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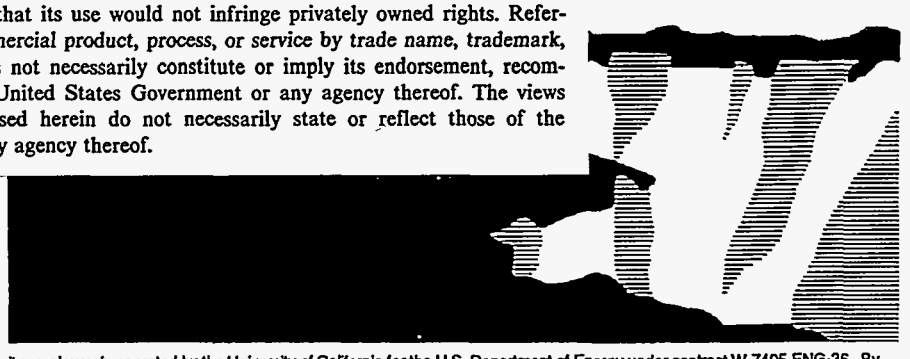

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SYNTHESIS AND PROPERTIES OF BULK METALLIC GLASSES IN Pd-Ni-P AND Pd-Cu-P ALLOYS

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SYNTHESIS AND PROPERTIES OF BULK METALLIC GLASSES IN Pd-Ni-P AND Pd-Cu-P ALLOYS

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ABSTRACT

Bulk amorphous Pd-Ni-P and Pd-Cu-P alloy rods with diameters ranging from 7 to 25 mm have been synthesized over a wide composition range using a fluxing technique. For most bulk amorphous Pd-Ni-P alloys, the difference $\Delta T = T_x - T_g$ between the crystallization temperature T_x and the glass transition temperature T_g is larger than 90 K, while for bulk amorphous Pd-Cu-P alloys, ΔT varies from 27 to 73 K. $Pd_{40}Ni_{40}P_{20}$ has the highest glass formability, and 300-gram bulk amorphous cylinders, 25 mm in diameter and 50 mm in length, can be easily produced. This size, however, is not an upper limit. The paper presents the glass formation ranges for both ternary alloy systems and data on the thermal stability of the amorphous alloys, as well as their specific heat, density, and elastic properties.

INTRODUCTION

Bulk glass formation in metallic systems is usually difficult. Unlike traditional oxide glasses which can be easily formed using low cooling rates, metallic glasses can, in general, only be formed using high cooling rates. This is because undercooled metallic melts have high atomic mobility and thus cooling rates on the order of 10^6 K/sec are needed to prevent the melt from crystallizing while it is cooled from its melting temperature, T_m, to the glass transition temperature, T_g. Recently, a number of multicomponent metallic alloy systems have been found to have extraordinary glass forming ability. These alloy systems include La-Al-(Ni,Cu) [1], Mg-(Cu,Ni)-Y [2], Zr-Al-(Cu,Ni,Co) [3,4], Zr-Ti-Cu-Ni-Be [5], Nd-Al-(Cu,Ni,Co,Fe) [6], and Ti-Zr-Ni-Cu [7]. Most of these alloys can be quenched from the melt into a bulk amorphous state at a relative cooling rate of 1~100 K/sec. By bulk we mean a sample with minimum dimensions of about 1 mm. Because bulk amorphous alloys have large technological potential, understanding their synthesis and finding new compositions are topics of great scientific interest.

$Pd_{40}Ni_{40}P_{20}$ was one of the first bulk amorphous alloys discovered. By quenching the melt in water, Chen produced amorphous $Pd_{40}Ni_{40}P_{20}$ alloy rods with diameters of 1-3 mm [8]. Using surface etching and thermal cycling to eliminate the surface impurities, Drehman *et al.* [9] successfully produced amorphous $Pd_{40}Ni_{40}P_{20}$ solids with minor diameters up to 5.3 mm; and by fluxing molten $Pd_{40}Ni_{40}P_{20}$ with dehydrated B_2O_3, Kui *et al.* [10] were able to prepare amorphous $Pd_{40}Ni_{40}P_{20}$ buttons with the minimum dimension of about 10 mm. These previous studies have concentrated on the particular composition of $Pd_{40}Ni_{40}P_{20}$. In recent publications, we reported the homogeneity range for bulk glass formation in the Pd-Ni-P system [11,12]. In this paper we report a new ternary bulk glass forming system, Pd-Cu-P. The properties of bulk Pd-Cu-P and Pd-Ni-P glasses are compared and discussed.

