Original Article

Selenium transfer to metal phase at Pd–Bi alloy/Se-containing borosilicate glass interface

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ABSTRACT

During reductive heat-treatment of bismuth borosilicate glass with palladium and selenium, palladium is extracted along with bismuth as a liquid metal phase. Selenium may then be extracted from the oxide phase in a subsequent water-leaching step. However, selenium extraction can be hindered by partial transfer of the selenium to the metal. To suppress such selenium transport, the effect of varying bismuth and palladium proportions in the metal on selenium transfer was investigated. Thermodynamic equilibrium calculations predicted that bismuth, selenium, and palladium should coexist in all composition ranges. However, the experimental results demonstrated that the presence of palladium in the metal suppressed selenium transfer to the metal. Auger electron spectroscopy results indicated that the bismuth in the metal was more easily oxidized than palladium. At higher bismuth contents, the oxidized bismuth may enhance adhesion between the metal surface and the glass phase, leading to more selenium adsorption. For this reason, as heating time increased, the amount of selenium transfer also increased. Cross-sectional microscopy observations demonstrated that the selenium was present not only on the surface but also in the interior of the metal.

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1. Introduction

Reprocessing of spent nuclear fuel in Japan generates high-level liquid waste (HLLW) containing radioactive nuclides. To prevent leakage of these highly radioactive nuclides, HLLW is vitrified using borosilicate glass to immobilize the nuclides in the vitrified material for disposal [1–3]. In Japan, the vitrified materials are stored in the reprocessing facility in Rokkasho Village before disposal, and the storage will increase along with the generation of the vitrified materials. However, the radioactive nuclides contain long-lived fission products (LLFPs) with long half-lives [4], which require long-term storage of the generated vitrified materials, and the availability of disposal sites is limited in Japan. It is imperative to develop new storage solutions for the existing vitrified materials to address this problem. We focused on the vitrified glass as a target material, which is already stored and will be generated from the reprocessing facility, not the liquid waste.
One possible option will be to separate LLFPs from the glass and transmute them into short-lived or stable nuclides using nuclear transmutation technologies [4-6]. To develop LLFP recovery techniques, the program "Impulsing Paradigm Change through Disruptive Technologies (ImPACT)" is currently underway in Japan [5]. Under the ImPACT program, we are studying new LLFP separation techniques from vitrified materials, including palladium and selenium as a target for separation. The palladium in the vitrified materials can be recycled as valuable resources if the separated radioactive palladium is transmuted to stable palladium. Selenium (Se)-79 is a beta emitter produced by 235U fission in nuclear reactions. Due to its long half-life (about 10^5 years) [7-9] and potential ability to migrate into the environment via leaching and dissolution [10-12], extraction of selenium from vitrified materials and transmutation of the radioactive selenium are crucial to reducing nuclear waste hazards.

To date, separation of the elements from HLLW solutions has been studied by various researchers [8,13-18]. However, to the best of our knowledge, separation of them from the vitrified waste material in a controllable manner has not yet been reported. For this reason, we previously proposed an advanced phase separation method to extract palladium and selenium from the glass phase. In this method, a heavy metal soda-potash-borosilicate glass containing palladium, selenium, and cesium (also one of LLFPs) was melted at 1000 °C in a CO-containing atmosphere. During the melting process, the heavy metal oxides in the glass were reduced to metallic substances by the CO [19-23] and palladium segregated into the resulting liquid metal, which was separated from the molten oxide phase in the form of agglomerates. In the proposed method, bismuth was employed as a heavy metal for the extraction of palladium due to its low toxicity, and palladium-bismuth alloy was obtained from the process with palladium extraction of 88%. The molten oxide was subsequently annealed at 700 °C to generate phase separation of a Na-K-rich material on the surface of the oxide in contact with the gas phase (referred to as the "contact surface") [24]. According to our previous results, cesium and selenium were simultaneously transferred to the Na-K-rich material. We also found evidence indicating that the phase separation technique enhanced the leachability of cesium in water [23]. In addition, large quantities of selenium were extracted from the Na-K-rich material in water. Therefore, the above-mentioned heat-treatment enables selective extraction of palladium, selenium, and cesium with high efficiency. However, depending on the heat-treatment conditions, selenium can also be transferred to the bismuth metal together with palladium, which is the focus of this paper. Uptake of selenium by the metal phase decreases the efficiency of selenium extraction from the Na-K-rich material by water leaching, requiring further separation of selenium from the metal, which increases the extraction costs. To limit the transfer of selenium to the metal, the main factors influencing the transfer process need to be identified. To our knowledge, selenium transfer to a palladium-containing bismuth metal from vitrified material has not yet been performed. This study investigates the factors influencing the selenium transfer at metal/molten glass interface in such a system with a focus on the composition of the palladium-containing bismuth metal as a main determining factor.

