

Hard X-ray photoelectron spectroscopy study for transport behavior of CsI in heating test simulating a BWR severe accident condition: Chemical effects of boron vapors



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HIGHLIGHTS

- We have clarified the temperature-dependent chemical forms of Cs/I products.
- We have examined the CsI-decomposing effects of B₂O₃ vapor.
- The possibility of Cs re-evaporation from CsI-deposited surface is suggested.
- We have demonstrated the usefulness of HAXPES on FP chemistry.

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ABSTRACT

Transport behavior of CsI in the heating test, which simulated a BWR severe accident, was investigated by hard X-ray photoelectron spectroscopy (HAXPES) with an emphasis on the chemical effect of boron vapors. CsI deposited on metal tube at temperatures ranging from 150 °C to 750 °C was reacted with vapor/aerosol B₂O₃, and the chemical form of reaction products on the sample surface was examined from the HAXPES spectra of core levels, e.g., Ni 2p, Cs 3d and I 3d levels, and valence band. For the samples at ~300 °C, while the chemical form of major product on the sample surface without an exposure to B₂O₃ was suggested to be CsI from the HAXPES spectra, an intensity ratio of Cs/I was dramatically reduced at the sample surface after the reaction with B₂O₃. The results suggest the possibility of significant decomposition of deposited CsI induced by the chemical reaction with B₂O₃ at specific temperatures.

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1. Introduction

For the improvement of prediction method for source term and radionuclide distribution inside reactor under severe accidents in boiling water reactor (BWR), such as the Fukushima Dai-ichi Nuclear Power Plant (1F-NPP) accident, information about the transport behavior of cesium (Cs) and iodine (I) is vitally important, because these nuclides are important in views of both high radiological impact and high radiation dose (Miwa et al., 2015). Especially in the case of BWR, where boron carbide (B₄C) is used as control rod material, Cs/I chemistry for the release and transport behavior may have been critically altered by the chemical reaction

with boron (B). Several experiments have been performed previously to investigate the chemical reaction between B and fission products (FPs) (Hidaka et al., 2000; Shibasaki et al., 2000; Girault et al., 2009; Haste et al., 2009a, 2009b, 2013; Grégoire and Haste, 2013; Girault and Payot, 2013). These previous studies indicated the possible influences of B on the transport behaviors of Cs and I. However, since the experimental environments of the previous studies were close to the real situations in nuclear reactors, intermixture of complex factors made the interpretation of results difficult. Thus, basic experiments performed in simplified and well-controlled experimental setup may also be necessary to understand what kind of chemical form would be produced through the chemical reaction between B and Cs/I under specific experimental conditions (Miwa et al., 2015; Sato et al., 2014).

Recently, Sato et al. (2015) have investigated the transport behavior of cesium iodide (CsI) deposited on the thermal

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gradient tube (TGT), which was exposed to boron oxide (B_2O_3) vapor after the deposition of CsI. This study was aimed to investigate the situation simulating the chemical reaction between B vapor, which would be produced from molten B_4C blade, and Cs/I, which are deposited on the surface of reactor body, e.g., reactor coolant system, on the way of transport. It is expected in real situation of BWR severe accidents that B_4C would be oxidized to form B_2O_3 under steam atmosphere, and at high temperatures the liquid B_2O_3 would directly evaporate or would react with H_2O to form boric acids (Steinbrück, 2003; Repetto et al., 2007). Although boric acids are most plausible as B vapor in BWR severe accidents, high volatility of boric acids at considerably low temperatures makes it difficult to judge whether the chemical reaction between B vapor and Cs/I takes place at the TGT surface or at the vicinity of crucibles used for evaporation of reagents. Therefore, in this study, B_2O_3 was selected as a material simulating B vapor on the way of Cs/I transport. On the other hand, the experiment was performed under inactive gas atmosphere to restrict additional factors of chemical reactions, which would complicate interpretation of the results. It was suggested from the results that vapor/aerosol B_2O_3 decomposed a part of deposited CsI, resulting in the possible formation of gaseous $CsBO_2$ and I_2 , which might be transported into the colder regions of TGT. However, the discussion was based on the result of mass analysis using inductively coupled plasma mass spectrometry (ICP-MS), and it lacks direct observation of the chemical form of products on the sample surface, which is indispensable for precise understandings of the transport behavior of CsI and the chemical effects of B_2O_3 .

Therefore, in the present study, we have investigated the chemical forms of products on surfaces of the same samples, which were prepared and were used in the experiments of Sato et al. (2015), by means of hard X-ray photoelectron spectroscopy (HAXPES). HAXPES, which uses the X-rays with photon energy of typically above 5 keV, is significantly more bulk-sensitive than conventional photoelectron spectroscopy (PES) using photon energy of vacuum-ultra-violet (VUV) or soft-X-ray (SX) regions (Kobayashi, 2009). Therefore, HAXPES has an advantage that measurements without surface cleaning process are capable, while the surface cleaning process is inevitable for conventional PES in VUV or SX regions because their spectra should be strongly dominated by outermost surface layers that should be heavily contaminated by oxygen and carbon. In addition, atomic subshell photoionization cross sections for electronic states of heavy elements in valence-band region, relative to those of light elements, are high in the case of HAXPES compared to the case of conventional VUV or SX-PES (Yeh and Lindau, 1985). Therefore, HAXPES would be useful to observe the signal of heavy elements such as Cs and I in the valence band spectra composed of complex electronic structures. We have measured HAXPES spectra of core levels (e.g., Ni 2p, Cs 3d and I 3d levels) and valence band for the samples at representative temperatures of 650 °C, 300 °C and 150 °C, and have compared the obtained spectra between the cases with and without the exposure to B_2O_3 vapor at each temperature.

