LA-UR- 00 - 7 5 3

Approved for public release;
distribution is unlimited.

Title: Optimizing the Metalloid Content in Bulk Metallic Glasses

Author(s): O Jin, MST-8
R.B. Schwarz, MST-8
F.M. Alamgir, Lehigh Univ., Bethlehem, PA
H. Jain, Lehigh Univ., Bethlehem, PA

Submitted to: For publication in Nucleation and Growth Processes in Materials
Proceedings of Symposium E
Mat. Res. Soc. - Fall, 1999 Meeting, Boston, Dec., 1999

Los Alamos

NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

OPTIMIZING THE METALLOID CONTENT IN BULK METALLIC GLASSES¹

O. JIN¹, R. B. SCHWARZ¹, F. M. ALAMGIR², and H. JAIN²

¹Materials Science and Tech. Division, Los Alamos National Laboratory, Los Alamos, NM 87545.

²Dept. of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015-3195.

ABSTRACT

We have studied the effect of phosphorus content on the formation and properties of bulk Pd-Cu-P and Pd-Ni-P metallic glasses. It was found that the molar volumes of the Pd-Ni-P bulk glasses plotted as a function of P content follow a straight line whereas those for the Pd-Cu-P glasses follow two straight lines of different slopes, intersecting at a critical P concentration. The transition in molar volume behavior is attributed to a change in the alloy's short-range order with increasing P content. The origin of this structural change is discussed based on x-ray photoelectron spectroscopy (XPS) measurements.

RECEIVED
OCT 04 2000
OSTI

¹. to appear in "Nucleation and Growth Processes in Materials", Proceedings of Symposium E, Mater. Res. Soc. Fall 1999 Meeting, Boston, Dec. 1999.

INTRODUCTION

Bulk metallic glasses are receiving increasing attention for their potential in applications, and for allowing unprecedented studies of the structure of liquids and glasses. For conventional metallic glasses (prepared at cooling rates on the order of 10^6 K/s) it has long been believed that the metalloid content should be near 20 at.%. Therefore, the search for new bulk metal-metalloid glass-forming alloys (prepared at cooling rates on the order of 10^2 K/s) has been mostly devoted to adjusting the type and content of the metal atoms, while the effect of metalloid content on glass forming ability has received less attention. It is expected, however, that the optimization of the metalloid content will play a crucial role in maximizing the size of the glassy product [1].

This paper reports molar volume measurements in $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$, $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$, and $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{100-x}\text{P}_x$ bulk metallic glasses. For each alloy class, we determined the glass forming range. The dependence of molar volume on P concentration is correlated with electronic structure measurements using XPS.

EXPERIMENT PROCEDURE

Powders of $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ and $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ were prepared by ball-milling 6-gram mixtures of elemental Pd (99.95%), Cu (99.999%) and P (99.9999%) powders. The milling was done for 10 hours using a tungsten carbide vial and a single 12-gram tungsten-carbide ball. The mill was located inside an argon-filled glove box containing less than 0.1 ppm oxygen. The ball-milled powders were then loaded into fused silica tubes together with dehydrated B_2O_3 . Upon heating the tubes, the alloy melts and the B_2O_3 dissolves the oxides (fluxing) [2]. After fluxing, the fused silica tubes containing the purified melts were quenched in water. Bulk glassy rods of 7-mm and 8-mm in diameter were prepared for $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ and $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$, respectively. We used the same technique to prepare 8-mm diameter bulk glassy rods of $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{100-x}\text{P}_x$ with the purpose of comparing its properties with those of the Pd-Cu-P alloys.

The densities of the glassy rods were measured by the Archimedes method using distilled water as immersion fluid. The rods were then sectioned with a diamond-impregnated low-speed saw to prepare samples for X-ray diffraction and X-ray photoelectron spectroscopy (XPS) measurements. The XPS measurements were done on a Scienta ESCA-300 spectrometer using

Al K_{α} (1486.7 eV) x-rays from a rotating anode, and a high-resolution hemispherical electrostatic analyzer. Before recording an XPS spectrum, the surface of each specimen was mechanically cleaned in high vacuum (10^{-7} Pa) with a diamond tool.

RESULTS AND DISCUSSION

We used X-ray diffraction to determine which cast alloys were amorphous. Single phase amorphous rods were obtained for alloys with phosphorus content, x , from 15.5 to 19 at.% for $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses, from 17 to 21 at.% for $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ glasses, and from 16 to 22 at.% for $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{100-x}\text{P}_x$ glasses. For the three alloy systems, the glass forming ranges are centered at phosphorus content lower than 20 at.%. Although we were able to prepare 7 and 8 mm-diameter amorphous rods of $\text{Pd}_{50}\text{Cu}_{30}\text{P}_{20}$ and $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, respectively, we were unable to prepare a similar rod at the composition $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$. This clearly shows that $\text{Pd}_{40}\text{Cu}_{40}\text{P}_{20}$ is not the optimum composition for bulk glass formation in the $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ system. It further suggests that to maximize the dimensions of the bulk glass (i.e. lower the critical cooling rate), one has to carefully optimize the metalloid content in the alloy. The factors that determine the best alloy composition for bulk glass formation are poorly understood.