Pd-Cu-P System

The bulk glass forming range for 7-mm diameter amorphous Pd-Cu-P rods is shown in Fig. 2. Similar to Pd-Ni-P system, the glass formation range is restricted to near 20 at.% phosphorus. However, the palladium content for bulk glass formation is limited to 40-60 at.%, which is narrower than that for Pd-Ni-P alloys. Clearly, the glass forming ability for the Pd-Cu-P system is not as good as that of the Pd-Ni-P system.

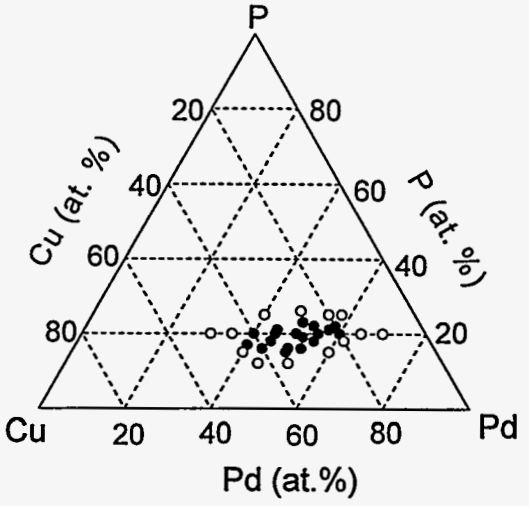

Figure 2. Bulk glass formation range in the Pd-Cu-P system. Filled circles denote the formation of glassy rods with diameters of at least 7 mm.

Pd-Cu-Ni-P

The bulk glass-forming ability of the Pd-Ni-P and Pd-Cu-P ternary alloys can be substantially enhanced by going to the quaternary Pd-Ni-Cu-P system. Indeed, it has been reported recently that a 40-mm diameter glassy rod of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ can be prepared by water quenching [17]. We have found that using the B_2O_3 flux, a 16-mm diameter amorphous rod can be prepared by cooling the same melt in air. The composition range for bulk glass formation in the Pd-Cu-Ni-P system is being investigated.

THERMAL STABILITY

When the temperature is increased to above T_g, the amorphous solid becomes an undercooled liquid and its viscosity decreases drastically. Since crystallization does not occur until the temperature is further increased to approach T_x, the temperature interval $\Delta T = T_x - T_g$ is a measure of the thermal stability of the undercooled liquid. The values of ΔT must be associated with a given heating rate, which here is 20 K/min. Fig. 3 shows the DSC traces for several bulk glassy Pd-Cu-P, Pd-Ni-P, and Pd-Cu-Ni-P alloys. These bulk glass formers are characterized by large values of ΔT. For all the 10-mm diam. glassy Pd-Ni-P rods we prepared, $\Delta T > 60$ K, with the alloys near the $Pd_{40}Ni_{40}P_{20}$ composition reaching $\Delta T > 100$ K [11]. For the glassy Pd-Cu-P alloys, ΔT ranges from 27 K to 73 K.

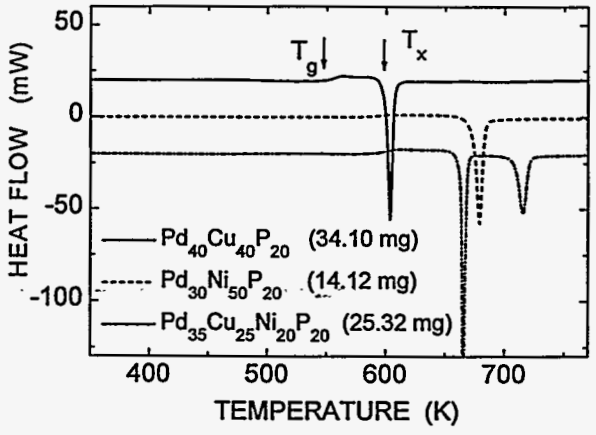

Figure 3. DSC traces for three bulk glassy Pd-(Cu,Ni)-P alloys, scanned at 20 K/min.

