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Author(s): Ricardo B. Schwarz, CMS
Yi He, CMS

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BULK METALLIC GLASS FORMATION IN THE Pd-Ni-P and Pd-Cu-P ALLOY SYSTEMS

R. B. Schwarz and Y. He

Center for Materials Science, MS K-765
Los Alamos National Laboratory, Mail Stop K765
Los Alamos, NM 87545, U. S. A.

1. INTRODUCTION

Since the first successful synthesis of glassy Au-Si and Pd-Si by P. Duwez and co-workers [1], the production of amorphous alloys has been associated with the rapid solidification of melts at cooling rates on the order of 10^6 K/sec. In these and many other alloys, high cooling rates are necessary to avoid the crystallization of the undercooled melt while it is quenched from the liquidus temperature T_l to the glass transition temperature, T_g. The required fast cooling rate restricts at least one of the dimensions of the amorphous products to less than about 50 μm. Because amorphous metallic alloys have many potential technological applications, the recent discovery that certain alloy melts can be quenched into bulk amorphous states has received great attention.

Formation of a metallic glass by melt-quenching requires bypassing the crystallization of the melt within the temperature regime T_l to T_g. This, in turn, requires avoiding both the heterogeneous and homogeneous nucleation of crystalline embryos. Heterogeneous nucleation can be minimized by removing from the melt all foreign inclusions (e.g. oxides). When this is achieved, the major competition to glass formation comes from homogeneous nucleation. Turnbull [2,3] studied homogeneous nucleation in undercooled melts and showed that the most important single parameter describing the nucleation rate is the ratio of T_g to T_l, called the reduced glass transition temperature T_{rg}. The solid curves in Figure 1 show homogeneous nucleation rates for various values of T_{rg} calculated using the parameters listed in [4]. The nucleation rate is negligible for $T \rightarrow T_l$ (because the thermodynamic force for crystallization approaches zero) and for $T \rightarrow T_g$

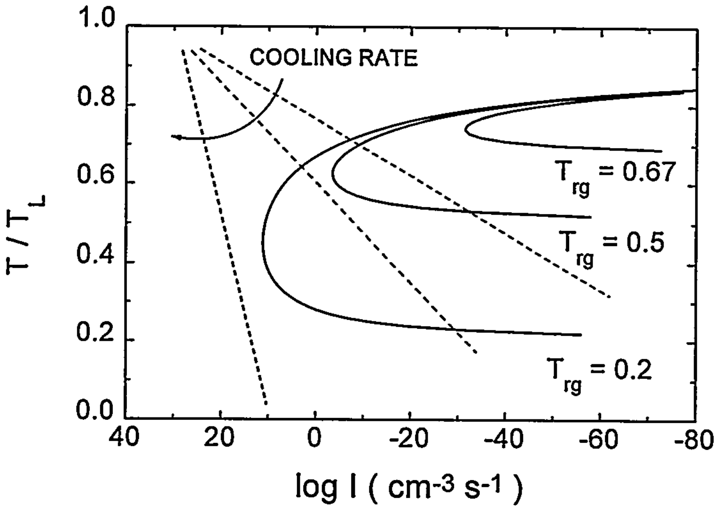

Figure 1. Calculated homogeneous nucleation rate for various values of T_{rg} as a function of temperature.

(because the nucleation rate is kinetically suppressed by the increasing glass viscosity). If we associate a smaller nucleation rate (positive abscissa) with a larger time period during which the undercooled liquid can exist without crystallizing, the homogeneous nucleation rate curves in the figure become equivalent to the customary T-T-T curves for crystallization. It is then clear that the larger the value of T_{rg}, the smaller the critical cooling rate required to avoid crossing the nose of the T-T-T curve, as indicated schematically by the three dashed lines.

For any given alloy system, the composition range for glass formation depends on its T_{rg} value (usually, T_g is weakly composition dependent) and on the imposed cooling rate. Because the liquidus temperature is lowest at and near eutectic compositions, glassy metallic alloys are easier to form by quenching melt of those compositions. The Pd-P and Ni-P binary systems have eutectics near the composition $M_{80}P_{20}$ (M = Pd, Ni). Both $Pd_{80}P_{20}$ and $Ni_{80}P_{20}$ can be prepared as thin amorphous ribbons at cooling rates > 10^4 K/s. The ternary alloy $Pd_{40}Ni_{40}P_{20}$ has $T_{rg} = 0.65$ [3]. By quenching the melt in water, Chen produced bulk amorphous $Pd_{40}Ni_{40}P_{20}$ alloy rods with diameters of 1-3 mm [5]. Using surface etching and thermal cycling to eliminate surface impurities, Drehman *et al.* [6] were able to produce amorphous $Pd_{40}Ni_{40}P_{20}$ buttons with minor diameters of up to 5.3 mm; then, by fluxing molten $Pd_{40}Ni_{40}P_{20}$ with dehydrated B_2O_3, Kui *et al.* [7] were able to further increase the minimum sample dimension to about 10 mm. These last two works demonstrate that in addition to a large T_{rg}, bulk glass formation requires the careful removal of heterogeneous nucleation centers. Several alloy compositions, listed in Table 1, have been found to be amenable to bulk glass formation with sample dimensions ranging from several *mm* to several *cm*. These sample dimensions could not have been achieved unless the critical cooling rates were on the order of 100 K/s, or lower. It is clear from the table that all these alloys have large values of T_{rg}. Most recently, Fe-based ferromagnetic bulk amorphous alloys have been synthesized [8,9] which may have important technological applications.