2. Experimental

Experimental setup to prepare the TGT samples is illustrated in Fig. 1 (Sato et al., 2015). CsI in the yttria-stabilized zirconia (YSZ) crucible and B_2O_3 in platinum crucible were mounted in induction furnace below TGT made of nickel metal. First, the entire amount of CsI was vaporized by heating at 1050 °C for 5 min and the vaporized materials were transported into TGT. The completion of CsI vaporization in the abovementioned heating conditions of temperature and time scale was confirmed from the vaporization rate measured using thermogravimetry-differential thermal analysis (Sato

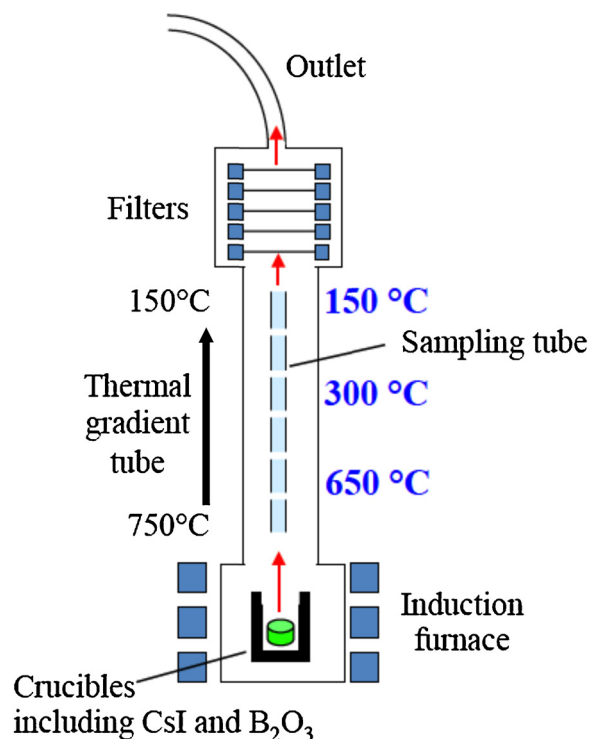


Fig. 1. Sample preparation system including thermal gradient tube (TGT) (Sato et al., 2015).

et al., 2015). Inside TGT, there were Ni-made sampling tube (4.2 mm ID) to trap deposited materials according to the TGT temperature. After the completion of CsI vaporization, heating temperature of crucibles was raised up to 1700 °C and maintained for 30 min to vaporize B_2O_3 . The platinum crucible was used for B_2O_3 to prevent direct reaction between solid/liquid CsI and B_2O_3 (Sato et al., 2015). The chemical reaction between gaseous Cs/I and B_2O_3 vapor in the vicinity of crucibles was also prevented because the vaporization of CsI was completed before the start of B_2O_3 vaporization. Therefore, it is expected that chemical reaction between B_2O_3 and CsI occurred at the tube surface, not at the vicinity of crucibles. During the whole heating process, TGT was held at temperatures from 750 °C at the bottom to 150 °C at the top with continuous temperature gradient. Because the present study was aimed to observe the effect of chemical reaction between CsI and B_2O_3 more clearly by restraining complex reactions in gaseous phases, an atmosphere inside TGT was filled with inactive Ar gas, not with steam atmosphere, that might be closer to real situation in BWR severe accidents. High purity Ar gas (O_2 and H_2O impurities were approx. 1 ppm) flew through TGT with a flow rate of 1 L/min⁻¹. Sampling tube from bottom to top was cut and decomposed into 14 parts. Separated pieces of sampling tube inside TGT will be called 'TGT samples' hereafter. TGT samples corresponding to the temperatures at 650 °C, 300 °C and 150 °C were picked up for HAXPES measurements. Details of sample preparation are described in Sato et al. (2014, 2015).

HAXPES experiments were performed using a laboratory HAXPES system equipped with a monochromatic Cr-K α X-ray source (Kobata et al., 2010; Kobayashi et al., 2013). In this system, the incident Cr-K α X-rays (5.4 keV photon energy) are monochromatized and are focused into the typical spot size of $\sim 100 \mu m$ at the sample position. Energies of emitted photoelectrons are analyzed using VG-SCIENTA R4000 analyzer combined with a wide-acceptance objective lens. Total energy resolution in the present study was ~ 0.5 eV. Probing depth was supposed to be about 10–20 nm for the valence band spectra obtained in the present study. Since the products at the sample surface, including CsI, were considered to be

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