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### **Abstract**

This is the final report for a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). The objective of this work was to develop the competency for the synthesis of novel bulk amorphous alloys. We researched their synthesis methods and alloy properties, including thermal stability, mechanical, and transport properties. The project also addressed the development of vanadium-spinel alloys for structural applications in hostile environments, the measurement of elastic constants and thermal expansion in single-crystal TiAl from 300 to 750 K, the measurement of elastic constants in gallium nitride, and a study of the shock-induced martensitic transformations in NiTi alloys.

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## Background and Research Objectives

Metallic glasses have many technologically important properties that are not found when the alloy is in its crystalline form. These include high strength (in excess of 2 GPa), ductility in tension, and high corrosion resistance (especially for metal-metalloid glasses containing phosphorus). In addition, some ferromagnetic metallic glasses have extremely low hysteretic losses when used as cores of transformers and motors operating at 60 Hz. Other applications of ferromagnetic metallic glasses include toroidal magnetic cores for high-frequency transformers, targets in article surveillance systems, sensors, transducers, and high-energy pulsed-power devices.

Amorphous or glassy alloys can be prepared by cooling the melt at a rate sufficiently high to bypass crystallization while the undercooled melt is in the region  $T_1 - T_g$ . Here,  $T_1$  is the liquidus temperature and  $T_g$  is the glass-transition temperature. For most metallic alloys, the critical cooling rate to bypass crystallization is very high, on the order of  $10^6$  K/s. Because of the high cooling rate, at least one dimension of the amorphous product must be small, typically less than 50  $\mu\text{m}$ .

Since the 1980s, a few metallic melts have been known to require much lower critical cooling rates, enabling the production of "bulk" metallic glasses having thicknesses of at least a few millimeters. Since 1990, a serious effort on this topic has been carried out by Prof. Inoue and his collaborators at the Tohoku University in Sendai, Japan. In 1993, W. L. Johnson started research on beryllium-containing glasses at the California Institute of Technology (CalTech). The objective of our project was to develop at LANL the competency for the synthesis of bulk metallic glasses. The project started as a collaboration with Prof. Johnson (making use of our beryllium facilities), and continued as a study on the synthesis and properties of metallic glasses using fluxing techniques. Although our LDRD project has ended, continued research on this topic has been funded by DOE/BES.

## **Importance to LANL's Science and Technology Base and National R&D Needs**

Metallic glasses have many interesting properties that can be exploited for energy conservation. The clearer example relates to the low hysteresis losses of ferromagnetic metallic glasses. This property alone makes metallic glasses of national importance and of clear relevance to the DOE mission. As a point of illustration, it is interesting to evaluate the potential savings that could be achieved by replacing the current distribution transformers in the US electrical power network by similar devices built from metallic glass cores. The core losses in these transformers constitute approximately 1% of the total power generated. By 1990 this loss was estimated to be 60 billion kW-hr/yr, worth over \$4 billion at \$0.07/kW-hr. The use of metallic glasses enables reducing the energy loss by 60-70%, meaning that the savings would amount to billions dollars per year [1].

Although the advantageous properties of soft ferromagnetic glasses have been known for the last 30 years [2], the science and engineering needed to manufacture these metallic glasses in the form best suited for industrial applications has been slow to develop. Allied Signal (Parsippany, NJ) perfected techniques for glassy ribbon production and commercialized the manufacture of thin foils of about 30- $\mu\text{m}$  thick, 0.2-m width, and centimeters in length. Such soft ferromagnetic glass ribbons were introduced in 1978 at a price of about \$300/kg. Since then, the price has decreased almost linearly, and the current price for a 30- $\mu\text{m}$  thick glassy ribbon is comparable to the price of the 0.28-mm thick oriented crystalline Fe-3.2Si alloy, traditionally used in the manufacture of most transformers and motors operating at 60 Hz.

In spite of these developments, ferromagnetic metallic glasses have only been used to a small extent, mainly because the products are still only 30- $\mu\text{m}$  thick. Such thin foils are difficult to process into the shapes of solid cores and wound with continuous copper coils. Thus, the cost of manufacturing transformers and motors using metallic glasses is high not only because of the slightly higher cost of the core material, but also because of the more complicated manufacture. The manufacture problem would be largely alleviated with the availability of mm-thick ferromagnetic foils.