Table 1. Bulk glass forming alloy systems and the production methods. ***d*** is the smallest sample dimension.

Alloy system	**Typical Composition**	T_{rg}	**Synthesis method**	***d*** **(mm)**	**Ref.**
Pd-Cu-Si	$Pd_{78}Cu_6Si_{16}$	0.63	WQ	1-3	[5]
Pd-Ni-P, Pt-Ni-P	$Pt_{48}Ni_{32}P_{20}$	~ 0.60	WQ	1-3	[5]
$Pd_{40}Ni_{40}P_{20}$	$Pd_{40}Ni_{40}P_{20}$	0.59	FX	5-10	[6,7]
Pd-Ni-P	$Pd_{40}Ni_{40}P_{20}$	0.59	FXWQ	10-25, > 25	[10]
Pd-Cu-P	$Pd_{40}Cu_{40}P_{20}$	0.64	FXWQ	7	This work
Au-Pb-Sb	$Au_{55}Pb_{22.5}Sb_{22.5}$	0.63	QLN	1.5	[11]
La-Al-Ni, La-Al-Cu	$La_{55}Al_{25}Ni_{20}$	0.68	DC	3	[12]
Zr-Al-Ni-Cu	$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$	0.58	WQ	16	[13]
Mg-Cu-Y, Mg-Ni-Y	$Mg_{65}Cu_{25}Y_{10}$	0.60	MC	4	[14,15]
Zr-Ti-Cu-Ni-Be	$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$	0.67	MC	> 14	[16,17]
Ti-Zr-Cu-Ni	$Ti_{34}Zr_{11}Cu_{47}Ni_8$	0.59	MC	4	[18]
Fe-based alloys	$Fe_{73}Al_5Ga_2P_{11}C_5B_4$		MC	1-2	[8]
Pd-Cu-Ni-P	$Pd_{40}Cu_{30}Ni_{10}P_{20}$	0.71	WQ	40	[19]
Nd-Fe-Al	$Nd_{70}Fe_{20}Al_{10}$	*	MC, SC	4-12	[20,21]

DC = die casting; FX = fluxing; MC = mold casting; WQ = water quenching;
FXWQ = fluxing followed by water quenching; SC = suction casting;
QLN = quenching into liquid nitrogen. * No glass transition observed.

Although bulk amorphous $Pd_{40}Ni_{40}P_{20}$ has been known for about 20 years, the *bulk* glass-forming range in the Pd-Ni-P system had not been investigated. It has been known, however, that using melt-spinning techniques (associated with cooling rates on the order of 10^6 K/s), amorphous $Pd_{80-x}Ni_xP_{20}$ alloys can be produced over the whole metal composition range, i.e., from $x = 0$ to $x = 80$ [5]. Because a cm-size metallic sample cannot be cooled at a rate faster than about 100 K/s, the metal composition range for *bulk* glass formation in the Pd-Ni-P system is narrower. Using an improved fluxing technique, we have recently studied bulk glass formation in the Pd-Ni-P system, and found that bulk amorphous alloy rods with diameters of 10 mm can be synthesized over a wide composition range [10,22]. We have also found, for the first time, that bulk amorphous rods with diameters up to 7 mm can be produced in the Pd-Cu-P and Pd-Ni-Fe-P systems [23]. Compared to the other bulk glass systems listed in Table 1, the Pd-Ni-P and Pd-Cu-P systems have the advantage of having only three elements, and being relatively easy to prepare. In this paper, we report the composition ranges for bulk glass formation in the Pd-Ni-P and Pd-Cu-P systems and the thermal and elastic properties of these bulk amorphous alloys.

2. EXPERIMENTAL

The bulk amorphous alloys were prepared by two synthesis methods. To prepare the Pd-Ni-P alloys, commercial Ni_2P powder (99.5% pure) was arc melted under a purified argon atmosphere to produce Ni_2P ingots. Then, solid Ni_2P, palladium (99.99% pure), and nickel (99.99% pure) were arc-melted to form alloy ingots of the desired composition. These alloys were placed in fused silica tubes, and repeatedly purified in molten B_2O_3, as described in Refs. [6,7]. Finally, the fused silica tubes containing the melt and the flux were quenched in water.

To synthesize bulk amorphous Pd-Cu-P alloys, we started by ball-milling elemental powders of Pd (99.95% pure), Cu (99% pure), and P (99.99% pure) in a SPEX 8000 laboratory ball mill for about 10 hours. The ball-milling was carried out inside an argon-filled glove box containing less than 0.1 ppm oxygen. The ball-milled powder was then placed in a fused silica tube together with dehydrated B_2O_3 and processed as described above. The quenched Pd-Ni-P and Pd-Cu-P rods were sectioned with a low-speed diamond saw to prepare samples for x-ray diffraction, differential scanning calorimetry, and elastic moduli measurements.