Figure 1 shows the molar volumes of the alloys as a function of phosphorus content. The molar volumes were deduced from measured densities, the nominal compositions, and the known atomic weight of the elements. Two features are apparent in this figure. First, the bulk glass forming range of the $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{100-x}\text{P}_x$ glasses is wider than that of the $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ and $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses, indicating that Pd-Ni-P is overall a better glass-forming system than Pd-Cu-P. Second, the molar volumes of the $(\text{Pd}_{0.5}\text{Ni}_{0.5})_{100-x}\text{P}_x$ glasses follow a single straight line, whereas those of $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ and $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses show clear discontinuities at 19 and 17.5 at.%, respectively.

The molar volume data for the Pd-Cu-P bulk glasses for phosphorus contents below and above the respective discontinuities can be fitted by two straight lines. The intersection of these lines define the critical phosphorus concentrations $c_{1:1}^* = 17.5$ and $c_{5:3}^* = 19$ for the two Pd-Cu-P alloys with Pd/Cu ratios of 1:1 and 5:3, respectively. An extrapolation of these lines to the pure-phosphorus ordinate enables us to deduce the partial molar volumes of phosphorus, $\bar{V}_P$, given in the last column of Table 1. Notice that the molar volumes deduced from the extrapolation of the

lines with negative slopes have comparable values of, $\bar{V}_P = 7.18, 6.85,$ and $7.10 \text{ cm}^3 \text{ mole}^{-1}$. Similarly, the $\bar{V}_P$ values deduced from the extrapolation of the lines with positive slopes are also of comparable values, 9.2 and $8.95 \text{ cm}^3 \text{ mole}^{-1}$. This suggests that $\bar{V}_P$ assumes one value (close to 7.1) for the two Pd-Cu-P bulk glasses below their respective critical phosphorus concentration, and a different value (close to 9) for glasses above the critical phosphorus concentrations.

An extrapolation of the lines fitted to the molar volumes of the Pd-Cu-P bulk glasses to the zero-phosphorus ordinate enables us to deduce the combined partial volume of Pd and Cu in these glasses, weighted by the molar ratios between these elements. Based on the previous analysis, we assume that, as for phosphorus, the metal atom partial molar volumes have only two values: one for all the Pd-Cu-P bulk glasses fitted by the two lines of positive slope, and another for the alloys fitted by the two lines of negative slope. With this assumption we obtain two equations that enable us to calculate the partial molar volumes of Pd and Cu. These values are given in Table 1.

Figure 1 and Table 1 indicate that the partial molar volumes of Pd, Cu, and P in the Pd-Cu-P glasses change abruptly at critical concentrations of phosphorus. We interpret these abrupt changes to reflect changes in the local atomic environment (short-range order, SRO). For all the Pd-Cu-P alloys belonging to the lines with negative slope in Fig. 1, the partial molar volumes of Pd, Cu, and P are approximately 9.0, 7.6, and $7.0 \text{ cm}^3 \text{ mole}^{-1}$, respectively. When the phosphorus content increases beyond the critical phosphorus concentrations, the partial molar volume of Pd *decreases* by 3.3% to 8.7, that of Cu *decreases* by 10.5% to 6.8, and that of phosphorus *increases* by 30% to 9.1.

The $\bar{V}_P$ value in the Pd-Ni-P glasses, deduced from the single fitted line in Fig. 1, is approximately 7.2, thus close to the $\bar{V}_P$ values in the Pd-Cu-P glasses *below* their respective critical concentrations. This observation justifies making the additional assumption that $\bar{V}_{Pd}$ is the same for all the glasses whose molar volumes have been fitted by lines of negative slope. This assumption enables us to deduce the partial molar volume of nickel in the Pd-Ni-P glasses to be $6.66 \text{ cm}^3 \text{ mole}^{-1}$.

These results suggest further that the SRO in the Pd-Ni-P bulk glasses is similar to that of the Pd-Cu-P bulk glasses for phosphorus contents *below* their respective critical concentrations.

Finally, in Fig. 1, the molar volume of the $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{79}\text{P}_{21}$ glass does not seem to belong to either of the two lines fitting the rest of the molar volume data. This alloy, very rich in phosphorus, may contain nano-sized crystalline inclusions that were not detected by x-ray diffraction.

