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Electron irradiation effects of SrZrO$_3$ ceramic for radioactive strontium immobilization

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Abstract

The perovskite structure is widely considered ideal host phases for Sr immobilization. To investigate the radiation tolerance on ceramic waste forms, the as-prepared SrZrO$_3$ ceramics were irradiated by external electron beam. The results indicated that the electron irradiation had different influence on the surface and inside of the SrZrO$_3$ ceramic. The no-crystallizing can be produced on the surface of SrZrO$_3$ ceramic, and electron beam heating promoted grain growth in the inside of SrZrO$_3$.

Keywords: Ceramics; immobilization; Electron irradiation; Microstructure

1. Introduction

The stabilization and immobilization of radioactive waste continues to attract much attention due to radioactive hazards. In order to reduce threat to the environment, radioactive wastes must be treated or immobilized prior to final disposition, especially to the high level waste (HLW) such as long half-time minor actinides and fission products$^1$. In the immobilization process, a critical scientific contribution to this problem is the development of robust materials science solutions that encapsulate radioisotopes for long periods of time. In the past few decades, various glasses had been extensively employed as candidates for immobilizing HLW$^{2,4}$. However, glass is unsuitable for radioactive waste disposal due to the poor radiation tolerance and leaching resistance. In recent years, most results indicated that ceramic forms exhibit excellent chemical durability, long-term stability and radiation tolerance to glass forms, and have been in a hot research topic to disposing high-level radioactive waste$^{3,6}$. As

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crystalline waste-forms, ceramics are stable compounds with definite thermodynamics and kinetics properties, and expected to be more robust than for glasses. Therefore, it is considered an excellent host for immobilizing complex actinide and fission wastes.

It is well known that $^{90}$Sr have relatively long half-life of 28.1 years, it is typical high level radioactive wastes generated from spent nuclear fuels. In $^{90}$Sr host phases, $^{90}$Sr decay to daughter $^{90}$Y, the $^{90}$Y decay to stable $^{90}$Zr by emitting beta particles. The stability of crystalline waste forms comprised of $^{90}$Sr is likely to be affected by daughter product formation and beta particles. As an oxide ceramic, SrZrO$_3$ contains parent $^{90}$Sr and stable daughter $^{90}$Zr, so it is useful to investigate beta irradiation effects of SrZrO$_3$ ceramic. In this work, the prepared SrZrO$_3$ ceramic was irradiated by external electron beam, used to simulate beta irradiation of strontium. Based on characteristics of the microstructure, the radiation resistance of the SrZrO$_3$ ceramic was investigated before and after electron irradiation.

2. Materials and methods

SrZrO$_3$ ceramics were synthesized from powders prepared by Sol-thermal spraying method (STSM). Firstly, 0.1 M solutions of Sr$^{2+}$ and Zr$^{4+}$ were prepared by dissolving Sr(NO$_3$)$_2$ and Zr(NO$_3$)$_4$·3H$_2$O in deionized water with heating and stirring on a hot stirrer set at 60 ºC for 2 h. Subsequently, the two solutions were mixed corresponding to nominal compositions of SrZrO$_3$ and stirred at 60±5 ºC for 1 h. To obtain a stable precursor solution, citric acid and polyethylene glycol were added to the solution containing Sr and Zr ions according to 8g C$_6$H$_8$O$_7$H$_2$O and 5 g in 100 ml Solution. The precursor solution prepared was added into spray pyrolysis equipment and pyrolysed at 823 K under air environment by a heater. A black precipitate was obtained which was further heated in a conventional furnace at 900 ºC for 2 h. Green The circular plates with 15 mm diameter and 2 mm thickness produced by hydraulic pressing (HP) at a pressure of 15 MPa. The plates were then sintered at 1250 ºC for 12 h in air.

To evaluate irradiation effects of SrZrO$_3$ ceramic, the circular plates sintered were subjected to an electron irradiation with energy of 1.8MeV and flux of $1.5\times10^{13}$ electrons/cm$^2$/s. The effects of electron irradiation on the microstructure of SrZrO$_3$ ceramics were identified by X-ray diffraction analysis (XRD), Fourier transform Raman (FT-Raman) and field scanning electron microscope (FSEM).

3. Results and discussions

Fig. 1 shows the XRD patterns of the SrZrO$_3$ ceramics before and after electron irradiation. It was clear found that no secondary phase was observed by XRD on the SrZrO$_3$ before electron irradiation, the SrZrO$_3$ sintered is a single phase with orthorhombic perovskite structure, and consistent with previous reports. The sharp and well-defined diffraction peaks indicated that the obtained ceramic has a high degree of crystallinity. The lattice parameters of SrZrO$_3$ determined from XRD are $a = 0.5795$ nm, $b = 0.5817$nm, $c = 0.820$ nm.