3. BULK GLASS FORMATION RANGE

(a) Pd-Ni-P

Using the B_2O_3 fluxing technique, amorphous Pd-Ni-P alloy rods with a critical diameter of 10 mm can be formed over a wide composition range. The phosphorus content is restricted to around (20 ± 5) at.%, whereas the palladium concentration can vary from 25 to 60 at.%, as illustrated in Figure 2. Among these alloys, $Pd_{40}Ni_{40}P_{20}$ has

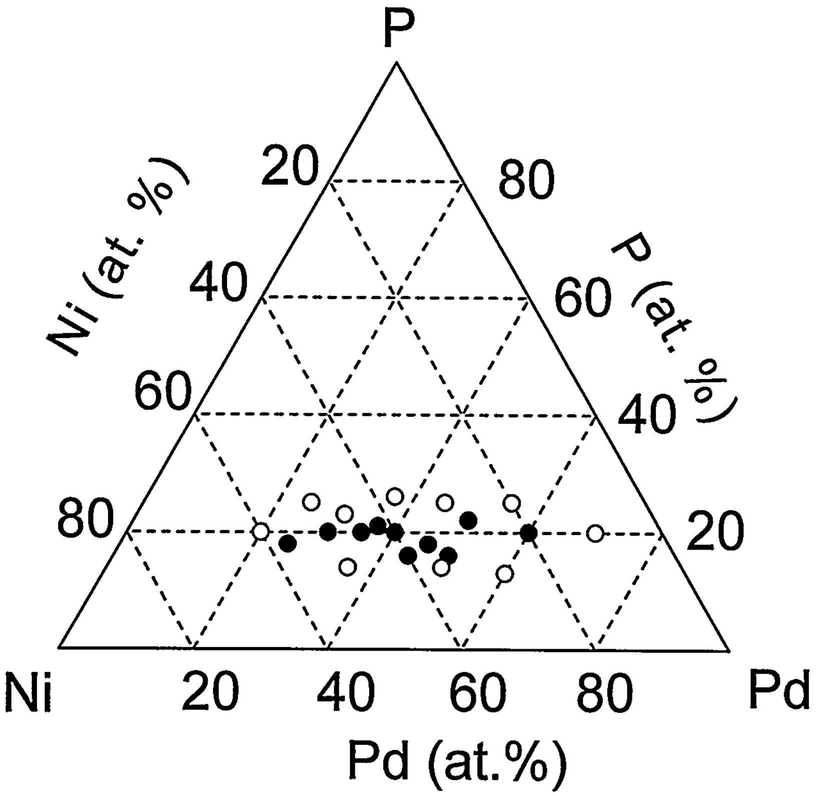

Figure 2. Bulk glass formation range in Pd-Ni-P system. Filled circles denote the formation of amorphous phase, open circles denote the formation of crystalline phases.

the highest glass forming ability, and a 300-gram bulk amorphous cylinder, 25 mm in diameter and 50 mm in length, can be easily synthesized [10]. The cross section of this cylinder was examined by x-ray diffraction and it showed that the whole sample was amorphous. Clearly, this size is by no means the upper limit for bulk glass formation in $Pd_{40}Ni_{40}P_{20}$.

(b) Pd-Cu-P

As shown in Fig. 3, bulk Pd-Cu-P glasses also require about 20 at.% P. The palladium concentration needed to form bulk amorphous rods with diameters of 7 mm is restricted to 40 - 60 at.%, which is narrower than that for Pd-Ni-P glasses. During these tests, we noticed that upon replacing part of the Cu by Ni, the glass forming ability of the Pd-Cu-P alloys can be enhanced drastically. For example, amorphous $Pd_{40}Cu_{30}Ni_{10}P_{20}$ cylinders with a diameter of 16 mm can be readily obtained by fluxing followed by air-cooling (*i.e.* without quenching the molten alloy in water), while water quenching enables the formation of amorphous $Pd_{40}Cu_{30}Ni_{10}P_{20}$ cylinder of 40 mm in diameter [19]. The glass formability in the Pd-Ni-Cu-P system is under investigation.

