

V-C Electronic Structure and Phase Stability of Bulk Metallic Glass

In this project, we have investigated the electronic structure and chemical bonding of the bulk metallic glasses, bulky multi-element amorphous alloys, experimentally by means of the synchrotron light photoemission spectroscopy and theoretically by the electronic structure calculation for their characteristic clusters, in order to understand the origin of their large glass forming ability from the microscopic point of view. Bulk metallic glasses show very high resistance against the crystallization of the super-cooled melt and a clear glass transition in spite of their thermodynamically metastable phase, and they have drawn much attention as new materials possessing useful engineering properties such as high mechanical strength, high corrosion resistance, good shaping ability, and soft-magnetic properties.

V-C-1 Electronic Structure of Bulk Metallic Glass $Zr_{55}Al_{10}Cu_{30}Ni_5$

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[*J. Electron. Spectrosc. Relat. Phenom.* **144-147**, 585–587 (2005)]

The electronic structure of a bulk metallic glass $Zr_{55}Al_{10}Cu_{30}Ni_5$ has been studied by means of photoelectron spectroscopy in order to understand the origins of its large glass formation ability and unique mechanical properties from the microscopic point of view. The valence-band photoelectron spectra show three bands ascribed to the Zr *4d*, Ni *3d* and Cu *3d* states. Remarkable feature of these bands is the highly-symmetric spectral shape with the high binding energy and narrow width in comparison with the *d* bands of the crystalline transition metals. This is attributed to the lack of the crystalline periodicity in the metallic glass as well as the reduction in the neighboring atoms to hybridize with those transition metals. High-resolution valence-band spectrum also reveals the intensity reduction near the Fermi level, which implies that the pseudo-gap in the electronic structure may be one of the important factors for the glass formation.

V-C-2 Free-Energy Estimation of the Zr-Ni-Al Bulk Metallic Glass from the Local Atomic Arrangements of the Relevant Crystals

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[*Mater. Trans.* **46**, 2791–2798 (2005)]

Free-energy of Zr-Ni-Al bulk metallic glass (BMG) was estimated by making full use of coordination clus-

ters in the relevant crystals. The clusters in the BMG were determined by using the BMG's experimentally determined radial distribution functions, and the electronic structure of the identified clusters was calculated by the DVX α cluster calculation. The local atomic arrangements in the Zr-Ni-Al BMG are found to be characterized by the prism clusters with Zr or Ni atom in their center and the Kasper polyhedrons about Al atoms. It was concluded, as a consequence of the present analysis, that the Zr-Ni-Al BMG are stabilized by the low internal energy of the constituent local atomic clusters assisted by the large entropy caused by the freedom in the bond-direction between the prism clusters and the Kasper polyhedrons.

V-C-3 Investigation of Stability of the Zr-Ni-Al Bulk Amorphous Phase from Local Atomic Arrangements of the Relevant Crystals

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[*J. Jpn. Soc. Powder Metallurgy* **53**, 100–106 (2006)]

Stability of the Zr-Ni-Al bulk metallic glass (BMG) was investigated by making full use of its relevant crystals. The local atomic arrangements (characteristic atomic clusters) commonly existing in the BMG and its relevant crystals were identified by the experimentally determined radial distribution functions. We found that the local atomic arrangements of the BMG were characterized by the prism clusters with a transition element, Zr or Ni, in their center and the Kasper polyhedron about an Al atom. Internal energy of these clusters was investigated by combinational use of the DVX α cluster calculation and the high-resolution photoemission spectroscopy. The prism clusters about the transition metal elements were confirmed to possess a low internal energy. We propose, as a consequence of present analysis, that the Zr-Ni-Al BMG is stabilized by the low internal-energy of the cluster and the large entropy caused by the freedom in the bond-direction between the clusters.

V-C-4 Electronic Structure of Zr-TM-Al (TM = Ni, Cu) Bulk Metallic Glasses

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[*J. Jpn. Soc. Powder Metallurgy* **53**, 107–110 (2006)]

The valence-band electronic structures of Zr-TM-Al (TM = Ni, Cu) bulk metallic glasses have been investigated by means of synchrotron-radiation photoelectron spectroscopy. Their valence-band spectra show Zr 4d-

Ni 3d- and Cu 3d-derived bands at the binding energies of 0.5, 2.0 and 3.6 eV, respectively. The Zr 4d-derived band becomes prominent around the excitation photon energy $h\nu$ of 40 eV. It is found that the wider the super-cooled liquid region $\Delta T_x = T_x - T_g$ (T_x : the crystallization temperature, T_g : the glass transition temperature), the larger the peak binding energy of the Zr 4d-derived band becomes. For the photoexcitation at $h\nu \sim 18$ eV, where the Zr 4d states less contribute to the spectrum, the spectral intensity reduces towards the Fermi level. This may imply the formation of a pseudogap in the sp bands. It is also found that the width of the pseudogap for the occupied states becomes wider as ΔT_x is increased. These spectral findings suggest that both the strength of the chemical bonding around Zr and the reduction in the electronic energy because of the pseudogap formation and the chemical bonding contribute to the large glass formation ability of the Zr-Cu-Al metallic glasses.

V-D Electronic Structures of Fe₂VAl Intermetallic Compound and Its Related Alloys

In this project, we have studied the electronic structures of the Heusler-type intermetallic compound Fe₂VAl and related alloys experimentally with use of the synchrotron light photoemission spectroscopy and theoretically by both the band structure calculation with a super cell and the cluster calculation, in order to clarify the mechanisms of its unusual transport properties and of the large enhancement of their thermoelectric properties. Fe₂VAl and related alloys have been received much attention because of not only the scientific interest in the anomalous transport properties at low temperatures but also their potential application for thermoelectric materials.

V-D-1 Surface and Bulk Electronic Structures of Heusler-Type Fe₂VAl

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[*J. Vac. Sci. Technol., A* **24**, 1464–1467 (2006)]

Surface and bulk electronic structures of Heusler-type ($L2_1$ -type) Fe₂VAl have been investigated by photoelectron spectroscopy, in particular, for the valence band and V 2p core level regions, in order to elucidate the changes in the valence band electronic structures for the surface and bulk regions. In the valence band spectrum, the intensity at the Fermi level E_F is increased for the surface-sensitive low photon energy excitation in comparison to the bulk-sensitive high photon energy excitation. It is also found that the intensity around a binding energy of 0.4 eV is enhanced for large photoelectron takeoff angles for the bulk-sensitive photoelectron spectrum. The V 2p core level spectrum shows a surface-derived shoulder structure on the low binding energy side of the main feature, which suggests that the valence electron concentration around V may be large in the surface layers in comparison to the bulk. These facts suggest that a pseudogap is formed around E_F in the

bulk electronic structure, as predicted by band calculations, and that it is destroyed in the surface layers by the V 3d states as well as the Fe 3d states emerging in mid pseudogap of the bulk electronic structure.