_{40}P_{20}$ (Fig. 5). Usually the free volume increases with a larger unit cell. The Mn_3P cell is as large as that of Fe_3P. Due to the denser packing of glasses with Mn_3P the solubility is less. The Co_2P structure unit is totally different from the (Mn,

TABLE IV Dimensions of the unit cells and their free volumes

Alloy	Unit cell volume, U (nm^3)	Molecules per unit cell	Metal radius, r_M (nm)	Metalloid radius, r_N (nm)	Free volume, V_f (nm^3)	
					Per unit cell	Per molecule
Mn_3P	0.386	8	0.135	0.095	0.275	0.0344
Fe_3P	0.370	8	0.126	0.095	0.274	0.0343
Co_2P	0.131	4	0.125	0.095	0.084	0.0210
Ni_3P	0.352	8	0.124	0.095	0.259	0.0324
Pd_3P	0.230	4	0.137	0.095	0.173	0.0431
"Pd_4P"	0.217	4	0.137	0.095	0.163	0.0408
Ni_3B	0.151	4	0.124	0.075	0.112	0.0280
Pd_3B	0.201	4	0.137	0.075	0.151	0.0377

Fe, Ni)$_3$P structure units. It has the smallest free volume. However, since there are only two cobalt atoms in the phosphide structure there is more metal phase in $Pd_{40}Co_{40}P_{20}$ than in $Pd_{40}Ni_{40}P_{20}$. These metal atoms are deposited in between the phosphide structure units, thus leading to a more disordered short-range order. Co_2P and Pd–Co are densely packed and the helium solubility is low; however, helium atoms may be deposited between the Co_2P units and the metal phase. The significantly higher solubility indicates a different solution mechanism.

In glasses of the system $(Pd_{50}Ni_{50})_{1-y}P_y$ it is supposed that helium occupies sites similar to the sites of phosphorus atoms. Since the boron atom is smaller than the phosphorus atom, the helium solubility in $Pd_{40}Ni_{40}B_{20}$ should be increased compared to that in $Pd_{40}Ni_{40}P_{20}$. This is confirmed by Fig. 5. The free volume in Pd_3B and Ni_3B is smaller than the free volume in the corresponding phosphides. The higher solubilities are obviously due to the fact that the distributed free volume becomes smaller, whereas the voids for helium solution grow. Since nothing is known thus far on Pt–P compounds it is not possible to understand the high helium solubility in $Pt_{40}Ni_{40}P_{20}$ glass melt.

5. Conclusions

The method used here is capable of measuring very low gas solubilities in metallic glass melts. The solubilities obtained are sensitively dependent on the free volume and hence on the structure of the respective glasses and glass melts. The results enable one to prepare metallic glasses with higher or lower gas solubilities.

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