The decade of the 1970s saw a rapid development of ferromagnetic glasses. This development was motivated by (1) the oil embargo of 1973 (and the realization that electricity was no longer "penny cheap"); (2) the need of high performance materials for

high-energy pulsed-power systems for accelerators and lasers; (3) the development of new applications in magnetic pulse-compression techniques using saturable-core reactors; and (4) the need for energy-efficient switched-mode power supplies (in use in almost all televisions and personal computers). The relatively low price of oil in the last decade has slowed the research efforts on these materials and institutions such as Allied Signal have discontinued research on metallic glasses, except for tests in direct support of market applications. However, the lessons of history, and a possible future need to reduce CO<sub>2</sub> emissions suggests that efforts be made in the US to advance the science of amorphous metallic glasses, especially on the synthesis of ferromagnetic glasses.

The recent discovery that a number of metallic glasses can be prepared at cooling rates of 1 to 100 K/s has generated great interest because these alloys can be prepared in bulk form, where all dimensions are at least a few millimeters, or even centimeters. These alloys can be grouped into the classes RE-Al-TM (RE=rare earths, TM=transition metals), Mg-RE-TM, Zr-Al-TM, and Zr-Ti-Cu-Ni-Be. Most new alloy compositions for bulk metallic glasses have been developed in Japan and are protected by international patents. The beryllium-containing alloy  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  was developed at CalTech and, being non-magnetic, has only been commercialized into sporting equipment.

### **Scientific Approach and Accomplishments**

This LDRD project addressed the synthesis and properties of bulk metallic glasses. We started by studying the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy immediately following its discovery by Pecker and Johnson at CalTech [3]. Making use of the LANL beryllium facility, we were the first to show that this alloy can be manufactured as inch-diameter rods by simply arc-melting the alloy components in a grooved water-cooled copper hearth and turning the arc power off to let the alloy cool at a natural rate on the order of one hundred degrees per minute (Fig. 1). About 2-kg of this alloy were then shipped to Amorphous Alloys International (Laguna Niguel, CA), a small company interested in commercializing this alloy. At Los Alamos, we characterized the  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy by measuring its elastic properties, thermal expansion, and structural relaxation near the glass transition temperature. This work resulted in



Publications 1 and 2, and an invited presentation at the International Conference on Liquid and Amorphous Solids, Chicago, IL, 1996. It soon became apparent that we could not continue researching beryllium-containing alloys at Los Alamos because all sample preparation (cutting, polishing, etc.) had to be done within the beryllium facility, which is inaccessible to post-doctoral researchers and students lacking security clearances.

Our research work then switched to the  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  system. Millimeter-size bulk metallic glasses of this composition had been prepared by D. Turnbull and co-workers using a  $\text{B}_2\text{O}_3$  fluxing technique. The purpose of our research was:

1. to perfect the fluxing technique to produce much larger bulk metallic glasses,
2. to investigate the composition range for the formation of bulk metallic glasses in the Pd-Ni-P system (until then, bulk metallic glasses were known only at the  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  composition),
3. to investigate the possibility of using the fluxing method to prepare metallic glasses containing other elements (in particular, can the fluxing technique be applied to the synthesis of bulk glasses that contain no palladium?), and
4. to investigate the possibility of using the fluxing method to prepare ferromagnetic bulk metallic glasses.

The approach and results of the work are described in Publications 3 through 9. In Publication 3, we reported the formation of a 1 inch-diameter rod of amorphous  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ , shown in Fig. 2. At the time, this was the largest piece of metallic glass ever prepared. The one-inch diameter was determined by our supply of palladium at the time and is by no means an upper limit to the product that can be prepared by this technique. To achieve such a large amorphous sample, the alloy melt must be carefully purified to remove all heterogeneous nucleation centers. Usually, these centers are tiny oxide inclusions that move through the melt. These inclusions provide potent nucleation centers at which the melt crystallizes before one can sufficiently undercool it to reach the glassy state. To achieve glass formation, all such nucleation centers must be removed. In improving the flux-melting technique, we realized that we had made important innovations to the method to warrant a US patent disclosure. The Laboratory patent review office agreed with this evaluation and a US patent application has been submitted.

The research continued with the investigation of the glass-forming range in the Pd-Ni-P system. Figure 3 shows that bulk metallic glasses can be prepared over a wide composition range. Of particular interest is the fact that 10-mm diameter amorphous rods can be prepared at the composition  $\text{Pd}_{25}\text{Ni}_{57}\text{P}_{18}$ . For all these alloys, the difference between the crystallization temperature and the glass transition temperature exceeds 60 K, and for the  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  composition, it reaches more than 100 K. This opens a window for the manufacture of *near-net-shape* products using techniques based on injection molding.