Our objective is to identify the effect of the palladium content in the metal on selenium transfer from the selenium-containing borosilicate glass during reductive heat-treatment. Samples of a simulated soda-borosilicate glass containing non-radioactive selenium and palladium-containing bismuth metal with different palladium proportions were heated in an atmosphere that contained increased concentration of CO generated by carbon combustion in a reactor. In this CO-containing atmosphere, oxygen also coexisted and can partially oxidize the surface of the metal. Such oxidation affects the surface property of the metal and selenium absorption on the metal. Therefore, we also investigated the oxidation of the metal surface in the atmosphere.

2. Materials and methods

2.1. Preparation of simulated glass and test metal samples

A simulated borosilicate glass containing selenium was prepared using a mixture of standard chemical reagents. Table 1 shows the batch compositions of the reagent mixtures. These non-radioactive reagents (purchased from Wako Chemical Co. Ltd., Osaka, Japan) were mixed uniformly in a 100-ml alumina crucible, on which an alumina cover was placed. Then, the crucible was placed in an electric furnace, and the temperature was raised to 1000 °C at a heating rate of ca. 30 °C/min. When the target temperature was reached, the mixture was allowed to melt for 2 h under atmospheric conditions. Then, the crucible was removed from the furnace using fire tongs, and the melt in the crucible was allowed to cool naturally and rapidly at room temperature. The as-prepared glass was ground into powder with a particle size below 1 mm in a mortar. The obtained glassy material is referred to as the simulated glass.

For preparation of the metallic alloy, bismuth and palladium metal powders were mixed uniformly in a 30-ml alumina crucible. The proportions of bismuth and palladium were varied as shown in Table 2. To avoid oxidation of the metal, each 30-ml alumina crucible containing a metal mixture was placed inside a 100-ml alumina crucible containing activated carbon (3 g, Wako Chemical Co. Ltd.). An alumina cover was then placed on the 100-ml crucible. The reaction container was placed in the electric furnace, and the furnace temperature was raised to 1000 °C over 30 min. The target temperature was held and the mixture was allowed to melt at 1000 °C for 1 h. Afterward, the 100-ml crucible was removed from the furnace using fire tongs and the 30-ml crucible was

<table>
<thead>
<tr>
<th>Table 1 - Compositions of reagent mixtures used for the preparation of batches of simulated glass.</th>
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</thead>
<tbody>
<tr>
<td>Reagents</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>B₂O₃</td>
</tr>
<tr>
<td>NaOH</td>
</tr>
<tr>
<td>Se</td>
</tr>
</tbody>
</table>
removed from the 100-mL crucible and tilted at a certain angle to allow the liquid metal to agglomerate at room temperature in air. The solidified metal was separated from the crucible by cracking the 30-mL crucible using a hammer. The material obtained by this procedure is referred to as the test metal. Seven types of test metal were prepared using different proportions of palladium and bismuth (test metals 1–7).

2.2. Heat-treatment experiments

The heat-treatment procedure used here was based on that described in our previous reports [19–23]. A 30-mL alumina crucible containing the simulated glass (5 g) and the test metal was placed in a 100-mL alumina crucible containing activated carbon (3 g) with an alumina cover. The reaction container was placed in an electric furnace and heated to a temperature of 1000 °C at a rate of ca. 30 °C/min. The temperature was maintained for a given time, after which the melt was allowed to cool naturally to room temperature inside the furnace. The metal was physically separated from the oxide phase by cracking the 30-mL alumina crucible using a hammer. The obtained metal is referred to as the metal product.