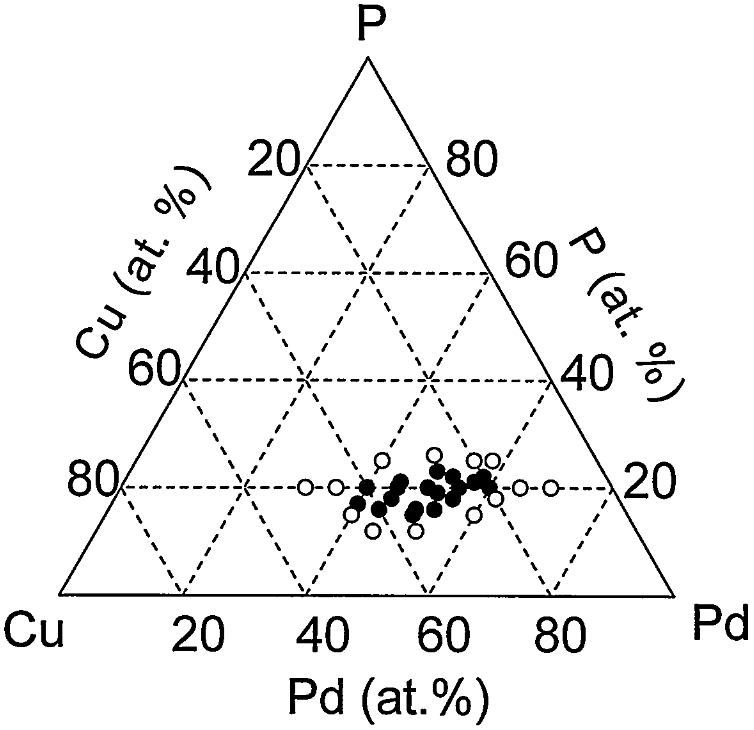

Figure 3. Bulk glass formation range in Pd-Cu-P alloys. Filled symbols are the compositions where amorphous rods with diameter of 7 mm can be formed, open circles represent the formation of crystalline phases.

4. GLASS TRANSITION AND CRYSTALLIZATION

The values of T_g and T_x are of technological importance. For most metallic glasses, T_x is close or even lower than T_g. Bulk glasses, however, are characterized by a large value of ΔT. This may be due to the fact that bulk glasses are usually formed at or near the compositions of deep eutectics. Thus, in the absence of metastable crystalline phases at the eutectic composition, crystallization would require extensive solute partitioning and long-range diffusion. In practice, a large value of ΔT is important because within the temperature range T_x - T_g, the amorphous alloy can be used to produce near-net shape components using techniques such as injection-molding. Figures 4 and 5 are the DSC traces of a number of selected bulk amorphous Pd-Ni-P and Pd-Cu-P alloys obtained at a scanning rate of 20 K/min. The values of T_g, T_x, ΔT, and ΔH_x are listed in Table 2.

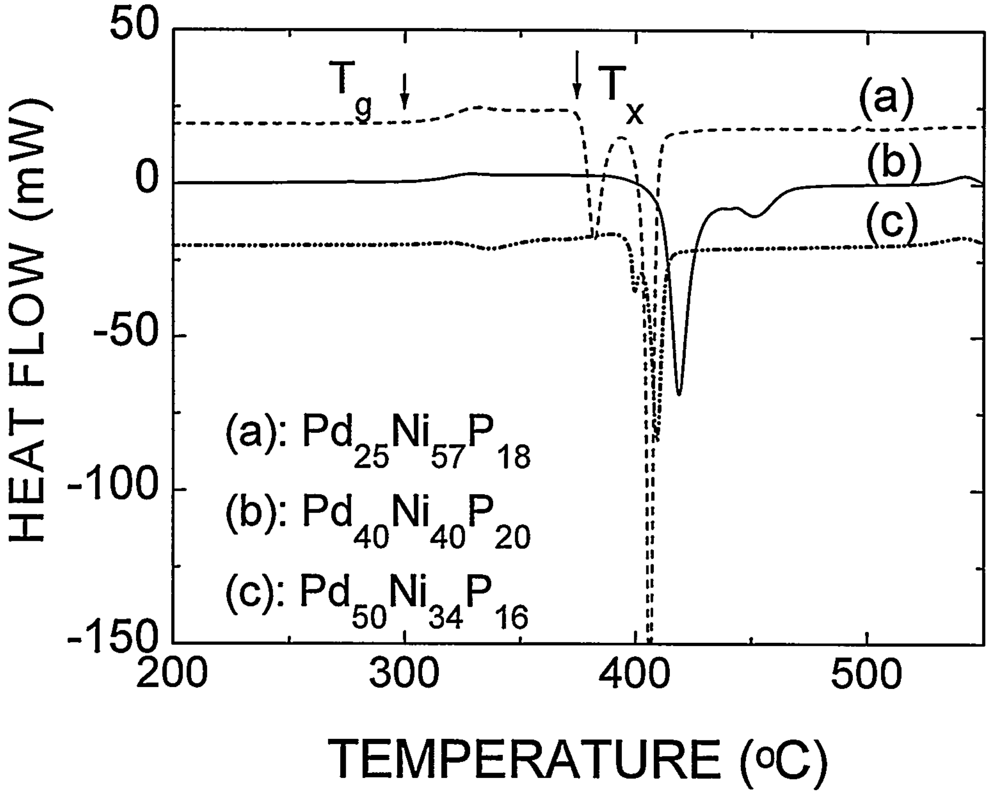

Figure 4. DSC traces for three bulk glassy Pd-Ni-P alloys at the heating rate of 20 K/min.

