Highly processable bulk metallic glass-forming alloys in the Pt–Co–Ni–Cu–P system

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Highly processable bulk metallic glass alloys in the Pt–Co–Ni–Cu–P system were discovered. The alloys show low liquidus temperature below 900 K, excellent processability with low critical cooling rate reflecting in maximum casting thicknesses in quartz tubes of up to 20 mm, and a large supercooled liquid region. The $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ composition has a liquidus temperature of 795 K, a glass transition temperature of 508 K with a supercooled liquid region of 98 K. For medical and jewelry applications a Ni-free alloy, $Pt_{60}Cu_{16}Co_{2}P_{22}$ was discovered with a liquidus temperature of 881 K, a glass transition temperature of 506 K, and a supercooled liquid region of 63 K. Glass formation was observed in a wider composition range. Vickers hardness of these alloys is in the 400 Hv range. The alloys can be processed in the supercooled liquid region in air without any measurable oxidation. In this region, a large processing window is available in which the material does not embrittle. Embrittlement in these alloys is correlated with crystallization. It can be avoided as long as substantial crystallization does not take place during isothermal processing in the supercooled liquid region. Also, liquid processing can be performed in air when flux with B_2O_3.
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Platinum-based alloys are finding more and more applications in fields like jewelry, medical, dental, automotive, microtechnology and nano-technology. They are inert, possess high strength, an esthetic appearance, and a high catalytic potential. Processing of these alloys, however, is very difficult because of their high liquidus temperature in the 2000 K range. Reaction with the crucible, tarnishing and oxidation, and shrinkage are just some problems resulting from the required high processing temperature.

In the last two decades several alloys based on Pd,[1–3] La,[4] and Zr[5,6] were discovered which form an amorphous phase during cooling of up to several centimeters at cooling rates of 100 K/s or less. These bulk metallic glasses (BMGs) all have in common that their composition is close to a deep eutectic composition. Consequently, their melting temperature is much lower than the linear interpolation of the alloy's constituents liquidus temperatures. The resulting low liquidus temperature is an attractive property for casting alloys. Most uniquely, BMGs show a large temperature difference between glass transition temperature and the crystallization temperature, the so-called supercooled liquid region. In this temperature region the BMG is in a highly viscous liquid state and can be super plastically deformed, a processing method typically used for plastics.

The best BMG forming alloys were found in the Pd–Cu–Ni–P system.[1–3] This system is based on the metal-metalloid Pd–P eutectic. Critical casting thicknesses of 72 mm[7] and critical cooling rates[8] of 0.005 K/s were measured under special fluxing conditions. Due to similar phase diagrams of Pt–P and Pd–P, the Pt–P was chosen as the basic system and Ni, Cu, and Co were added.

Four different composition regions are studied: An alloy region with maximum processability with a platinum content of at least 85% by weight; a region with maximum processability with a platinum content of at least 85% by weight that does not contain any nickel; an alloy that consists of at least 75% by weight with high processability; and an alloy that consists of at least 75% by weight with high processability and consists of no more than three elements. Criteria used to

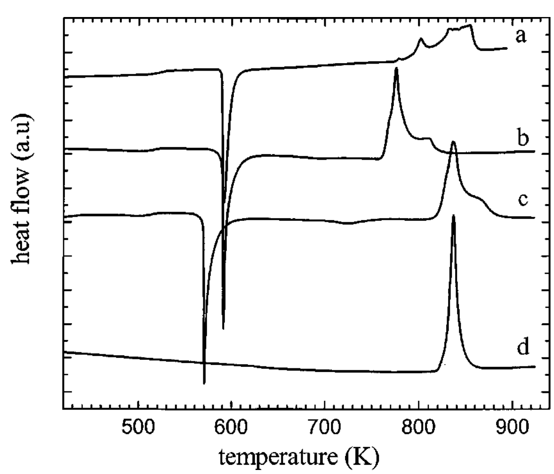

FIG. 1. DSC thermogram determined by heating with 20 K/min of Pt-based alloys of various compositions that were cast in various size quartz tubes. (a): $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ cast in 20 mm quartz tube, (b): $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ cast in 16 mm quartz tube, (c): $Pt_{60}Cu_{16}Co_{2}P_{22}$ cast in 12 mm quartz tube, and (d): $Pt_{60}Cu_{20}P_{20}$ cast in 4 mm quartz tube.

