

FIG. 2. ESR spectrum for pure silica optical fiber with a 70 μm diameter.

remarkably with increasing surface area ratio while the E' -center ESR intensity was kept almost unchanged. Moreover, the hfs ESR intensity was almost directly proportional to the surface area ratio. These results suggest that the hfs is present at or near the fiber surface.

As already mentioned, the VAD preforms contain extremely low hydroxyl ion content. For the γ -ray irradiated water-free VAD preform, we observed the E' center, but not the hydrogen hfs. Vitko has not observed the hfs for the γ -ray irradiated low water silica either.⁸ These results indicate that the hydrogen hfs is not present inside the optical fiber.

In spite of the water-free VAD optical fiber, the possibility of the hydrogen hyperfine interaction, however, is present near or at the surface. It is well known that silica contains considerably high concentrations of the hydroxyl group. Moreover, physically adsorbed water molecules exist at the optical fiber surface at RT, and it is possible that the water molecule may be dissolved and diffused into the optical fiber from the surface. Vitko also suggested that the formation of the 119-G doublet might involve the migration of hydrogen. From these results and the fact shown in Fig. 3, it can be concluded that the hfs is due to hydrogen interaction at the optical fiber surface.

In conclusion, the hydrogen hf doublet with splitting of 119 G, which is due to an electron trapped at a hydrogen

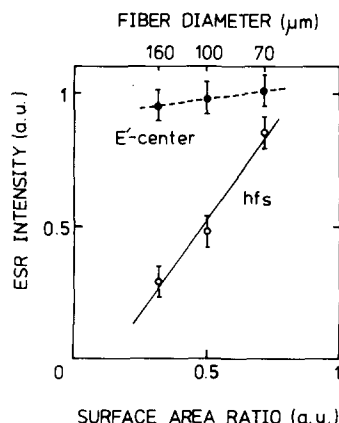


FIG. 3. Relationship between ESR intensities per unit sample mass and optical fiber surface area ratio.

compensated substitutional germanium, was observed for the silica optical fibers. The hfs ESR intensity increased with increasing the fiber surface area. These results suggest that the hydrogen hf interaction takes place at or near the optical fiber surface.

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Formation of bulk metallic glass by fluxing

H. W. Kui, A. L. Greer,^{a)} and D. Turnbull

Division of Applied Sciences, Harvard University, Cambridge, Massachusetts 02138

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Bulk specimens (0.4–4 g mass) of the alloy $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ have been undercooled consistently to the glass state, with no detectable superficial crystallinity, in a molten flux of dehydrated boron oxide. The minimum dimension of the most massive glass specimen, so formed, was 1.0 cm. The absence of crystallinity in the specimens was confirmed by x-ray diffraction, scanning electron microscopy, and calorimetry.

Drehman, Greer, and Turnbull¹ reported that when subjected to certain surface and annealing treatments the alloy $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ can be quenched from its molten to glass state in virtually bulk form at cooling rates of only 1 °C/s.

^{a)}Present address: Department of Metallurgy and Materials Science, University of Cambridge, Cambridge CB2 3QZ, England.

The largest ingot had a mass of 2.3 g and minimum dimension 0.6 cm. It exhibited some superficial crystallinity which included less than 2% of its total mass. This behavior reflects a high resistance in this alloy to homogeneous nucleation which was attributed to its exceptionally high reduced glass temperature $T_{rg} \sim 0.67$.² The treatments employed to remove the heterogeneous nucleation centers, which initiate

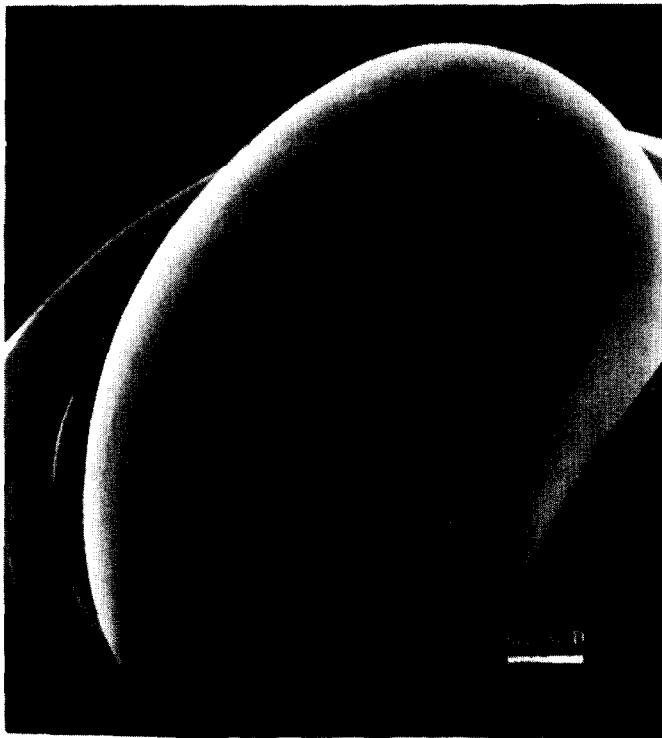


FIG. 1. Cross section of largest glassy ingot.