The formation of amorphous alloys via the undercooling of melts requires we prevent the melt from crystallizing while its temperature is reduced from the liquidus temperature T_l to T_g. The reduced glass transition temperature $T_{rg} = T_g / T_l$, has been shown to be a measure of the

alloy's glass forming ability [18,19]. The values of T_g, T_x, T_l, T_{rg}, and the enthalpy of crystallization ΔH_x are listed in Table 1 for a selected number of glassy alloys. In this table, the T_{rg} value for $Pd_{40}Ni_{40}P_{20}$ was calculated using the (upper) liquidus temperature, $T_l = 991$ K. If we use the solidus temperature for this alloy, $T_s = 875$ K, then T_{rg} is 0.66, as often quoted in the literature [19].

Table 1 T_g, T_x, ΔT, T_l, T_{rg}, and 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 (K)	T_x (K)	ΔT (K)	T_l (K)	T_{rg}	ΔH_x (kJ/mole)
$Pd_{30}Ni_{50}P_{20}$	583	673	90	1010	0.58	5.94
$Pd_{40}Ni_{40}P_{20}$	576	678	102	991	0.58	7.37
$Pd_{50}Ni_{28}P_{22}$	584	676	92	972	0.60	6.06
$Pd_{40}Cu_{40}P_{20}$	548	599	51	843	0.65	2.66
$Pd_{50}Cu_{30}P_{20}$	562	619	57	863	0.65	3.92
$Pd_{60}Cu_{20}P_{20}$	596	660	64	916	0.65	4.04

SPECIFIC HEAT

The specific heat, C_p, of the Pd-Ni-P and Pd-Cu-P glassy alloys near T_g was measured by DSC at a heating rate of 20 K/min. A sapphire single crystal was used as reference material. All the specimens used in these measurements were cut from 7-mm diameter amorphous rods. Fig. 4 shows the results for $Pd_{40}Cu_{40}P_{20}$. The open circles show C_p of the as-prepared glass whereas the open triangles are measurements for the same glass after heating it to 563 K and immediately cooling it to room temperature. The difference between these two curves between 475 and 560 K is due to an irreversible structural relaxation in the as-prepared glass. The solid symbols show C_p for the crystallized glass (after annealing it at 673 K for 30 min.). The peak centered at about 565 K in the C_p curves of the glass in the both the as-prepared and relaxed states is due to the reversible glass transition. The two open-symbol curves show that the as-prepared glass, obtained by water-quenching a 7-mm diameter rod, contains a significant amount of excess free volume, which relaxes upon annealing. Similar C_p measurements for glassy Pd-Ni-P alloys suggest that in this system, the as-prepared glasses contain smaller amounts of excess free volume. Nevertheless, the difference in free volume between the as-prepared and

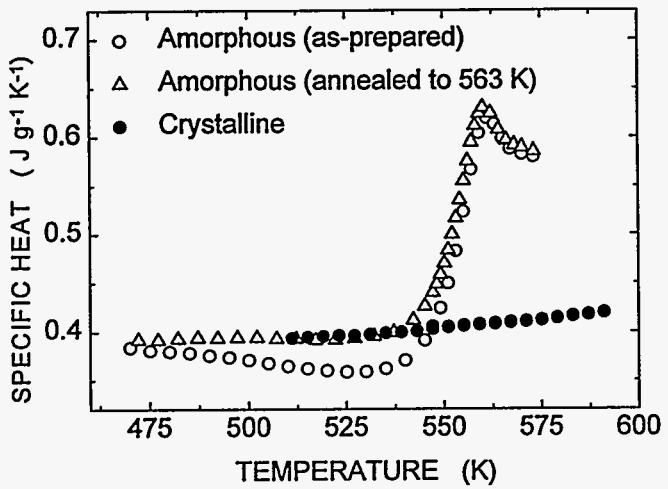

Fig. 4. Specific heat of glassy and crystallized $Pd_{40}Cu_{40}P_{20}$.

amorphous rods can be formed in alloys containing between 25 to 60 at.% Pd. Bulk glass formation in Pd-Cu-P system, which is reported here for the first time, has a relatively narrower glass-forming range. Preliminary results show that the glass forming ability of the quaternary Pd-Ni-Cu-P system is higher than that of either the Pd-Ni-P or the Pd-Cu-P systems. All the ternary bulk glasses are characterized by large values of $\Delta T = T_x - T_g$. The bulk Pd-Cu-P glasses, obtained at estimated cooling rates of 100 K/s, have appreciable excess free volume which give clear signatures in the specific heat measurements.