There are various other elements that can be purified using the  $\text{B}_2\text{O}_3$  flux. These include Fe, Cu, and Ni. Our research showed that the fluxing technique could be applied to the synthesis of Pd-Cu-P, Pd-Cu-Ni-P, and Pd-Fe-Ni-P glasses over a wide composition ranges (Figures 4, 5, and 6). These are new bulk metallic alloy compositions, never reported before. Figures 5 and 6 show the composition ranges for bulk glass formation in the latter two alloys. Of particular interest is the fact that in the Pd-Fe-Ni-P system, glass formation requires the Fe content to be lower than 20 at.%. Unfortunately, none of the bulk Fe-containing glasses prepared by this method was ferromagnetic. However, the  $\text{Pd}_{40}\text{Ni}_{22.5}\text{Fe}_{17.5}\text{P}_{20}$  bulk glass showed strong spin-glass behavior, as indicated in Fig. 7. Its associated magnetocaloric effect suggests that these glasses may be used in magnetic refrigeration.

The capability developed under this LDRD project for the synthesis of metallic glasses has benefited various other DOE projects. Samples prepared under this project have been supplied to researchers at universities and national laboratories. These collaborations include:

- With M. Miller (ORNL), we are studying the atomic structure of these glasses using field emission atom probes. We are interested in relating the atomic structure with the ease of glass formation. In particular, we want to investigate whether the resistance to crystallization is due to the presence of strong short-range ordering in the undercooled melt. Parts of this work have been reported in Publication 8.
- With T. Egami and W. Dmowski (Univ. of Pennsylvania), we are studying the microstructure of our metallic glasses using the National Synchrotron Light Source at

Brookhaven National Laboratory. These studies are complimentary to those described above. Results of this work have been reported in Publication 9.

- With G. Kwei and M. Hundley (LANL), we are using neutron diffraction (at Argonne National Laboratory) to investigate the phonon structure of these bulk glasses. Of particular interest is the existence of a peak in the low-temperature specific heat (the so-called Boson peak) that is ubiquitous to all amorphous structures (metallic, oxides, etc). The Boson peak reflects a large density of phonon states of low energies and suggests the existence of lattice resonant modes with low restoring constant and/or high effective mass.

It is clear then that our first three goals were achieved during the duration of this LDRD project, and the fourth goal has also been achieved in FY1998 under DOE/BES funding.

The remainder of this report describes some additional short-term activities pursued during this three-year LDRD project.

Mechanical alloying techniques were used to prepare a novel vanadium-spinel alloy that is quite resistant to degradation in radiation environments (i.e., no swelling or bubble formation). The composite has a hardness in excess of 12 GPa. With only 20 vol.% vanadium, the toughness was about 5 times that of pure spinel, which is still too low for structural applications. We found that the toughness was limited by the formation of an oxygen-stabilized tetragonal vanadium phase. New alloys were prepared with the addition of percent levels of titanium and chromium. In the new alloys the oxygen content is below 1 at.% and show no tetragonal vanadium phase. The mechanical properties of these alloys are being measured. The work started by this LDRD project will continue during FY1998 with support from DOE/BES. Results of this work have been reported in Publications 10 and 11.

Gallium nitride is a wide band gap (3.4 eV) compound semiconductor. Due to a breakthrough in 1992 that made it possible to dope GaN to *p*-type, *p-n* junctions of GaN can now be fabricated. This has opened the way for the development of blue light emitting diodes (which are already commercialized) and, more recently, laser diodes. In addition, the wide band gap and high melting point of GaN make it, along with SiC, a promising material for high-power and high-temperature electronic devices. To fabricate devices based on GaN using heteroepitaxy methods, one must know accurately the five

independent elastic moduli of GaN. These material constants were poorly known since the measurements were made on thin films using low-accuracy techniques. In 1996, we obtained a unique GaN single crystal (2 x 2 x 0.2 mm) grown at the Ioffe Physico-Technical Institute (Russia). Although this crystal was too small for any measurement based on an acoustic echo technique, its size proved to be sufficient for using the resonant ultrasound techniques developed at LANL. The five elastic moduli were measured and the results were reported in Publication 12.

Intermetallic compounds based on TiAl are considered potential lightweight materials for high temperature structural applications. In spite of its clear technological importance, the elastic constants of TiAl had not been measured. We used the resonant ultrasound technique to measure, for the first time, the six independent elastic moduli of a single crystal of  $\gamma$ -TiAl (Ti<sub>44</sub>Al<sub>56</sub>) from room temperature to 500°C. We used the elastic moduli to calculate the Young's and shear moduli along various crystal directions and the anisotropy factors. This work was reported in Publications 13 and 14.

