

## Soft X-ray Emission Spectroscopy of Pd-based Bulk Metallic Glasses

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## Introduction

We have studied the electronic structure of bulk metallic glasses (BMG) *i.e.* bulky multi-component amorphous alloys, in order to clarify the origin of their high glass forming ability (GFA) from a microscopic point of view of their electronic structure. BMG have useful engineering properties such as high mechanical strength, good shaping ability, high corrosion resistance, and soft magnetic properties [1]. In spite of their thermodynamically metastable phase, they show very strong resistance to crystallization of the supercooled melt and the clear glass transition. Although their GFA has been often discussed in terms of the empirical rules [2], Pd-based BMG do not satisfy the rules and the origin of the GFA has not been well understood yet. Recently the importance of local clusters has been suggested in Pd-based BMG [3], where the strong chemical bond between P and transition metals may be formed. In this report, we will show the results of the P  $K\alpha$  and Pd  $L\beta_{2,15}$  X-ray emission (XES) measurement on Pd-based BMG.

## Experimental

Specimens, Pd<sub>40-x</sub>Ni<sub>40+x</sub>P<sub>20</sub>, Pd<sub>40-x</sub>Cu<sub>40+x</sub>P<sub>20</sub>, and Pd<sub>42.5</sub>Ni<sub>7.5</sub>Cu<sub>30</sub>P<sub>20</sub>, of 3 mm in length and 2 mm in diameter were prepared by a casting method and their amorphous phases were confirmed by X-ray diffraction measurement. Their P  $K\alpha$  and Pd  $L\beta_{2,15}$  XES spectra were measured at BL-11B with use of a Ge(111) double crystal monochromator for excitation and a Yohan-type spectrometer ESCARGOT for XES measurement. The photon energy for both the monochromator and the spectrometer was calibrated by the measurement of the P  $K$ - and Pd  $L_3$ -edge X-ray absorption spectra of InP and Pd, respectively.

## Results and Discussion

In Fig.1, the P  $K\alpha$  XES spectrum of Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> is compared with its hard X-ray and vacuum ultraviolet photoemission (HXPS and UPS) spectra [4] and the partial density of states (DOS) per atom calculated by the DV- $X\alpha$  method [5] for a Pd<sub>3</sub>Ni<sub>6</sub>P trigonal prism cluster shown in the inset. Here, the binding energy for the XES spectrum was estimated from the binding energy 2143.54 eV of the P 1s core level obtained by HXPS with the correction by 0.1 eV due to the recoil effect. The Pd<sub>3</sub>Ni<sub>6</sub>P cluster was extracted from a related crystal [3] and its electronic structure does not depend so much on the arrangement of Pd and Ni in

the cluster. In the upper and lower UPS spectra, the Ni 3d and Pd 4d bands, respectively, become dominant, while the *sp* states are enhanced in the HXPS spectrum [6]. Although the XES spectrum indicating the P 3p DOS seems slightly shifted to the high binding energy side, which may be caused by the ambiguity of the photon energy calibration, all the experimental results are quite well understood by the electronic structure of the trigonal prism cluster. This indicates the predicted strong *p-d* bond between P and its surrounding Pd and Ni and the presence of the trigonal prism clusters in Pd-Ni-P BMG. The network of such clusters can be formed by sharing their vertices and sides because of the highly stable covalent nature of P-(Pd, Ni) bonds in the cluster and the large flexibility in the inter-cluster connection, as the SiO<sub>4</sub> clusters in the silica glass.

In summary, we have found the strong chemical bond in the Pd-Ni-P clusters, which may result in the reduction of the internal energy and the resistance to crystallization; the formation of the flexible network of the clusters may also increase the entropy. These lead to the high GFA of Pd-based BMG.

## References

- [1] M. Telford, *Materials Today* **7** (2004) 36.
- [2] A. Inoue, *Acta Mater.* **48** (2000) 279.
- [3] T. Takeuchi *et al.*, *Mater. Trans.* **48** (2007) 1292.
- [4] K. Soda *et al.*, *AIP Conf. Proc.* **879** (2007) 1821.
- [5] H. Adachi *et al.*, *J. Phys. Soc. Jpn.* **45** (1978) 875.
- [6] J. J. Yeh and I. Lindau, *Atomic Data and Nucl. Data Tables* **32** (1985) 1.

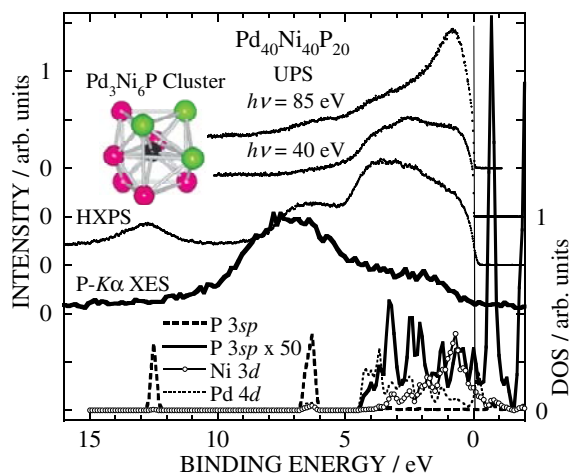


Fig.1 P  $K\alpha$  XES spectrum of Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> BMG.