Coordination State of Oxygen Anions on Surface of Oxide Glass after Relaxation Analyzed by Soft X-ray Absorption Spectroscopy

Masanori Suzuki[1], Norimasa Umesaki[1], Hirona Yamagishi[2] and Toshiaki Ohta[2]

1) *Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*
2) *The SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan*

It has been considered that in ionic melts and molten oxides, surface structure relaxation such as ionic distance adjustment or ionic rearrangement would occur spontaneously to reduce surface excess energy, which significantly affects surface tension values of these melts [1]. For the accurate prediction of surface tension of oxide melts, it is required to qualify ionic arrangements on surface area after the relaxation.

Similar to the proposal for typical oxide crystals that oxygen anions are exposed to top surface and determine the surface energy of the crystals [2], the structural information on the rearranged coordination state of oxygen anions on the surface area should be significantly important to comprehend the nature of surface tension of molten oxides.

In the present study, we conduct O k-edge XANES (X-ray absorption near edge structure) measurement of oxide glass after surface structure relaxation, to examine the coordination state of oxygen anions. Here, we assume that microscopic structure in oxide glass is similar to that in the corresponding melt. Generally, oxygen anions in bulk of oxide melt are classified by either bridging oxygen (BO) or non-bridging oxygen (NBO). It has been suggested by previous researchers [3] that O k-edge XANES spectrum of oxide glass reflects various information on oxygen ions coordination including BO and NBO recognition. Additional advantage of soft X-ray absorption spectroscopy is that, coordination states around surface area could be reflected by electron yield (EY) method, which can be distinguished from those in bulk area analyzed by fluorescence yield (FY) method. Therefore, by comparison between the XANES spectrum by EY method and that by FY method could recognize original feature of microscopic structure around oxygen anions occupying surface area.

Experimental procedure is as follows: first, the oxide glass in the Al_2O_3-CaO system was prepared by quenching the corresponding melt by thick Cu plates. After crashing the quenched sample into powder to increase surface area, heat treatment was conducted at 873 K for 24 h in air atmosphere to promote surface structure relaxation. We verified by X-ray diffraction analysis that both samples before and after the heat treatment are glassy state. Then, the glass samples were set in the holder and included in the transfer vessel in Ar atmosphere, and the vessel was taken to the vacuum under 10^{-6} Pa. Finally, O k-edge XANES spectrum was measured for each sample in BL-11 in the SR center, Ritsumeikan University, by both TEY and TFY modes.

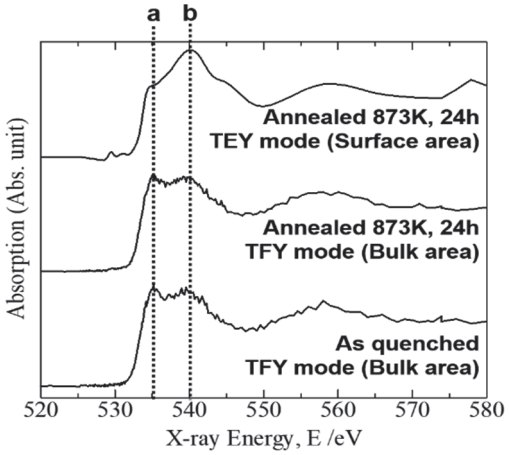

Fig. 1 Observed O k-edge XANES spectra of Al_2O_3-CaO glass after annealing to promote surface structure relaxation.

Fig. 1 shows the O k-edge XANES spectra of the Al_2O_3-CaO glass as quenched and after heat treatment. Each spectrum indicated two distinguished peaks (a, b) in absorbed X-ray energy. The peak a (535 eV) was attributed to non-bridging oxygen (NBO), while the peak b (540 eV) corresponded with bridging oxygen (BO). The XANES spectrum of the annealed glass by TEY mode clearly indicated that the proportion of BO increases rather than NBO in surface area, corresponding with the peak intensity ratio compared with that by TFY mode (reflecting oxygen coordination state in bulk area). Thus, it has been indicated that bridging oxygen tends to be preferentially distributed than non-bridging oxygen in surface area after structural relaxation occurs in the Al_2O_3-CaO glass.

References

[1] T. Tanaka, S. Hara, *Z. Metallkd.,* **1999**, *90*, 34.
[2] D. T. Livey, P. Murray, *J. Am. Ceram. Soc.*, **1956**, *39*, 363.
[3] G. S. Henderson, D. R. Neuville, L. Cormier, *Chem. Geology*, **2009**, *259*, 54.