High pressures generated by shock waves can be used to drive pressure-induced phase transformations. In some cases (e.g., graphite-to-diamond and hexagonal-to-cubic boron nitride), the high pressure state is retained upon decompression, enabling the synthesis of novel metastable materials. Indeed, the shock compaction of graphite with explosives is the commercial method for the synthesis of diamond powder for grinding applications. When a shock wave reaches a free surface, it is reflected as a rarefaction wave, a phenomenon that leads to spallation. Can spallation in materials be mitigated by the dissipation of energy through phase transformations? Very little is known about phase transformation induced by negative stresses. In collaboration with N. Thadhani (Georgia Inst. of Tech., we investigated phase transformations in NiTi alloys subjected to negative stress pulses. We demonstrated that shock-impact-generated, tensile-stress pulses induce a martensitic transformation from B2-to-monoclinic phase. Further results are described in Publication 15.

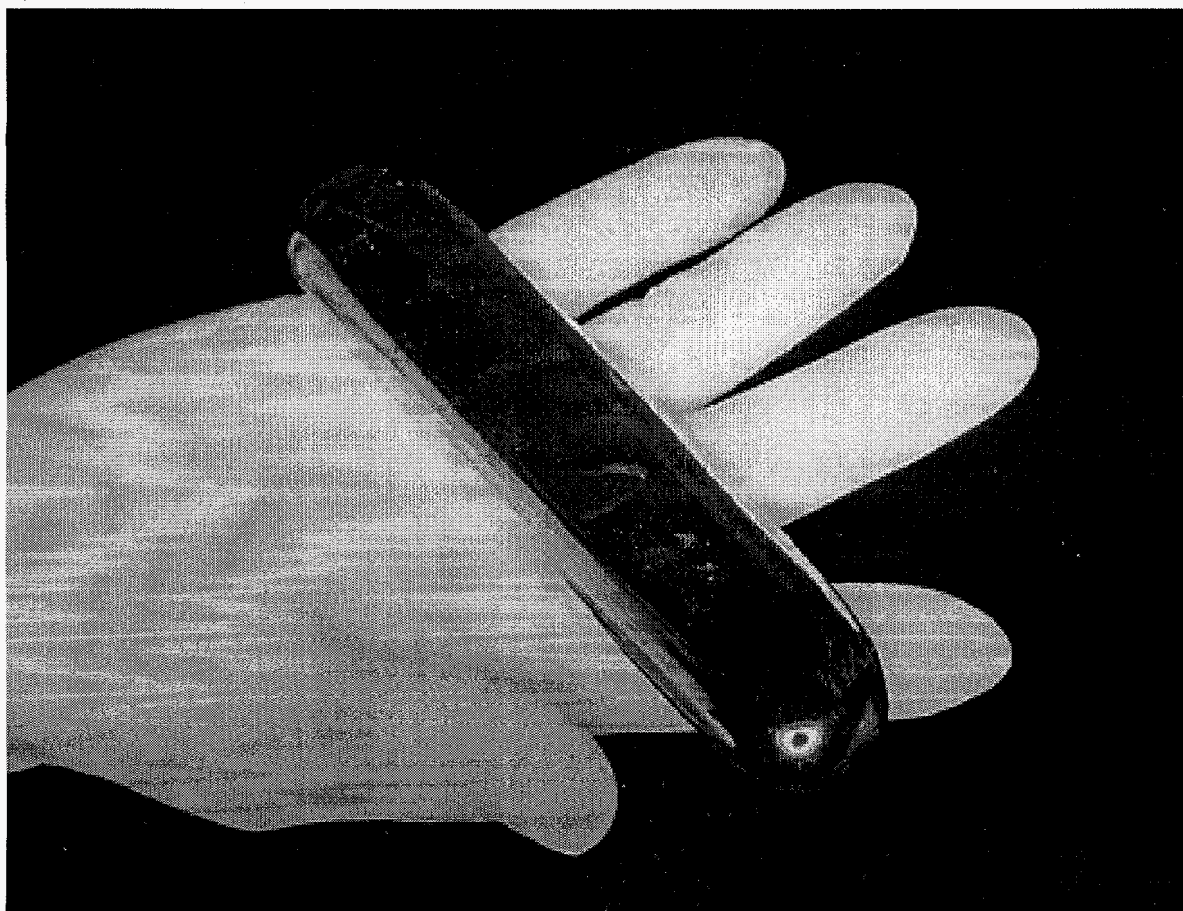
## Publications

1. Yi He, R. B. Schwarz, D. Mandrus, and L. Jacobson, "Elastic moduli, density, and structural relaxation in bulk amorphous  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy," *J. Noncrystalline Solids*, **205-207**, 602-606 (1996).
2. Y. He, R. B. Schwarz, and D. G. Mandrus, "Thermal expansion of bulk amorphous  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy," *J. Mater. Res.*, **11**, 1839-1841 (1996).
3. Y. He, R. B. Schwarz, and J. I. Archuleta, "Bulk Glass Formation in the Pd-Ni-P System," *App. Phys. Letters* **69**, 1861 (1996).
4. B. Schwarz and Y. He, "Bulk Metallic Glass Formation in the Pd-Ni-P and Pd-Cu-P Systems," in *Properties of Complex Inorganic Solids*, edited by Gonis et al. (Plenum Press, New York, 1997), p. 287-299.
5. R. B. Schwarz and Y. He, "Formation and Properties of Bulk Amorphous Pd-Ni-P Alloys," in "Synthesis and Properties of Mechanically Alloyed and Nanocrystalline Materials," Proceedings of the ISMANAM International Symposium, Rome, Italy, May 20-24, 1996. Edited by D. Fiorani and M. Magini. Also published in *Materials Science Forum (Trans Tech. Public.)* **235-238**, 231-240 (1997).