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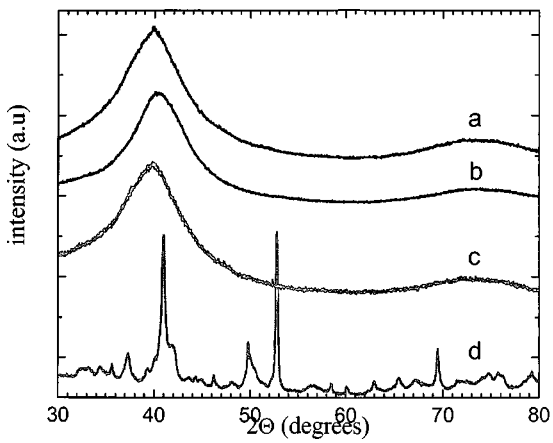

FIG. 2. X-ray diffraction thermogram of Pt-based alloys of various compositions that were cast in various size quartz tubes. (a): $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ cast in 20 mm quartz tube, (b): $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ cast in 16 mm quartz tube, (c): $Pt_{60}Cu_{16}Co_2P_{22}$ cast in 12 mm quartz tube, and (d): $Pt_{60}Cu_{20}P_{20}$ cast in 4 mm quartz tube.

identify highly processable compositions are large critical casting thickness, large supercooled liquid region, low liquidus temperature, and no embrittlement during thermoplastic processing.

Alloys were prepared by inductively melting the elements (Pt: 99.95, Cu: 99.999, Ni: 99.5, Co: 99.95 P: 99.999 purity) in quartz tubes. Subsequently, the alloy was exposed to a fluxing treatment. B_2O_3 was added to the alloy and heated to about 1200 K for 20 min. This fluxing treatment was found to improve the glass forming ability in various alloys.[1,9,10] Samples are water quenched in various diameter quartz tubes of a wall thickness of 1 mm.

Thermal analysis is performed in a differential scanning calorimeter (DSC) Netzsch DSC 404 c. X-ray diffraction is carried out on an Inel XRG 3000 using Cu $K\alpha$ radiation. Hardness test was performed on a Leco R-600. Compression tests were carried out on a MTS 810. A large number of compositions were investigated in each abovementioned composition range. From each range only one composition is discussed in detail.

Figure 1 shows the DSC thermogram obtained by heating with 20 K/min of the four Pt alloys. The thermogram in Fig. 1(a) is that of $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ that was cast in a 20 mm quartz tube, Fig. 1(b) shows $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ cast in 16 mm, Fig. 1(c) shows $Pt_{60}Cu_{16}Co_2P_{22}$ cast in 12 mm, and Fig. 1(d) shows $Pt_{60}Cu_{20}P_{20}$ that was cast in 4 mm tube. All compositions are in atomic percent. Except for $Pt_{60}Cu_{20}P_{20}$ all alloys show a glass transition and a crystallization peak suggesting that at least some fraction of the material was amorphous. The liquidus temperature of all alloys is below 900 K.

Figure 2 shows the x-ray diffractogram of the four alloys. The diffractogram in Fig. 2(a) is that of $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ that was cast in a 16 mm quartz tube, Fig. 2(b) shows $Pt_{60}Cu_{16}Co_2P_{22}$ cast in 12 mm, Fig. 2(c) shows $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ cast in 20 mm, and Fig. 2(d) shows $Pt_{60}Cu_{20}P_{20}$ that was cast in 4 mm tube. All alloys but the $Pt_{60}Cu_{20}P_{20}$ exhibited broad amorphous peaks with no sharp crystalline peaks. This confirms that all alloys but $Pt_{60}Cu_{20}P_{20}$ are x-ray amorphous.

The results of the various alloys are summarized in Table I. All alloys show very low liquidus temperature compared to commercially crystalline Pt alloys. $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ has a liquidus temperature of 795 K. With a glass transition temperature of 508 K the reduced glass transition temperature $T_{rg} = T_g/T_l = 0.64$, a value only seen among extraordinarily good glass formers. The supercooled liquid region for $Pt_{60}Cu_{16}Co_2P_{22}$ and $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ is larger than 60 K and for $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ it reaches 98 K. A large supercooled liquid region is crucial for thermo plastic processing. Also shown in Table I are the hardness numbers. For $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$, $Pt_{60}Cu_{16}Co_2P_{22}$, and $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ the Vickers hardness number is around $V_H = 400$. This is about twice as hard as conventional crystalline Pt alloys typically used for jewelry applications. The maximum casting thicknesses are also shown in Table I. Large maximum casting thicknesses of up to 20 mm for the $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$ were measured reflecting the good glass forming ability.

It should be mentioned that a larger composition range for all four alloys was studied. As an example in the range of the $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ alloy platinum was increased up to 63%, Ni was varied from 0% to 10%, Cu from 6% to 16%, and P from 18% to 25%. Among the constituents of the alloy, the P content has the strongest influence on the glass forming ability. For example $Pt_{60}Cu_{14.7}Ni_{5.3}P_{20}$ could not be cast amorphous in 10 mm tubes or larger, whereas Ni, Cu, and P could be varied in the abovementioned range and still be cast amorphous at least into 12 mm tubes.