ACKNOWLEDGMENTS

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SYNTHESIS OF BULK AMORPHOUS ALLOYS

The synthesis of bulk amorphous Pd-Ni-P and Pd-Cu-P alloys was based on an improved fluxing technique [11,12], which was pioneered by Turnbull and his colleagues [9,10]. The alloy synthesis starts by mechanically allying mixtures of elemental powders [13]. The alloyed powders are then purified in molten B_2O_3 which dissolves oxide impurities which would otherwise act as heterogeneous nucleation centers in the undercooled molten alloy. The bulk amorphous alloy was formed by quenching the molten alloy in water. The cooling rates are estimated at no more than 100 K/s. The structure and properties of the amorphous alloys was investigated by X-ray diffraction, optical microscopy, scanning electron microscopy, scanning differential calorimetry (DSC), and resonant ultrasound spectroscopy (RUS).

BULK GLASS FORMATION RANGE

Pd-Ni-P System

Using the fluxing technique, bulk amorphous Pd-Ni-P alloy rods with a critical diameter of 10 mm can be formed over a wide range of metal compositions, as indicated in Fig. 1. For bulk glass formation, however, the phosphorus concentration must be maintained close to 20 at.%. Previous research has shown that the glass forming ability correlates with the difference $\Delta T = T_x - T_g$. For the Pd-Ni-P system, ΔT is largest for $Pd_{40}Ni_{40}P_{20}$ and we have found that amorphous $Pd_{40}Ni_{40}P_{20}$ cylinders, 25 mm in diameter and 300 g in weight, can be easily produced [11]. Clearly, this size is not the upper limit for bulk glass formation in $Pd_{40}Ni_{40}P_{20}$.

Drehman and Greer [14] studied the kinetics of crystal nucleation and growth in $Pd_{40}Ni_{40}P_{20}$ glass. They determined that for this alloy the steady-state homogeneous nucleation rate is as low as 10^6 m^{-3} s^{-1}, which is the lowest value reported in any metallic glass. The crystal growth rate at 590 K is estimated to be less than 10^{-10} m/s. Based on these data, and provided heterogeneous nucleation has been effectively suppressed, the critical cooling rate for glass formation in $Pd_{40}Ni_{40}P_{20}$ is estimated to be as low as 10^{-3} K/s. Experimentally, we have 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 [15], while an upper bound of the critical cooling rate of 0.17 K/s has also been reported for $Pd_{40}Ni_{40}P_{20}$ [16]. With such a low critical cooling rate, it should be possible to prepare much larger bulk glasses in this alloy system.

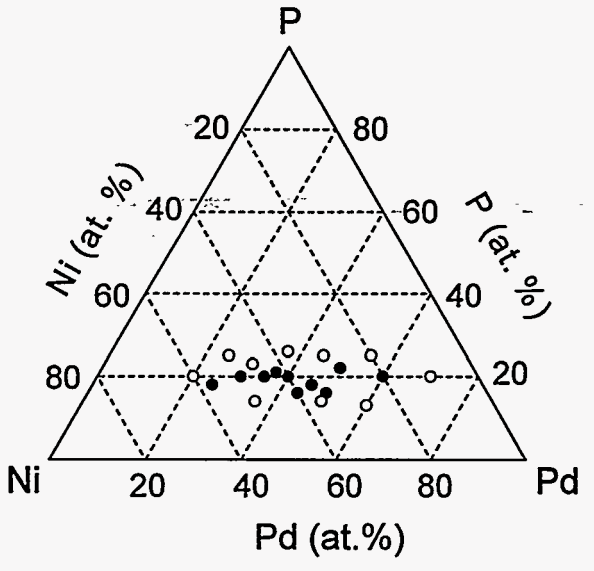

Figure 1. Bulk glass formation range in Pd-Ni-P system. Filled circles denote the formation of glassy rods with diameters of at least 10 mm. For the open circles, the 10-mm diameter rods were crystalline.