6. Y. He and R. B. Schwarz, "Synthesis and Properties of Bulk Metallic Glasses in the Pd-Ni-P and Pd-Cu-P Systems," Fall 1996 Meeting of the Mater. Res. Soc., Boston, MA, Dec. 2-6, 1996 (in press).
7. Yi He, TongDe Shen, and R. B. Schwarz, "Bulk Amorphous Metallic Alloys: Synthesis by Fluxing and Properties," *Metallurgical Transactions* (in press, 1997).
8. M. K. Miller, D. J. Larson, R. B. Schwarz, and Yi He, "Decomposition in  $Pd_{40}Ni_{40}P_{20}$  Metallic Glass," *Mater. Sci. And Engineering A*, (in press, 1997).
9. T. Egami, W. Dmowski, Yi He, and R. B. Schwarz, "Structure of Bulk Amorphous Pd-Ni-P Alloys Determined by Synchrotron Radiation," *Metallurgical Transactions* (in press, 1997).
10. E. Üstündag, K. E. Sickafus, Y. He, R. B. Schwarz, P. C. Panda, and R. Raj, "Metal-Ceramic Composites for Hostile Environment Application," in "Advances in Ceramic Matrix Composites III," ed. N. P. Bansal (Amer. Ceramic Soc., Westerville, OH, 1996). Also in *Ceramic Transactions Vol. 74* (in press, 1997).
11. R. B. Schwarz, C. J. Wetteland, T. D. Shen, E. Ustundag, and K. E. Sickafus, "Vanadium-Spinel Composites for Structural Applications in Hostile Environments," *Materials Science and Engineering A*, (in press, 1997).
12. R. B. Schwarz, K. Khachatryan, E. R. Weber, "Elastic Moduli of Gallium Nitride," *Applied Phys. Lett.* **70**, 1122-1124 (1997).

13. Y. He, R. B. Schwarz, A. M. Migliori, and S. H. Whang, "Elastic Constants of Single Crystal  $\gamma$ -TiAl," *J. Mater. Research* **10**, 1187 (1995).
14. Yi He, R. B. Schwarz, T. Darling, M. Hundley, S. H. Whang, and Z. M. Wang, "Elastic Constants and Thermal Expansion of Single Crystal  $\gamma$ -TiAl from 300 to 750 K," *Materials Sci. Eng Engineering A*, (in press 1977).
15. M. Thakur, N. N. Thadhani, and R. B. Schwarz, "Shock-Induced Martensitic Transformations in Near-Equiatomic NiTi Alloys," *Metall. Transactions* **28A**, 1445-1455 (1997).