It is interesting to compare the current partial molar volumes of palladium, copper and nickel in bulk glasses to their known elemental values, also listed in Table 1. The previous discussion suggests that all the glasses studied can be classified into two groups: (1) glasses with $\bar{V}_P \approx 7$; and (2) glasses with $\bar{V}_P \approx 9 \text{ cm}^3 \text{ mole}^{-1}$. For the first group, the partial molar volume of the metal atoms is slightly larger in the glass than in elemental form, whereas the opposite is true for the second group. If indeed these two groups of glasses have different SRO, the partial molar volume results suggest that the change in SRO is accompanied by a change in the electronic bonding.

XPS measurements were performed to elucidate the driving force for a possible change of SRO in the Pd-Cu-P glasses. Figure 2 shows XPS data for $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, and for three $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses with $x = 16.5, 17.5$, and 19 . It is customary to present the XPS spectra with the zero of the energy scale at the Fermi energy, so that the abscissa represents binding energy. In Figure 2 we used a different energy normalization: we shifted the abscissa of each curve so as to superimpose the high-energy edges of the d -band for all XPS curves and placed this edge at $x = 0$. By doing this, one can more clearly see the different contributions to electronic bonding in these glasses. A detailed study of the valence band of Pd-Ni-P glasses as a function of Pd/Ni ratio has been published before [3]. The XPS signal for the Pd-Ni-P glasses has a broad density of states with a sharp high-energy edge, characteristic of a transition metal with a filled, or partially filled, d -band. The XPS spectra for the Pd-Cu-P glasses have similar broad d -type bands but, in addition, have high-energy tails, characteristic of higher energy s and p -states. This indicates that the d -bands in the Pd-Cu-P glasses are full and that excess electrons occupy s and p states of energy higher than that at the top of the d -bands.

The inset to Fig. 2 (left) is an enlargement of the highest energy range of the XPS signals for the Pd-Cu-P glasses. The inset clearly shows that the phosphorus increase causes an increase in the occupancy of the s - and p -bands. The energy increase is about 0.08 eV per atom percent increase in phosphorus. We use these observations to explain the structural changes implied by the changes in partial molar volumes in Fig. 1.

in these glasses. The latter glasses, containing more Pd, have a larger density of unoccupied *d*-states, which can accommodate a larger fraction of the electrons donated by the phosphorus. The *s* and *p* states above the *d*-band are thus less populated in the latter alloys and the polymorphic transition occurs at a higher phosphorus concentration.

The molar volume data for Pd-Ni-P glasses show no indication of a polymorphic transition. Figure 2 shows that the density of states for amorphous Pd₄₀Ni₄₀P₂₀ is characterized by a partially filled, or just filled, *d*-band. This agrees with the fact that nickel has a lower number of valence electrons than copper. Thus, in these alloys, an increase in the phosphorus concentration does not cause a significant increase in the alloy's Fermi energy. Increasing the phosphorus concentration by a large amount may eventually cause a polymorphic transition similar to that observed in the Pd-Cu-P glasses. However, this transition may occur at phosphorus concentrations well beyond the glass-forming range for these alloys.

The optimum phosphorus concentration for bulk glass formation in the Pd-Ni-P system is at the center of its homogeneity range, $x = 19$. For the Pd-Cu-P glasses, the optimum phosphorus concentration for bulk glass formation is close to $c_{1:1}^* = 17.5$ and $c_{5:3}^* = 19$ at.% (Fig. 1). We arrived at these conclusions by measuring thermal properties such as glass transition temperature, crystallization temperature, and enthalpy of crystallization. These data will be presented separately. However, none of the Pd-Cu-P compositions was as good a bulk-glass former as the Pd₄₀Ni₄₀P₂₀ glass. The XPS data suggest that *s* and *p* bonding at energies above the *d*-band is present in all our Pd-Cu-P glasses and that this bonding type is less favorable to bulk glass formation.

CONCLUSIONS

Metalloid concentration has significant effect on the glass forming ability of metal-metalloid glasses. To minimize the critical cooling rate, and thus maximize the size of the bulk metallic glasses, the metalloid content needs to be optimized.

Partial molar volume measurements suggest that Pd-Cu-P glasses sustain a polymorphic change with increasing phosphorus content. This change is driven by an increase in the electronic contribution to the alloy's free energy. Before the occurrence of the polymorphic change, the SRO in the Pd-Cu-P glasses is similar to that in the Pd-Ni-P glasses. The polymorphic transition in the Pd-Cu-P glasses, and the difference between the glass-forming

Describing SRO in metal-metalloid glasses has concerned researchers for a long time. Some understanding of the SRO has been obtained by simulating the structure of these glasses by computer models. A comparison of measured and calculated atom pair distribution functions was taken as a measure of the model accuracy. It was found that the models reproduced the measured atom-pair distribution functions only when constructed following special algorithms that favor the development of specific types of SRO. Examples are the algorithm of Boudreaux and Gregor [4], which bias the alloy against metalloid-metalloid nearest neighbors, and the algorithm of Gaskell [5], which bias the alloy towards containing a large number of trigonal prismatic units. These units have a metalloid atom at the center and metal atoms at the corners and near the faces. Clearly, the glass could adopt many other SRO configurations. It is now accepted that metal-metalloid glasses can exhibit polymorphism. Furthermore, polymorphism can be more prevalent in ternary (and higher component) glasses, which have a higher degree of freedom for packing tetrahedral atom units [6].