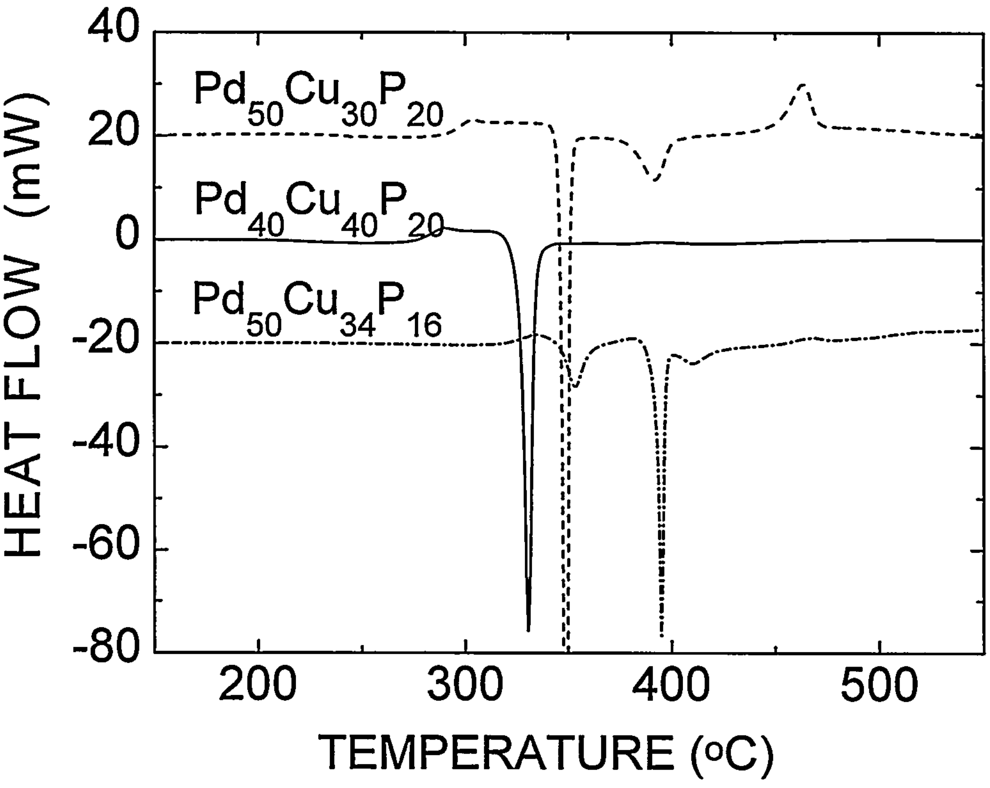

Figure 5. DSC traces for three bulk glassy Pd-Cu-P alloys at a heating rate of 20 K/min.

From Table 2, it is clear that the variations of the glass transition temperature as a function of the composition for amorphous Pd-Ni-P alloys is small. The weak composition dependence of T_g in Pd-Ni-P alloys is consistent with previously reported results [24,25], where T_g of glassy $Pd_{80-x}Ni_xP_{20}$ alloys were found to be between 585 and 602 K when x varies from 0.15 to 0.8. In contrast, T_g for bulk amorphous $Pd_xCu_{80-x}P_{20}$ alloys increases gradually as the palladium concentration increases, as illustrated in Figure 6.

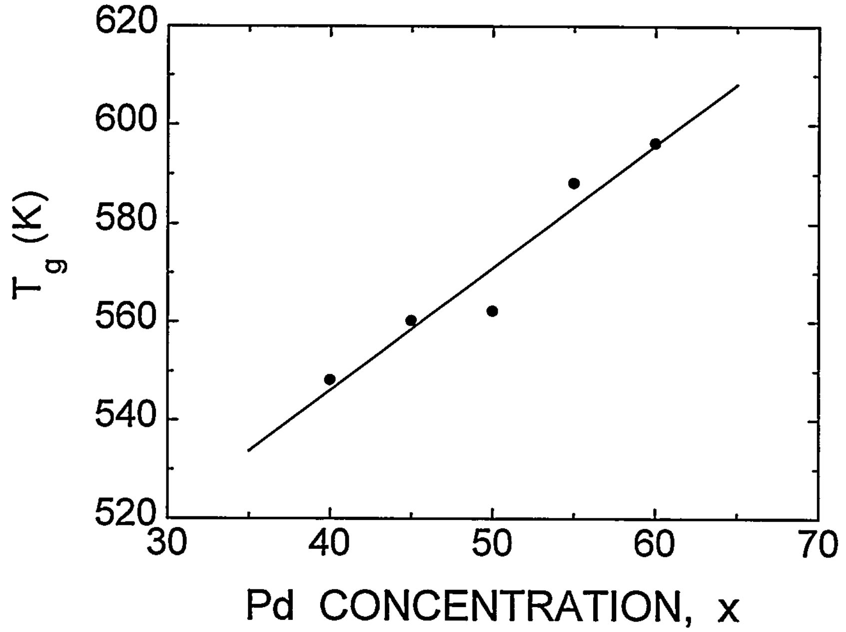

Figure 6. Composition dependence of the glass-transition temperature T_g for bulk amorphous $Pd_xCu_{80-x}P_{20}$.