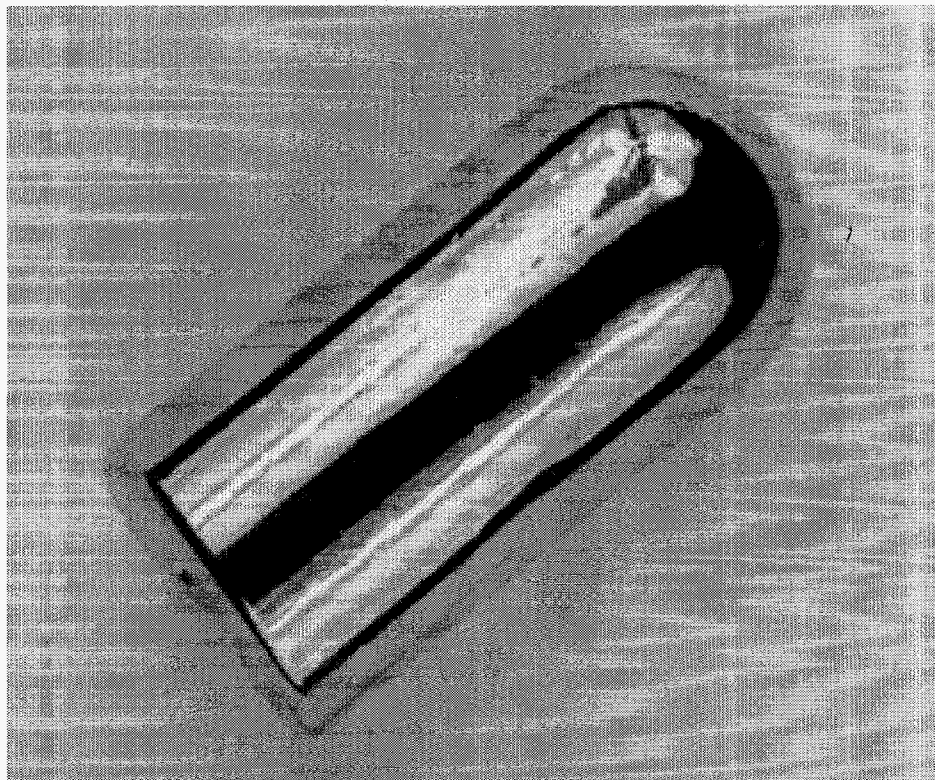
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- [2]. P. Duwez and S. C. H. Lin, *J. Appl. Phys.* **38**, 4097 (1967).
- [3]. A. Pecker and W. L. Johnson, *Appl. Phys. Lett.* **63**, 2342 (1993).



**Figure 1.** 270-g ingot of amorphous  $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$  alloy prepared by arc-melting the elements in a water-cooled copper hearth and letting the melt solidify after turning the arc off.

Figure 2. 300-g rod of bulk amorphous  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  with 25 mm in diameter prepared by fluxing in  $\text{B}_2\text{O}_3$  and water quenching, as described in Publication 1.





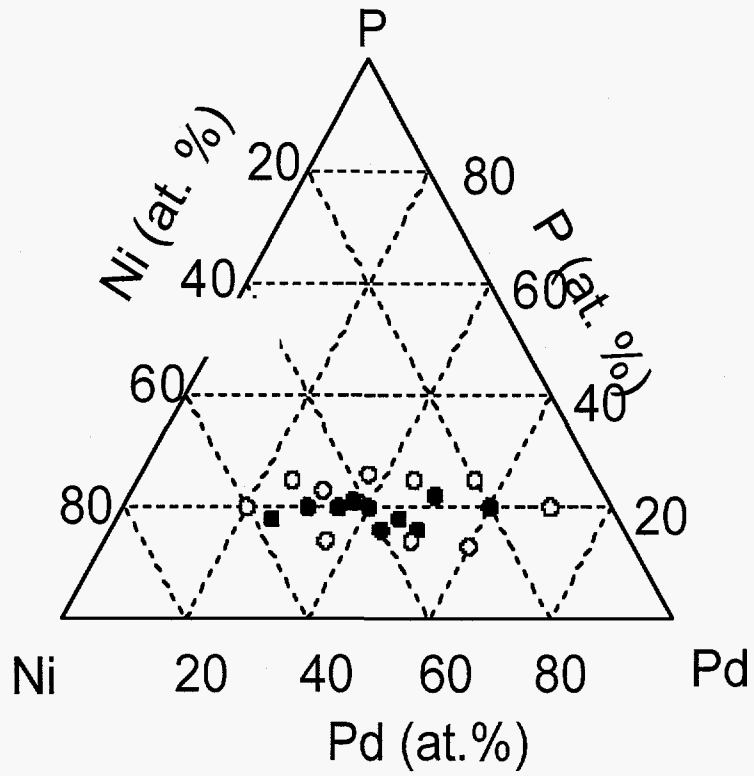


Figure 3. Compositional range for bulk amorphous phase formation in the Pd-Ni-P alloy system. Filled symbols denote the compositions where the products were 10-mm diameter amorphous rods; open symbols represent crystalline products (for this diameter rod).