Because the present bulk glasses were prepared by quenching the melt at relatively low cooling rates on the order of 100 K s^{-1} [7], the SRO trapped in the glassy state will most likely be that present in the undercooled melt as it approached the glass transition temperature. As the melt is undercooled, it will seek the SRO that minimizes its free energy at that temperature. Changes in the electronic contribution to this energy, brought about by changes in alloy composition, can cause changes in the SRO adopted by the undercooled melt.

The present XPS data (Fig. 2) shows that Pd-Cu-P glasses have filled *d*-bands. For these glasses, an increase in the phosphorus content causes a rapid increase in the electronic contribution to the free energy because the electrons from the additional phosphorus atoms can only populate empty *s* and *p* states of higher energy. We suggest that the increase in free energy with increasing phosphorus content forces the glassy alloy to perform a polymorphic change to a SRO structure of lower free energy. In the $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses, the polymorphic change occurs at $c_{11}^* = 17.5$. This structural change creates additional *d*-band states, as reflected by the widening of the *d*-band XPS signal when the P content is increased from $x = 17.5$ to $x = 19$ (Fig. 2, right). The availability of more *d*-band states means that the additional electrons do not have to populate *s* and *p* states of higher energy.

In the $(\text{Pd}_{0.625}\text{Cu}_{0.375})_{100-x}\text{P}_x$ glasses, the polymorphic change occurs at $c_{53}^* = 19$. This difference in critical phosphorus concentration is consistent with the difference in the Pd content

ability of the Pd-Cu-P and Pd-Ni-P glasses is related to differences in the electronic band structure of the alloys.

Table 1. Partial molar volumes of Pd, Cu, Ni and P deduced from extrapolations of density measurements for bulk metallic glasses as a function of phosphorus content. The table includes the known molar volumes of elemental Pd, Cu, and Ni with fcc structure.

Alloy	Phosphorus x-range	$\bar{V}_{\text{Pd}}$ cm ³ /mole	$\bar{V}_{\text{Cu}}$ cm ³ /mole	$\bar{V}_{\text{Ni}}$ cm ³ /mole	$\bar{V}_{\text{P}}$ cm ³ /mole
(Pd _{0.5} Ni _{0.5}) _{100-x} P _x	16 – 22	8.95	—	6.66	7.18
(Pd _{0.5} Cu _{0.5}) _{100-x} P _x	15.5 – 17.5	8.95	7.56	—	6.85
	17.5 – 19	8.68	6.83	—	9.20
(Pd _{0.625} Cu _{0.375}) _{100-x} P _x	17 – 19	8.95	7.56	—	7.10
	19 – 20	8.68	6.83	—	8.95
fcc Pd		8.90	—	—	—
fcc Cu		—	7.10	—	—
fcc Ni		—	—	6.59	—

Fig.1 Molar volumes of Pd-Ni-P and Pd-Cu-P glasses as a function of phosphorus content.

Fig. 2. XPS spectra for of $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ and for three $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses with $x = 16.5$, 17.5, and 19 (left), and expanded view of the top of the d-bands for the $(\text{Pd}_{0.5}\text{Cu}_{0.5})_{100-x}\text{P}_x$ glasses. The reference energy is chosen as explained in the text.

REFERENCES

1. Y. He, T. D. Shen, and R. B. Schwarz, *Metall. Mater. Trans.* **29A**, 1795 (1998).
2. A. J. Drehman, A. L. Greer and D. Turnbull, *Appl. Phys. Lett.* **41**, 716 (1982).

3. F. M. Alamgir, H. Jain, A. C. Miller, D. B. Williams, R. B. Schwarz, *Phil. Mag. B* **79**, no. 2, 239 (1999).
4. D. S. Boudreaux and J. M. Gregor, *J. Appl. Phys.* **48**, 150 (1977); *ibid*, **48**, 5057 (1977).
5. P. H. Gaskell, *J. Non-cryst. Solids* **32**, 207 (1979).
6. R. B. Schwarz and Y. He, *Mater. Science Forum* **235-238**, 231 (1997).
7. T. D. Shen and R. B. Schwarz, *J. Mater. Res.* **14**, 2107 (1999).

Acknowledgement: This work was supported by the US Department of Energy, Office of Basic Energy Sciences. The authors thank Dr. John Wills for helpful discussions.