The crystallization of glassy Pd-Ni-P and Pd-Cu-P alloys is complicated by the formation of metastable crystalline phases [26]. The final (stable) crystallization product consists of a mixture of a (Pd,Ni) or (Pd,Cu) fcc solid solution and more than one kind of metal phosphide of low crystallographic symmetry. Donovan *et al.* [27] used transmission electron microscopy (TEM) and X-ray microanalysis to study the microstructure of slowly cooled crystalline $Pd_{40}Ni_{40}P_{20}$. They identified the compositions of the metal phosphides to be $Pd_{34}Ni_{45}P_{21}$ and $Pd_{68}Ni_{14}P_{18}$.

Table 2: Values of T_g, T_x, ΔT and the crystallization enthalpy, ΔH_x, for bulk amorphous Pd-Ni-P and Pd-Cu-P alloys determined by DSC at a scanning rate of 20 K/min.

Composition	T_g (°C)	T_x (°C)	ΔT (K)	ΔH_x (kJ/mole)
$Pd_{25}Ni_{57}P_{18}$	285	377	92	5.71
$Pd_{30}Ni_{50}P_{20}$	310	400	90	5.94
$Pd_{35}Ni_{45}P_{20}$	308	410	102	5.94
$Pd_{37}Ni_{42}P_{21}$	310	405	95	5.36
$Pd_{40}Ni_{40}P_{20}$	303	405	102	7.37
$Pd_{44}Ni_{40}P_{16}$	300	395	95	6.10
$Pd_{46}Ni_{36}P_{18}$	300	389	89	6.20
$Pd_{50}Ni_{34}P_{16}$	292	396	104	4.76
$Pd_{50}Ni_{28}P_{22}$	311	403	92	6.06
$Pd_{60}Ni_{20}P_{20}$	315	371	56	3.37
$Pd_{40}Cu_{40}P_{20}$	275	326	51	2.66
$Pd_{40}Cu_{43}P_{17}$	281	324	43	3.18
$Pd_{44}Cu_{40}P_{16}$	300	331	31	3.59
$Pd_{45}Cu_{35}P_{20}$	287	360	73	3.52
$Pd_{50}Cu_{30}P_{20}$	289	346	57	3.92
$Pd_{50}Cu_{34}P_{16}$	316	344	28	4.41
$Pd_{50}Cu_{35}P_{15}$	312	340	28	4.04
$Pd_{50}Cu_{27}P_{23}$	292	319	27	3.83
$Pd_{55}Cu_{25}P_{20}$	315	382	67	3.75
$Pd_{58}Cu_{20}P_{22}$	323	372	49	2.91
$Pd_{60}Cu_{20}P_{20}$	323	387	64	4.04

5. ELASTIC PROPERTIES

The elastic properties of bulk amorphous $Pd_{25}Ni_{57}P_{18}$, $Pd_{40}Ni_{40}P_{20}$, $Pd_{50}Ni_{34}P_{16}$, $Pd_{40}Cu_{40}P_{20}$, $Pd_{50}Cu_{30}P_{20}$, and $Pd_{60}Cu_{20}P_{20}$ alloys were measured by resonant ultrasound spectroscopy (RUS). In this technique, the spectrum of mechanical resonances for a parallelepiped sample is measured and compared with a theoretical spectrum calculated for a given set of elastic constants. The true set of elastic constants is calculated by a recursive regression method that matches the two spectra [28,29].

An isotropic and non-magnetic amorphous alloy has only two independent second order elastic constants. The other elastic moduli are related through the equations [30]:

$$C_{12} = C_{11} - 2\,C_{44}, \tag{1}$$

$$E = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{(C_{11} + C_{12})}, \tag{2}$$

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \tag{3}$$

$$\nu = \frac{C_{12}}{C_{11} + C_{12}}, \tag{4}$$

where E, B, and ν are the Young's modulus, the bulk modulus, and the Poisson's ratio, respectively. The shear modulus G is simply C_{44}. Table 3 lists the elastic constants of a number of bulk amorphous Pd-Ni-P and Pd-Cu-P alloys. The typical experimental uncertainties of the RUS measurements are 0.8% for C_{11} and 0.05% for C_{44}.

Table 3 also lists the density ρ of these alloys, which was measured by the Achemedes' principle using pure ethanol as immersion fluid. To monitor the accuracy of the measurements, the density of 99.999% pure Al shots was also measured and it was found to be within 0.4% from its accepted value.

The Debye temperature of the bulk amorphous alloys was calculated from the relation:

$$\Theta_D = \frac{h}{k_B}\left(\frac{9\rho N}{4\pi M}\right)^{1/3}\left(\frac{1}{V_L^3} + \frac{2}{V_T^3}\right)^{-1/3}, \tag{5}$$

where h, k_B, and N are the Planck constant, the Boltzmann constant, and the Avogadro number, respectively; M is the mean atomic weight and ρ is the density. The longitudinal and the transverse ultrasound velocities V_L and V_T are given by

$$V_L = \sqrt{\frac{C_{11}}{\rho}}, \text{ and } V_T = \sqrt{\frac{C_{44}}{\rho}} . \qquad (6)$$

The calculated Debye temperatures are also listed in Table 3. From this table, it is clear that the elastic properties of the bulk amorphous Pd-Ni-P and Pd-Cu-P alloys change little with changing composition. The elastic moduli of the Pd-Cu-P alloys are slightly lower than those for the Pd-Ni-P alloys.