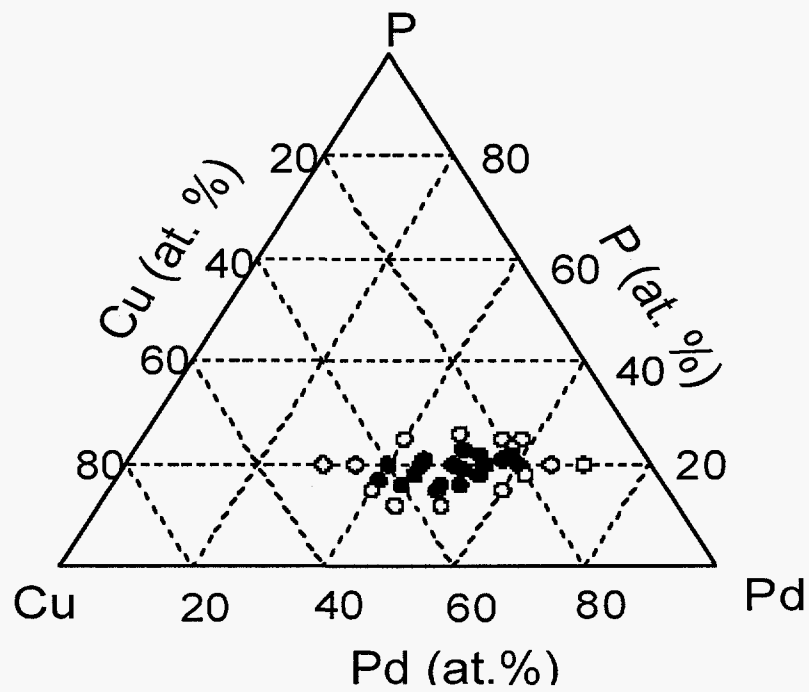


Figure 4. Compositional range for bulk amorphous phase formation in the Cu-Pd-P alloy system. Filled symbols denote the compositions where the products were 7-mm diameter amorphous rods; open symbols represent crystalline products (for this diameter rod).

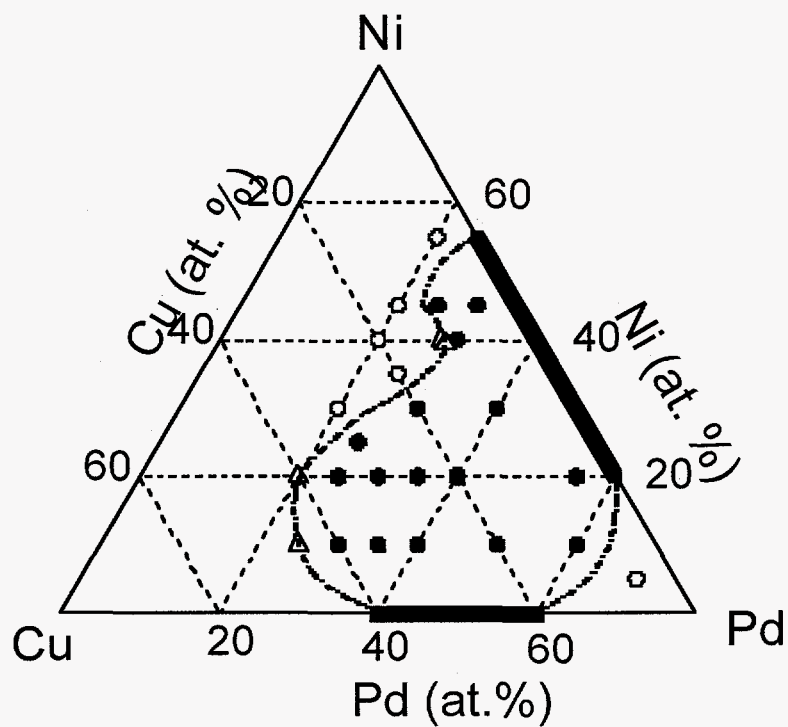
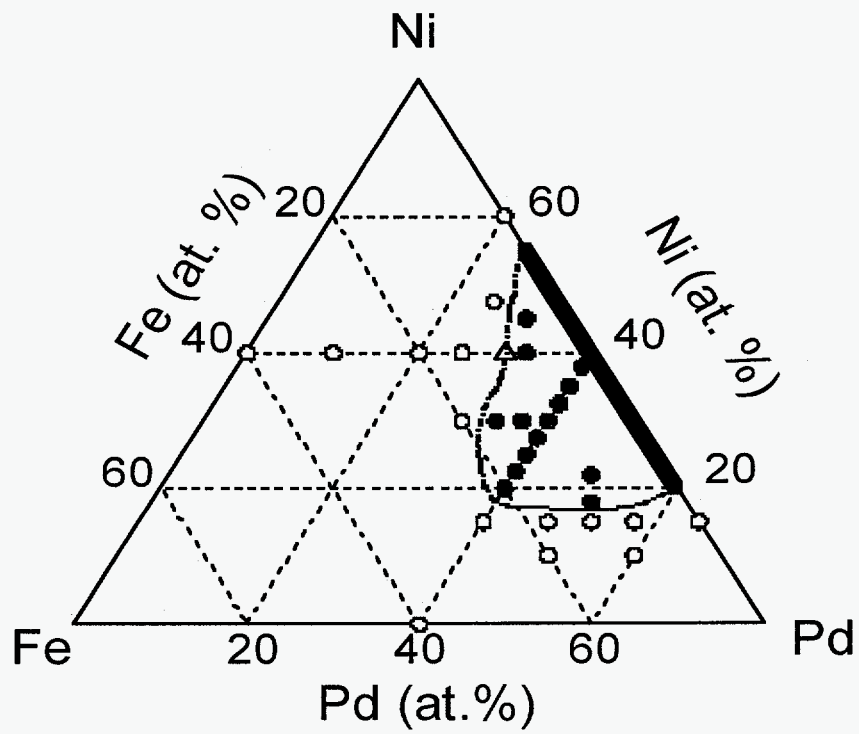