crystallization at reduced temperatures well above T_{rg} , were to subject the alloy to a succession of chemical etching treatments alternating with heating in vacuo to temperatures well in excess of the liquidus. An alternate approach to the removal of nucleating heterogeneities, which has been employed effectively in a number of investigations,^{3,4} is to heat and cool the molten metal while it is immersed in a molten oxide flux; after gravity segregation to the oxide-metal interface most heterophase impurities presumably are dissolved or deactivated (e.g., by being wet) by the molten oxide. In this letter we report the formation of bulk $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glass by cooling its melt in molten B_2O_3 fluxes. B_2O_3 is still molten at the glass transition temperature T_g ($\sim 330^\circ\text{C}$) of the alloy.

Boron oxide, nominally anhydrous and 99.995% pure, was obtained from Atomergic Chemical Corporation. To remove as much residual water as possible, it was preheated at 1000°C for 36 h in a Pt crucible contained in an evacuated (to $\sim 10^{-3}$ Torr) fused silica tube. After cooling it was stored in a vacuum desiccator until used.

To form the alloy Ni_2P (99.9% pure) powder was melted and solidified in vacuo in a fused silica tube and then alloyed with a Pd (99.9% pure) ingot by rf induction melting also in vacuo in a fused silica crucible.

In the experiment a resulting $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ ingot and B_2O_3 (just enough to immerse the whole alloy) were put together in a dry, cleaned fused silica tube (i.d. = 11 mm). The system was then subjected to a degassing treatment in which the alloy and B_2O_3 were melted under a vacuum of 10^{-3} Torr, held in the molten state ~ 2 min, and then cooled to a temperature (400°C) where B_2O_3 was still molten. Usually degassing was nearly complete after a second such melting-solidification cycle.

Following degassing the system was heated to a tem-

perature ($\sim 1000^\circ\text{C}$) and then cooled to a temperature below the alloy but above the B_2O_3 T_g , with the silica tube closed and the vacuum pump turned off to minimize vibrations. This cycle, duration usually ~ 3 min, was repeated until we judged from visual observation that the alloy remained amorphous through the cooling part of the cycle. The occurrence of crystallization during cooling was manifested by a change in reflectivity which followed the slow passage (~ 2 s) of the crystal melt interface across the alloy. After several thermal cycles the surface of the alloy became highly reflecting with no superficial film apparent. Eventually every alloy specimen tested, eight in number and with masses ranging from 0.4 to 4 g reached a condition, after many such cycles, in which no crystallization was exhibited and the surface of the alloy remained very smooth and highly reflecting. When this condition was realized we cooled the system to room temperature, removed the alloy specimen and examined it for evidence of crystallinity.

To prepare it for examination the specimen was cut into two halves and the exposed surfaces were polished and etched with aqua regia. No crystal boundaries were revealed by either optical or scanning electron microscopy. X-ray diffraction from several representative sections of the surfaces exhibited only the diffuse halos characteristic of the amorphous alloy; no crystalline diffraction peaks were detected. Differential scanning calorimetry, on specimens cut from the largest glassy ingot and reheated, at $10^\circ\text{C}/\text{min}$, indicated $T_g \sim 590$ K, crystallization onset at ~ 650 K, and a heat of crystallization of 5.5 ± 0.3 kJ/g atom; in fair agreement with the thermal results of Drehman *et al.*^{1,5} We concluded, therefore, that our specimens were entirely amorphous with no detectable superficial crystallinity.

The minimum linear dimension d_{\min} of our 4-g amorphous specimen (see Fig. 1) was about 1 cm (cf. with $d_{\min} \sim 0.6$ cm of the largest glass specimen reported by Drehman *et al.*¹). To our knowledge, this specimen is the thickest of any metallic glass yet formed by melt cooling. The extremely low probability of crystal nucleation in this alloy reflects a highly effective elimination of heterophase nucleants by our fluxing technique and that the steady nucleation frequency is very low and/or the transient times to steady state are relatively long.⁵

Our boron oxide fluxing method improves on our earlier one, based on surface etching pretreatments, by producing specimens which are wholly glassy and more massive and in producing them more consistently.

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