Comparative Study on Cold Immobilization of I–Cu@h–BN and I–Ag@h–BN

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***Keywords** : immobilization, cold sintering, leaching, nuclear waste management

1. Introduction

The immobilization of radioactive wastes generated in the nuclear fuel cycle has become one of the most important issues in the field of nuclear waste management. In particular, Iodine-129 (^{129}I) is a major environmental concern due to its extremely long half-life of 1.57 $\times 10^7$ years and a substantial amount of radioiodine is released during the reprocessing of spent nuclear fuels, necessitating effective treatment and immobilization to mitigate its environmental impact.

In radioactive waste management, conventional borosilicate glass faces significant challenges in incorporating iodine due to the high temperatures required for glass formation and vitrification, which often exceed the melting temperature of iodide compounds such as 606 °C for CuI. Vance et al. [1] proposed copper iodide (CuI) as a promising waste form, achieving over 60 wt% waste loading and up to 83% of the theoretical density using hot isostatic pressing (HIP) at 550 °C. However, CuI tends to decompose in the presence of water and iron powders, leading to substantial iodine release. To address this issue, CuI was encapsulated in a sintered pellet surrounded by Sn metal (melting point = 231 °C) and incorporated into the HIP canister at a lower temperature of 200 °C.

While this proposed method reduces waste loading compared to using CuI alone, our primary objective is to develop a low-temperature sintering technique that eliminates the need for additives and can effectively immobilize CuI waste while preventing its volatilization during the processing to a waste form. In response, we propose the use of cold sintering (CS), a pressure-assisted sintering technique, that enables sintering and densification of materials at significantly lower temperatures, often below 300 °C [2–4].

For a practical comparison, I–Cu@h–BN and I–Ag@h–BN were cold-sintered, and their elemental leaching behaviors were evaluated according to the ANSI/ANS-16.1-2019 protocols[5].

2. Methods and Results

In this section, the experimental mechanisms proposed in references [2,3] are used for the cold immobilization of I–Cu@h–BN and I–Ag@h–BN composites (**Fig. 1**). The specific sintering conditions are discussed in detail below.

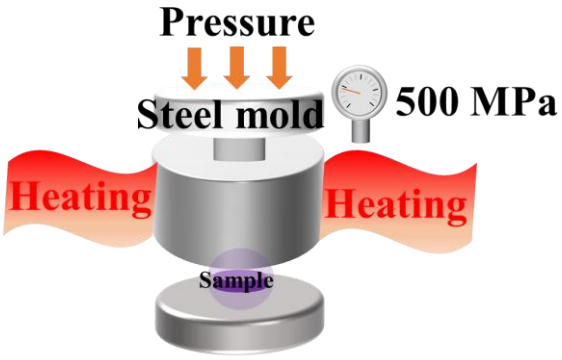

Fig. 1. Cold sintering setup

2.1 Cold sintering of I–Cu@h–BN and I–Ag@h–BN powders

0.4 g of I–Cu@h–BN and I–Ag@h–BN powders were placed in separate cylindrical steel molds with inner diameters of 8 mm and pressed under a uniaxial mechanical pressure of 500 MPa. The molds were then heated to 200 °C and held at this temperature for 10 mins. After allowing the sintered pellets to cool naturally to room temperature, the uniaxial pressure was gradually released. The resulting samples, labeled as CS_I–Cu@h–BN and CS_I–Ag@h–BN, were then retrieved for subsequent characterization.

2.2. Short-term leaching test

To assess the chemical durability of the sintered samples, a 5-d semi-dynamic leaching test was conducted in accordance with the ANSI/ANS-16.1-2019 standard procedure developed by the American Nuclear Society (ANS) [5].

$$L_i = \log\left(\frac{\beta}{D_{e,i}}\right) \quad (1)$$

where β is a defined constant (1.0 cm^2/s) and $D_{e,i}$ is the effective diffusivity of nuclide i calculated from the test data (cm^2/s).

3. Result and Discussion

The PXRD pattern of CS_I–Cu@h–BN (**Fig. 2a**) closely matches that of I–Cu@h–BN, which was attributed to the dominant phase of the CuI (cubic space group 216, F$\bar{4}$3m; PDF No. 01-075-0832). For I–Ag@h–BN (**Fig. 2b**), a combination of two phases, β-AgI (hexagonal space group 186, P63mc; PDF No. 00-009-0374) and γ-AgI (cubic space group 216, F$\bar{4}$3m; PDF No. 01-078-3284) commonly coexisted. At the same time, the PXRD pattern of CS_I–Ag@h–BN showed nearly identical diffraction peaks to I–Ag@h–BN but predominantly featuring cubic γ-AgI (PDF No.

01-078-3284). However, a broadening of peaks was observed in the cold-sintered samples, most likely due to high-pressure sintering causing the crystallite size to decrease.

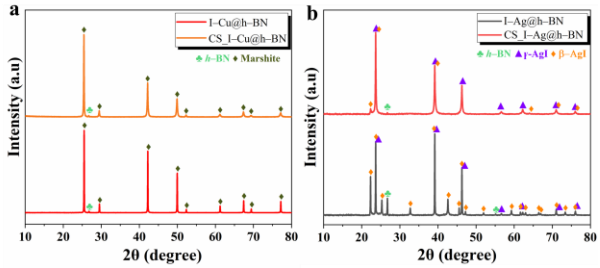

Fig. 2. PXRD patterns of (a) I–Cu@h–BN and (b) I–Ag@h–BN before and after sintering.

4. Conclusions

This study introduces a novel approach to fabricating I-129 waste forms through cold immobilization. By assessing the chemical durability of the waste forms, we gained valuable insights into the leaching behavior of the sintered samples. This research not only demonstrates the viability of cold sintering for immobilizing radioactive iodine but also highlights its potential for enhancing the stability and performance of waste forms in nuclear waste management.

Acknowledgments

This study is supported by the National Research Foundation of Korea (NRF-2021M2D2A1A02043946).

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