![Fig. 1. XRD patterns of SrZrO$_3$ ceramics before and after electron irradiation](image)
The theoretical density evaluated by XRD is 5.45 g/cm³. The average grain size of the samples is estimated using the Debye-Scherrer formula:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

(1)

Where \( K \) is the shape factor equal to 0.89, \( \lambda \) is the X-ray wave length for Cu Kα radiation (\( \lambda = 1.5406 \) Å), \( \theta \) is the Bragg’s angle and \( \beta \) is the full width of the diffraction line at the half maximum intensity. The grain size of the prepared powders calculated using this equation was in the range of 80-100 nm. Also, noted that the SrZrO₃ ceramic exhibits excellent radiation resistance under 1.8 MeV electrons irradiation with the flux of 1.5x10¹³ electrons/cm²/s. As seen in Fig. 1, the deleterious phases were not observed in irradiated sample, indicated that the electron irradiation does not destroy the crystal structure of SrZrO₃.

Fig. 2 displays the Raman spectra of SrZrO₃ ceramic in the frequency range 100-1000 cm⁻¹ before and after electron irradiation. At room temperature, SrZrO₃ is Orthorhombic with space group Pnma. The research indicated that there are 24 Raman-active modes to SrZrO₃, represented by 7Aₓ, 5B₁g, 7B₂g and 5B₃g. For SrZrO₃, 8 Raman modes were observed at 117, 144, 169, 255, 275, 349, 412 and 552 cm⁻¹. All peaks observed are characteristic of SrZrO₃ confirming the orthorhombic structure, and accordance with literatures. The bands at 117, 144 and 349 cm⁻¹ correspond to B₂g modes, and bands at 169, 255, 275, 412 and 552 cm⁻¹ are well defined as Aₓ modes. After electron irradiation, although the observed peak positions in Raman spectra are similar, the relative peak intensities decrease for different modes (see Fig. 3 b). It indicated that the irradiated SrZrO₃ had poor crystallinity. As known, Raman spectroscopy is sensitive to the structural changes on bulk crystals surface compared with the changes detected with XRD, implied that the irradiated SrZrO₃ could be no-crystallizing or amorphization on the surface, and this was further confirmed by FSEM experiment.

Fig. 2. Raman spectra of SrZrO₃ ceramics before and after electron irradiation

Fig. 3 shows the SEM images sintered of sample SrZrO₃ before and after electron irradiation. It was clearly found that SrZrO₃ ceramic was a large well crystal grain and distinct crystal boundaries. Moreover, the pores or microfractures did not observed in the SrZrO₃ ceramics, it indicated that the sintered sample had sufficiently densification with densities near the ideal value. The bulk density derived from the Archimedes method is about 5.38 g/cm³, which is greater than 97% of theoretical density (5.45 g/cm³). The dense microstructure is advantageous to reduce radioactive nuclides in long term nuclear waste disposal.

It may be noted that a dramatic difference was observed in the irradiated SrZrO₃ compared with the unirradiated bulk sample. Moreover, the microstructure changes were also difference on surface and inside of the irradiated SrZrO₃. The surface region responds to the visualized no-crystallizing, and an increased grain size was observed in
the inside of irradiated SrZrO$_3$ (see Fig.3b$_1$ and Fig.3b$_2$). The surface no-crystallizing may be attributable to the irradiation damage. To most ceramics, the displacement threshold values of the atom displacement was range from 100 to 800 keV. 1.8MeV was enough to the atoms of SrZrO$_3$ departed from primary position, under electron irradiation, a part oxygen atoms may be taken away from SrZrO$_3$ and the rest of oxygen atoms were portioned afresh, the vacancy at the beginning of the sequence was leaved and deposited the excess Sr atoms as an interstitial at the end of the sequence. Compared with surface, the growth of grain size in the inside of the irradiated SrZrO$_3$ may be attributed to short travel length of electron and beam heating effects caused by the electron irradiation. In this experiment, the dose rate is about 1.69×10$^3$Gy.s$^{-1}$, which is enough high to induced vacancies. The diffusion was enhanced via high concentration of radiation-induced vacancies, can promote the grain growth. As shown in Fig.3b$_2$, the average grain size was found to be ~ 5µm, it is much larger than the grain size in Fig.3a, indicated that electron irradiation may enhance annealing and/or recrystallization in SrZrO$_3$ ceramic, and consistent with a previous report$^{16}$. Combining with these results from XRD and RS, indicated that the electron irradiation has a notable damage on the surface, but nucleation at the inside was promoted by radiation exposure.

Fig. 3. SEM images of the SrZrO$_3$ ceramic, (a) unirradiated sample;(b$_1$) the surface of irradiated sample;(b$_2$) the inside of irradiated sample.

4.4. Conclusion

SrZrO$_3$ ceramics were synthesized from powders by STSM. The effect of electron irradiation on the microstructures of SrZrO$_3$ ceramic was investigated. Combining XRD, FSEM and RS, the electron irradiation induced changes on microstructures of SrZrO$_3$ ceramic as compared with the unirradiated sample. The electron irradiation induced no-crystallizing on surface of SrZrO$_3$ ceramic, and that electron beam heating enhanced the
growth of grain size at the interior of the irradiated SrZrO3 ceramic.

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