2020AG023 BL-7

Electronic Structures and Chemical Natures of Inhomogeneous Gd-TM (TM = Co, Ni, and Cu) Metallic Glasses

Shinya Hosokawa,[a] Jens R. Stellhorn,[b] Hitoshi Sato,[c] Jing Jiang,[d] and Hidemi Kato[d]

[a] *Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan*
[b] *Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima 739-8527, Japan*
[c] *Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima, 739-0046, Japan*
[d] *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

Keywords: Metallic glasses, Thermal rejuvenation effect, Heterogeneity, Chemical nature.

Recently, Ketov *et al.* [1] proposed a new type of the rejuvenation effect in metallic glasses, *i.e.*, a relaxation to a higher energy state, by a thermal cycle. According to their interpretation, if a glass is not elastically homogeneous, the thermal expansion coefficient has a distribution over the glass sample. By repeated temperature changes, magnitudes of thermal expansions are different depending on the positions in the glass, which surely induces shearing forces, and as a result, a rejuvenation effect occurs in the glass. They named this phenomenon as "Rejuvenation of metallic glasses by non-affine thermal strain". The validity of this logic is the subject to the discussion.

Yamazaki [2] intensively studied β-relaxation peaks in Gd-TM (TM = Co, Ni, and Cu) glasses. The β-peaks are remarkably larger than those of other metallic glasses, and thus, large heterogeneities are expected in these glasses. He also found that the heterogeneities highly depend on the transition metal elements, *i.e.,* Ni > Co > Cu.

In order to clarify the structural changes by the rejuvenation effect, we measured high-energy x-ray diffraction measurements. The rejuvenation of the glass samples was made by a thermal cycling between the liquid N_2 and room temperatures 40 times. The obtained pair distribution functions, $g(r)$, have two distinct peaks, where the shorter and longer ones (0.29 and 0.35 nm) correspond to the Gd-TM and Gd-Gd correlations, respectively. After the thermal treatments, slight decreases and distance shifts are observed in these peaks. We also performed anomalous x-ray scattering experiments to further investigate partial structures relating to the rejuvenation effect.

In this study, we start to investigate this thermal rejuvenation effect from another point of electronic views. We have recently measured valence-band and core-level photoemission spectroscopy (PES) on these metallic glasses *before the thermal treatments*.

The amorphous samples were prepared by melt spinning with a single Cu roll installed at the Institute for Materials Research, Tohoku University, Sendai, Japan. Ribbon samples with a thickness of about 20 μm and a width of ~ 2 mm were obtained.

The PES experiments were carried out by using a PES spectrometer installed at the beamline BL7 at Hiroshima Synchrotron Radiation Center in Hiroshima University, Higashi-Hiroshima, Japan. Ultraviolet photons generated from the HiSOR storage ring with the ring energy of 700 MeV and the ring current of 160-300 mA were monochromatized with a Dragon-type monochromator, covering the incident photon energy, $h\nu$, values from 20 to 450 eV. A PES spectrometer with a hemi-spherical photoelectron energy-analyzer (GAMMA-DATA, SCIENTA SES2002) attached to the analyzer chamber under the ultrahigh vacuum below 1×10^{-8} Pa at the end-station, was used for the PES experiments. The overall energy resolution, ΔE, of the spectrometer was about 0.1-0.5 eV depending on the $h\nu$ values of 20-450 eV. The details of the PES experimental setup are given elsewhere [3].

All the PES spectra were collected at room temperature. Clean surfaces were *in situ* obtained by sputtering the samples with Ar^+ ions in a sample preparation chamber with the base pressure below 1×10^{-8} Pa. The

energies of all spectra were defined with respect to the Fermi energy, E_F, of the sample or a freshly evaporated Au film.

Figure 1 shows the Gd 4*d* core-level PES spectra of (a) Gd-Ni, (b) Gd-Co, and (c) Gd-Cu glassy alloys. As clearly seen in the figures by arrows, the Gd 4*d* core levels have at least two doublets of $4d_{3/2}$ and $4d_{5/2}$ levels, indicating that the Gd atoms have at least two chemical sites. In the near future, we will detect the spectral changes after the thermal treatments.

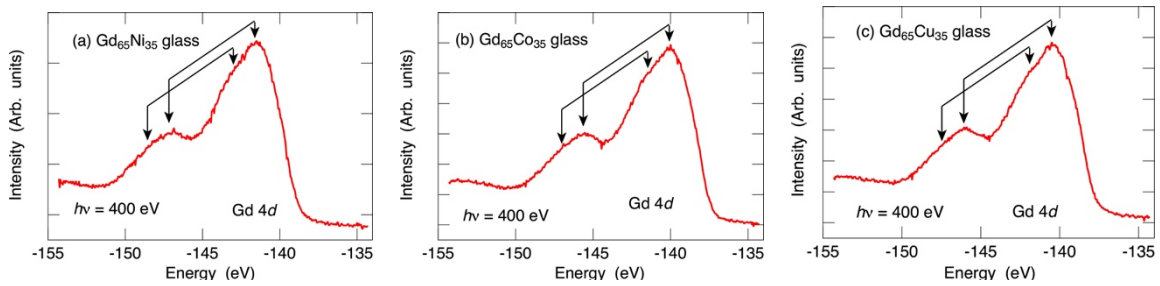

FIGURE 1. The Gd 4*d* core-level PES spectra of (a) Gd-Ni, (b) Gd-Co, and (c) Gd-Cu glassy alloys.

REFERENCES

1. S. V. Ketov, Y. H. Sun, S. Nachum, Z. Lu, A. Checchi, A. R. Beraldin, H. Y. Bai, W. H. Wang, D. V. Louzguine-Luzgin, M. A. Carpenter, and A. L. Greer, *Nature* **524**, 200-203 (2015).
2. Y. Yamazaki, *Thesis* (Tohoku University, 2016).
3. M. Taniguchi and J. Ghijsen, *J. Sync. Rad.* **5**, 1176-1179 (1998).