2.3. Thermodynamic calculations

Thermodynamic equilibrium calculations were performed using the FactSage 6.4 program (GTT Technologies) [25] to predict the theoretical phase diagram containing bismuth (Bi), palladium (Pd), and selenium (Se). These calculations are useful for estimating the affinity of selenium with bismuth and palladium during the formation of metallic droplets and the precipitation of complex intermetallic compounds. In the current study, the phase diagram for the Bi–Pd–Se ternary system was calculated at conditions of 1000 °C and 1 atm.

2.4. Characterization

The surface of the metal product was imaged using field-emission scanning electron microscopy (FE-SEM) on a Seiko Instruments/Zeiss ULTRA plus system (Seiko Instruments Co. Ltd., Chiba, Japan; Zeiss Co. Ltd., Oberkochen, Germany). Prior to the microscope observations, the metal product was covered with aluminum foil to prevent build-up of static charge during the observation. A 1-mm² piece of foil was cut from the cover on the sample, and the exposed area was observed at an accelerating voltage of 15 kV by FE-SEM. The elemental composition of the observed area was analyzed by an energy-dispersive X-ray spectrometer (EDS) (Bruker AXS Co. Ltd, Kanagawa, Japan) in the FE-SEM. Compositional measurements were also made along a cross-section of the metal product as follows. First, the metal product was placed in a hole prepared in a graphite plate. A thermosetting resin was subsequently poured into the hole to immobilize the metal product. The graphite plate containing the metal product was then heated at 70 °C for 5 min to solidify the resin and the metal product in the plate was polished using SiC sandpaper (average grit diameters: 35 μm, 21.8 μm, and 15.3 μm), Al₂O₃ sandpaper (roughness: 5 μm and 3 μm) and diamond sandpaper (roughness: 1 μm) in succession. The polished cross-section of the metal product was observed by FE-SEM in the same manner described above.

The proportion of palladium, bismuth, and selenium on the surface of each metal product was determined by X-ray fluorescence (XRF) analysis on a Shimadzu LAB CENTER XRF1800 system (Shimadzu Co. Ltd., Kyoto, Japan). Generally, detection limits of wavelength-dispersive XRF are 0.001–0.01 wt% for elements from sodium to uranium in periodic table [26]. The chemical states of the elements on the surface of the metal products were evaluated using Auger electron spectroscopy (AES) on a JEOL JAMP-9500F system (AES) (JEOL Co. Ltd., Tokyo, Japan).

3. Results and discussion

3.1. Effect of palladium in metal on selenium transfer from glass to metal

In a previous study of metal-oxide interfaces, the charge condition of the metal surface was found to be affected by its composition [27]. Because Pd-containing bismuth is generated during our treatment process [22], the palladium in the metal may influence the charge condition of its surface, which may also affect selenium transfer. For this reason, the effect of the palladium content in the metal product on selenium transfer was investigated. First, the metal product from test metal 1 with no palladium was evaluated. Fig. 1 summarizes the results of the FE-SEM analysis. As indicated by the EDS spectrum (Fig. 1d), peaks corresponding to Bi, Se, O, and C are present, demonstrating the presence of selenium in the metal product. The detection of C may be due to carbon and carbon dioxide contaminating on the metal product, because carbon monoxide can be decomposed to carbon and carbon dioxides [19]. The corresponding mapping images indicate that selenium was present on the surface of the product (Fig. 1b), whereas no selenium was detected in the interior of the product (Fig. 1c). This was confirmed by the EDS spectra from Points 1 and 2. The XRF analysis indicated that the selenium concentration in the metal product was 3.3 wt%.