In a recent publication Zhang and Inoue[11] observed a critical casting thickness for $Pt_{60}Cu_{20}P_{20}$ of at least 12 mm when casting in copper molds. In the present publication even in 4 mm quartz tubes the $Pt_{60}Cu_{20}P_{20}$ alloy could not be solidified amorphous. This discrepancy in the thicknesses the material can be cast amorphous in, can be explained by the different casting techniques used. Even for perfect wetting the low thermal conductivity of about 1.3 W/m K for quartz compared to about 10 W/m K, a typical value for BMGs, makes the quartz a thermal barrier for the cooling process. The heat flow kinetics through a 4 mm $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ sample in a quartz tube of 1 mm wall thickness is comparable to the heat flow through a $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ sample

TABLE I. Summary of the properties of the various Pt-based alloys. The maximum thickness the alloy could be cast amorphous, d_{max}, was determined for water quenching in quartz tubes of 1 mm wall thickness.

Composition [at. %]	T_g (K)	T_X (K)	ΔT (K)	T_1 (C)	$T_{rg} = T_1/T_g$	d_{max} quartz tube (mm)	Hardness, R_a
$Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$	508	606	98	795	0.64	16	402
$Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$	515	589	74	873	0.59	20	392
$Pt_{60}Cu_{16}Co_2P_{22}$	506	569	63	881	0.58	16	402
$Pt_{60}Cu_{20}P_{20}$				844		<4	

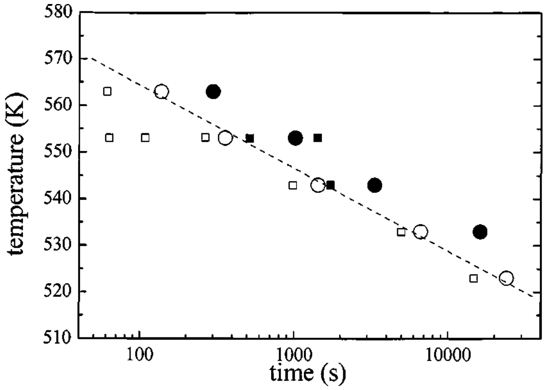

FIG. 3. Time-temperature-transformation diagram for amorphous $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ heated into the supercooled liquid region. Open circles depict onset of crystallization and closed circles the end of the crystallization. Squares indicate annealing conditions for failure mode determination. The open squares indicate a ductile behavior and the closed squares a brittle failure. The dashed line guides the eye to distinguish the region from ductile to brittle failure.

of about 18 mm. Therefore, critical casting thicknesses should only be compared with each other when the same quenching technique is used.

In order to explore the superplastic processability the time available before crystallization sets in was determined. Therefore, amorphous material was heated in the supercooled liquid region and processed isothermally until crystallization sets in. The onset of crystallization was determined by a heat release due to the release of the heat of fusion during crystallization. The isothermal studies on $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ result in a time temperature transformation (TTT) diagram which is shown in Fig. 3. A common phenomenon when BMGs are reheated into the supercooled liquid region is the embrittlement, a drastic decrease in the fracture toughness[12] which makes the material useless for most applications. An effective way to qualitatively estimate the embrittlement is a hardness test. It should be mentioned that this method allows one to determine a change in the fracture mode but is not capable of determining the absolute fracture toughness. The studied alloys show in the as-cast state a Vickers hardness around 400 Hv. $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ was annealed at different temperatures and times before and after the onset of crystallization as indicated by squares in Fig. 3. The embrittlement is evidenced by snapping of the disk shape sample during loading in the hardness test. Samples that snapped during loading are considered to be brittle and they are shown as solid squares. Samples that did not snap during loading were considered to be ductile and are shown as open squares. The hardness number measured on the material that did not snap remain unchanged within experimental scatter. For this alloy the embrittlement is correlated with the crystallization. This is in contrast to Zr-based alloys where embrittlement was observed prior to crystallization.[12] In order to further investigate the influence of annealing in the supercooled liquid region, the effect of the isothermal processing on the compressive yield strength was investigated. Therefore, a $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ sample that was subject to heat treatment of 180 s at 643 K and as-cast material was compared. Both samples show a yield strength of about 1.1 GPa.

The alloys' resistivity to oxidation was determined by processing both in air and in an argon atmosphere at 533 K for 30 min. Since with the naked eye no difference could be determined, x-ray photoemission spectroscopy (XPS) was utilized to determine oxidation. It turns out that between the differently processed samples no difference in the XPS spectrum could be revealed.

In conclusion, Pt-based alloys were developed that consist of at least 75% by weight of platinum, $Pt_{42.5}Cu_{27}Ni_{9.5}P_{21}$, an alloy that consists of at least 85% by weight of platinum, $Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5}$ of platinum and an alloy that consists of at least 85% by weight but does not consist of Ni, $Pt_{60}Cu_{16}Co_2P_{22}$. These alloys show low liquids temperature, large supercooled liquid region, large maximum casting thickness, and good processability both for casting and for thermoplastic processing. The fact that the alloys do not embrittle during isothermal processing prior to crystallization, and their large supercooled liquid region make them promising candidates for thermoplastic processing.

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