Table 3: Room-temperature elastic constants, density, and the Debye temperature Θ_D of a number of Pd-Ni-P and Pd-Cu-P bulk amorphous alloys. The elastic moduli are in units of GPa and the density ρ is in units of g/cm^3.

Sample	C_{11}	C_{12}	C_{44}	E	B	ν	ρ	Θ_D (K)
$Pd_{25}Ni_{57}P_{18}$	232	152	40.0	112	179	0.396	8.97	311
$Pd_{40}Ni_{40}P_{20}$	229	156	36.6	103	180	0.405	9.36	286
[a]$Pd_{40}Ni_{40}P_{20}$	236	159	38.6	108	185	0.403	9.41	301
$Pd_{50}Ni_{34}P_{16}$	230	152	39.2	110	178	0.397	9.84	285
$Pd_{40}Cu_{40}P_{20}$	202	136	33.2	93	158	0.402	9.30	269
$Pd_{50}Cu_{30}P_{20}$	205	139	32.7	92	161	0.405	9.46	262
$Pd_{60}Cu_{20}P_{20}$	210	145	32.3	91	167	0.409	9.78	254

[a] Data from ref. [31]: the elastic constants were measured by the pulse-echo technique; Θ_D was determined from low-temperature specific heat data.

6. DISCUSSION

DTA curves for the melting of $Pd_{40}Ni_{40}P_{20}$ and $Pd_{40}Cu_{40}P_{20}$ alloys are shown in Figure 7. Our DTA curve for $Pd_{40}Ni_{40}P_{20}$ is in agreement with previous results [32]. From this data, we calculate for these two alloys T_{rg} values as the ratio of T_g/T_l of 0.59 and 0.65, respectively. Notice that the melting of $Pd_{40}Ni_{40}P_{20}$ occurs over a temperature interval of about 100 K, starting at T_m and ending at T_l. If one defines T_{rg} as the ratio T_g/T_m, then the T_{rg} value for $Pd_{40}Ni_{40}P_{20}$ would be much higher, around 0.65, which is the value often quoted in the literature. The definition $T_{rg} = T_g/T_l$ is more appropriate.