Next, the effect of the palladium concentrations in the metal products on selenium transfer to the product is discussed. Fig. 2 shows the relationship between selenium and palladium concentrations on the surfaces of the metal products. The selenium concentrations were consistently high in the metal products with low palladium concentrations. With increasing palladium concentrations, the selenium

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Test metal 1</th>
<th>Test metal 2</th>
<th>Test metal 3</th>
<th>Test metal 4</th>
<th>Test metal 5</th>
<th>Test metal 6</th>
<th>Test metal 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic bismuth powder</td>
<td>1</td>
<td>0.95</td>
<td>0.9</td>
<td>0.85</td>
<td>0.8</td>
<td>0.65</td>
<td>0.5</td>
</tr>
<tr>
<td>Metallic palladium powder</td>
<td>0</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
<td>0.2</td>
<td>0.35</td>
<td>0.5</td>
</tr>
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</table>


concentrations decreased. At higher palladium concentrations, the selenium concentration remained low. This indicates that the palladium concentration is related to the selenium transfer to the metal from the selenium-containing borosilicate glass during the reductive heat-treatment.

Selenium transfer to the metal products was further investigated by FE-SEM observations. The metal products from test metals 3, 5, and 7 with different palladium proportions were observed and compared. Fig. 3a shows the morphology of the surface of the metal product from test metal 3, which was not in contact with the alumina crucible. The corresponding mapping images of Bi, Pd, and Se are also displayed. The mapping images indicate that Pd and Se occur in separate phases. The same trend was also observed for the other metal products (Fig. 3b and c). This is supported by the corresponding point analyses in Fig. 4. It can be seen in Fig. 3 that a decrease in the area of Se-rich regions corresponds to an increase of Pd-rich areas. Table 3 shows the elemental concentrations for the entire observed area based on EDS analyses. Although EDS analysis is a semi-quantitative technique, the elemental compositions of the metal products determined by EDS can be used as a reference to identify trends in compositional changes, such as those mentioned above.

The results indicate that the selenium concentration in the metal product from test metal 7, which has a higher palladium concentration, was low (Se=0.94 wt%).

Fig. 1 – FE-SEM observations of the metal product from the treatment of test metal 1: (a) secondary electron image and corresponding elemental mapping images of (b) Bi and (c) Se along with (d) EDS spectra.

Fig. 2 – Concentrations of palladium and selenium on the surface of the metal products determined by XRF analysis.
Fig. 3 – Secondary electron images and corresponding elemental mapping images of Bi, Pd, and Se in the metal products generated from: (a) treatment of test metal 3; (b) treatment of test metal 5; (c) treatment of test metal 7.

Fig. 4 – EDS spectra results for the metal product generated from the treatment of test metal 5.

comparing to the other metal products with lower palladium concentrations (Se = 6.9–9.6 wt%). This indicates that the presence of palladium suppressed selenium absorption at the surface of the metal. This explains why the selenium concentrations decreased with increasing palladium proportions in the metal product. The mechanisms underlying the limiting effect of palladium are discussed in the next section.

3.2. Discussion of selenium transfer to metal

3.2.1. Thermodynamic equilibrium analysis

The phase diagram of selenium, palladium, and bismuth obtained by the thermodynamic equilibrium calculation is shown in Fig. 5. Note that the objective of this section is to confirm the affinity among these elements, not to directly compare this calculation results with the above-mentioned experimental results. According to this theoretical phase diagram, Se and Pd are predicted to coexist in all composition ranges. Although such affinity is predicted, the palladium and selenium were observed in separate phases in the experimental results described in the previous section (Section 3.1). Therefore, the selenium absorption behavior cannot be explained by the affinity between Se and Pd. The possible reason for the behavior may be related to the rate of selenium

<table>
<thead>
<tr>
<th>Elements</th>
<th>Metal product from the treatment of test metal 3</th>
<th>Metal product from the treatment of test metal 5</th>
<th>Metal product from the treatment of test metal 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.5</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>O</td>
<td>1.7</td>
<td>2.2</td>
<td>4.3</td>
</tr>
<tr>
<td>Se</td>
<td>9.6</td>
<td>6.9</td>
<td>0.94</td>
</tr>
<tr>
<td>Pd</td>
<td>14</td>
<td>20</td>
<td>44</td>
</tr>
<tr>
<td>Bi</td>
<td>70</td>
<td>68</td>
<td>47</td>
</tr>
</tbody>
</table>
transfer to the metal, which is discussed in the following section.