Figure 5. Compositional range for bulk amorphous phase formation in the  $(\text{Pd-Cu-Ni})_{80}\text{P}_{20}$  alloy system. Filled symbols denote the compositions where the products were 7-mm diameter amorphous rods; open symbols represent crystalline products (for this diameter rod).

Figure 6. Compositional range for bulk amorphous phase formation in the  $(\text{Pd-Fe-Ni})_{80}\text{P}_{20}$  alloy system. Filled symbols denote the compositions where the products were 7-mm diameter amorphous rods; open symbols represent crystalline products (for this diameter rod).



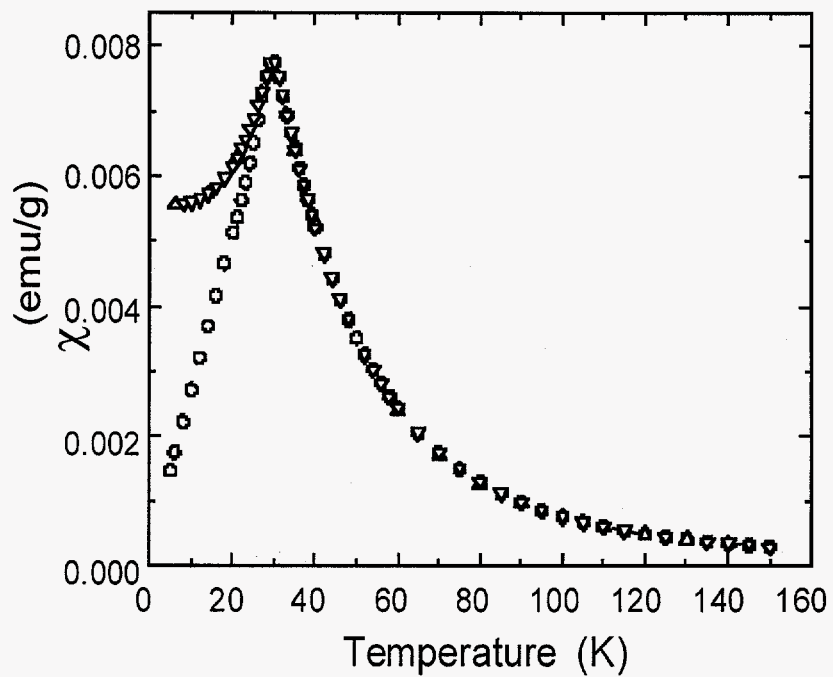


Figure 7. Temperature dependence of the susceptibility of amorphous  $\text{Pd}_{40}\text{Ni}_{22.5}\text{Fe}_{17.5}\text{P}_{20}$  alloys. Up-pointing and down-pointing triangles are data taken while cooling and warming the sample under an applied field of 10 Oe. Circles are data taken while heating the sample after it was cooled in zero applied field. The sharp cusp at about 30 K and the difference between the zero-field-cooled and field cooled data is indicative of spin-glass behavior.