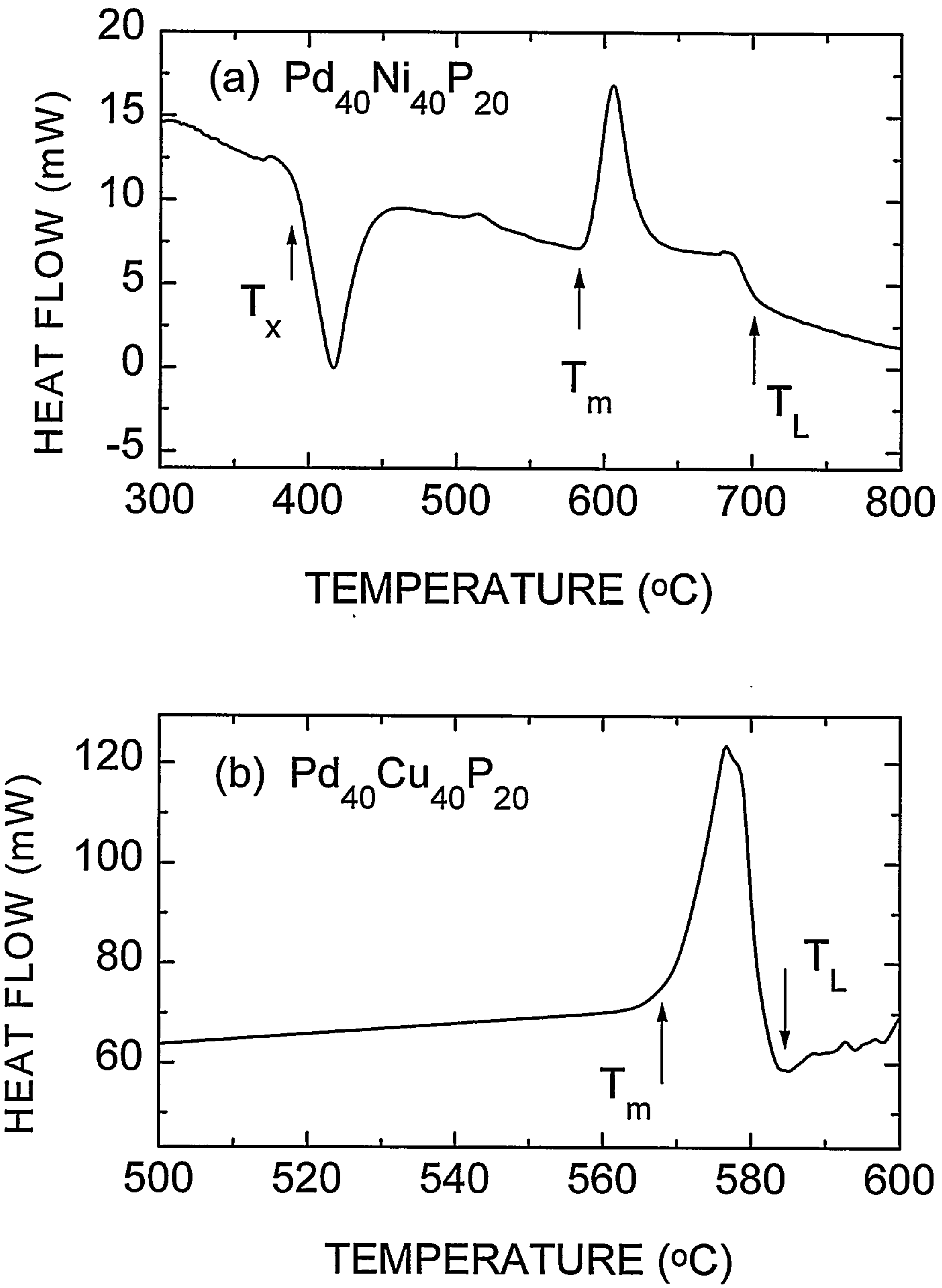

Figure 7. (a) DTA trace revealing the crystallization and melting of glassy $Pd_{40}Ni_{40}P_{20}$. (b) DSC trace of $Pd_{40}Cu_{40}P_{20}$ alloy near its melting point. T_m is the beginning of the melting, while T_l indicates the liquidus temperature where melting completes. The scanning rate used for DTA and DSC measurements is 20 K/min.

Using the fluxing technique, Lau and Kui [33] determined that the critical cooling rate for forming a 7-mm diameter bulk amorphous $Pd_{40}Ni_{40}P_{20}$ cylinder was ~ 0.75 K/sec. From this value, they estimated that the steady-state nucleation frequency was on the order of 10^4 m^{-3} s^{-1}. On the other hand, Drehman and Greer [34] estimated that the steady state nucleation frequency at 590 K is ~ 10^6 m^{-3} s^{-1}, which is also the maximum nucleation frequency. These two values are the smallest ever found in a metallic system. From the measured nucleation frequency and an estimated crystal growth rate of ~ 10^{-10} m/s at 590 K, follows that the *theoretical* critical cooling rate for glass formation in $Pd_{40}Ni_{40}P_{20}$ is 10^{-3} K/s. There have been various attempts to measure the critical cooling rate in $Pd_{40}Ni_{40}P_{20}$. Willnecker *et al.* [35] reported an upper bound of 0.17 K/s. Using the fluxing technique, we found that mm-size $Pd_{40}Ni_{40}P_{20}$ liquid can be vitrified without crystallization at a cooling rate of 0.34 K/s [23]. For such a low critical cooling rates, the thermodynamic properties of the undercooled $Pd_{40}Ni_{40}P_{20}$ liquid can be measured for the first time over the entire undercooling regime, from the melting temperature down to the glass transition temperature [32]. In comparison, the critical cooling rate for glass formation in the multi-component $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ alloy is ~ 1 K/s [17]. Thus the reported values of critical cooling rates for $Pd_{40}Ni_{40}P_{20}$ are about 6 times lower than those of the beryllium containing bulk amorphous alloys. Our work to date suggests that the critical cooling rates in the quaternary Pd-Cu-Ni-P alloys are even smaller than those reported for the ternary Pd-Ni-P alloys.

7. CONCLUSIONS

Bulk metallic glasses were prepared in the Pd-Ni-P and Pd-Cu-P systems using a fluxing technique. The formation of bulk amorphous Pd-Cu-P alloys was reported here for the first time. For both alloy systems, bulk glass formation requires maintaining the phosphorus content near 20 at.%. In the Pd-Ni-P system, 10-mm diameter amorphous $Pd_xNi_{80-x}P_{20}$ rods can be formed for $25 \le x \le 60$. In the Pd-Cu-P system, 7-mm diameter amorphous $Pd_xCu_{80-x}P_{20}$ rods can be produced for $40 \le x \le 60$.

From all the ternary alloys studied, $Pd_{40}Ni_{40}P_{20}$ has the highest glass formability, and 25-mm diameter amorphous cylinders, 50 mm in length, can be easily fabricated.

The glass stability of the Pd-Ni-P system is wider than that of the Pd-Cu-P system. For most bulk Pd-Ni-P glasses (10-mm diameter), $\Delta T > 90$ K. The ΔT values of bulk amorphous Pd-Cu-P alloys are considerably smaller, ranging from 27 to 73 K.

The elastic constants of bulk amorphous Pd-Ni-P and Pd-Cu-P alloys were determined using a resonant ultrasound spectroscopy technique. The Pd-Ni-P glasses are slightly stiffer than the Pd-Cu-P glasses. Within each alloy system, the Young's modulus and the bulk modulus show little change with alloy composition.

Of all the bulk glass forming systems so far investigated (Table 1), the ternary Pd-Ni-P system has the best glass formability. This alloy was one of the first bulk glasses discovered, yet it still remains the best in terms of glass formability. Upon replacing part of Ni by Cu, the critical cooling rates are expected to be further reduced.

8. ACKNOWLEDGMENTS

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