3.2.2. Influence of melting time on selenium absorption
To investigate the rate of selenium transfer, heat treatments were performed with various melting times from 5 min to 180 min. Test metal 1 with no palladium and test metal 6 with palladium were selected for comparison. Fig. 6 shows the selenium concentrations on the surfaces of the metal products at different melting times. In the case of test metal 1, the selenium transfer to the metal product increased as the melting time was extended from 5 min to 120 min. However, for test metal 6, the increase in selenium concentrations with time was smaller. Selenium transfer to the metal thus varies depending on the presence of palladium.

As explained above, different rates of selenium transfer were observed depending on the presence of palladium.

3.2.3. Adhesion properties between the alloy and borosilicate glass
The inhibition of selenium absorption by palladium is discussed in this section, where we focus on the adhesion properties between the metal and glass. As mentioned in Section 3.2, different surface morphologies of the metal products were observed. This implies that different adhesion characteristics between the metal product and that borosilicate glass result from the varied proportions of palladium and bismuth in the metal. The difference in adhesion can be also detected by examining the interface between the metal and the glass (Fig. 8a), and the surface of the metal products (Fig. 8b and c). When the proportion of palladium in the test metal was 10 wt% (test metal 3), the resulting metal product was not completely separated from the glass, with a portion of the metal remaining in the glass (Fig. 8a). In addition, the surface of the separated metal product was rough (Fig. 8b). However, when

**Fig. 5** – Phase diagram constructed from the thermodynamic calculation results at 1000 °C and 1 atm.

**Fig. 6** – Concentrations of selenium on the surface of the metal products with different melting times.
the proportion of the palladium in the test metal increased to 35 wt% (test metal 6), the resulting metal product was easily separated from the glass and its surface was relatively smooth (Fig. 8c). This implies that the presence of palladium on the metal surface decreased the possible contact between the metal and glass, limiting the selenium absorption. Fig. 7 contains EDS spectra, demonstrating that oxygen was found on the metal surface of the product of test metal 1, whereas it was not found for test metal 6, as represented by Points 5 and 8, respectively. Therefore, one reason for the different adhesion properties may be the difference in oxidation states on the metal surface. To evaluate these oxidation states, the surface of the metal product was analyzed by AES. For this analysis, we selected the metal product generated by the treatment of test metal 7, in which the palladium proportion was 50%. Fig. 9 summarizes the Auger electron spectra of the metal product, in which spectra for standard reagents (Pd, PdO, Bi, and Bi₂O₃) are included for comparison. Note that the analytical depth of AES is less than 10 nm, which is smaller than that of the EDS analysis at an accelerating voltage of 15 kV (around 1 μm). Therefore, the chemical states of the elements on the metal surface can be more precisely evaluated by AES. According to these spectra, the surface of the metal product contains not only bismuth and palladium (Fig. 9a and b), but also oxygen (Fig. 9c). This suggests that the metal surface was oxidized to a certain extent. In Fig. 9a, the mass ratio of Bi³⁺ to Bi⁰ on the surface of the product was calculated to be 2.4 from the spectra of the metal product and standard reagents. Additionally, Fig. 9b indicates that the ratio of Pd²⁺ to Pd⁰ was 1.4 and the ratio of oxygen in the bismuth oxide to that in the palladium oxide was calculated to be 80 from Fig. 9c. According to these results, the bismuth on the metal surface became relatively more oxidized than palladium during the heat-treatment.

Thus, when the proportion of bismuth in the metal was high, the surface of the metal was more easily oxidized. This enhanced the adhesion properties of the metal surface with the borosilicate glass and increased the absorption of selenium from the glass to the metal surface. When the proportion of palladium in the metal increased, adhesion of the metal
surface in contact with the glass declined, resulting in decreased selenium adsorption.

4. Conclusions

Metal composition is a key factor that affects the transfer of selenium to the metal phase during heat-treatment of selenium-containing borosilicate glass. We investigated the effect of the palladium content in the metal on selenium transfer and found that the presence of palladium decreased the affinity between the metal and glass because the palladium inhibited oxidation of the metal surface. The resulting decrease in contact between the metal and glass suppressed selenium absorption by the metal surface from the glass. These findings provide a new solution for designing higher-efficiency extraction processes from selenium-containing borosilicate glass through adjustments in alloy compositions.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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