Transport properties of iodine and tellurium in a thoria-2 mol% urania matrix

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Abstract

Diffusion properties of the volatile fission products iodine and tellurium inside the thoria based fuel matrix (ThO$_2$-2 mol% UO$_2$) were obtained by studying the release kinetics of the species from trace-irradiated fuel samples at different temperatures (1290–1790 K) in post-irradiation annealing experiments. Analysis of the kinetic data shows that the release through bulk diffusion is too low to be measurable below 1273 K. The apparent bulk diffusion coefficients for the two volatile species could be evaluated at higher temperatures in a well-defined powder sample (37–45 μm particle size, 24 m^2 kg^{-1} BET surface area) of the high-density fuel (>95% T.D.). Temperature dependences of the diffusion coefficients of iodine and tellurium derived from this study could be expressed in the form of Arrhenius equations as $\log D'_I \ (s^{-1}) = -(15\,000 \pm 1000)/T - 1.19 \pm 0.63$, and, $\log D'_{Te} \ (s^{-1}) = -(25\,600 \pm 1200)/T + 6.14 \pm 0.77$. Activation energies and frequency factors for diffusion of the two species as obtained from the Arrhenius equations are 286 kJ mol^{-1} and 6.4×10^{-2} s^{-1} for I and 491 kJ mol^{-1} and 1.38×10^6 s^{-1} for Te. The two sets of kinetic data are quite different and they suggest that the two species have different mechanisms of their transport in the fuel matrix. The results were compared with reported data in pure urania and thoria matrices.
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1. Introduction

Data on the transport properties of volatile fission products help in understanding their redistribution in nuclear fuel pins during the burn-up process. Under the steep temperature gradient across the pin, the fission products such as iodine and tellurium have the tendency to diffuse out of the fuel matrix and to settle at its interface with clad. A significant fraction of total Xe accumulation at the interface is due to the transport and release of less stable isotopes of the two volatile fission products, e.g., ^{132}Te and ^{131}I. The built up of concen-

trations of I, Te and Xe at the interface can result in stress corrosion cracking and failure of the clad [1,2]. Thus, one of the important parameters in carrying out simulation analysis for understanding the performance of a nuclear fuel/clad assembly [3] is the bulk diffusion coefficient of I and Te in the fuel matrix. For urania and plutonia based fuel there are ample measurements reported for diffusion properties of the two elements. However, this is not the case for a thoria based matrix envisaged as the fuel for advanced heavy water reactors in the third phase of the nuclear energy generation programme in India [4]. Discrepancy exists in the reported data on the transport and release kinetics of iodine in thoria based fuels [5,6]. Thus there was a need to generate more reliable data on the diffusion coefficients of the species, which are needed in evaluating the performance of thoria-based fuel.

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In this study the diffusion data were generated for the volatile fission products iodine and tellurium in the solid solution of thoria-2 mol% urania, which represents the typical fuel composition of the advanced heavy water reactor. The kinetic data for the transport and release of the volatile species were obtained by isothermal annealing of trace-irradiated fuel samples at different temperatures (1300–1800 K). The post-irradiation annealing technique used in this study was a modified version of that reported by Peehs and Kaspar [7]. In this technique the released fraction of the volatile components from irradiated fuel are collected in a defined geometry during isothermal annealing under high vacuum. The modified version of the present design allowed off-line assay of the released fraction of the volatile fission products iodine and tellurium as they were chemically fixed in situ on hot copper collectors following their release.

2. Experimental

A homogeneous solid solution of the cubic ThO_2-2 mol%UO_2 phase with an oxygen-to-metal ratio of 2.00 was procured in the form of high density (>95% T.D.) pellets from the Radiometallurgy Division of this Research Center (B.A.R.C.). The pellets were powdered and sieved to select the particle size of 37–45 μm that had a BET surface area of 24 $m^2 kg^{-1}$. The powder was heated in a hydrogen atmosphere at 1200 K to get rid of any hyperstoichiometry in its urania component that might have developed during handling the sample in air. The reduced powder was subdivided into several samples of approximately 1 g each sealed in individual quartz capsules under high vacuum. The samples were irradiated at a constant flux of 1×10^{16} neutrons $m^{-2} s^{-1}$ at ambient temperature ($\approx$300 K) using the APSARA reactor facility of this Research Center. Following the irradiation at a dose of 2×10^{20} fissions m^{-3} the respective samples were cooled typically for five days before loading into the apparatus for post-irradiation annealing study. A schematic view of the apparatus is shown in Fig. 1. The sample was placed inside a molybdenum cell having a lid with an orifice of 1.5 mm diameter and was heated isothermally by a tungsten resistor furnace in the vertical set-up inside the high-vacuum ($\approx$10^{-8} bar) system. It was seen in exploratory runs with un-irradiated samples that the sample did not show measurable (within 10 ppm) weight gain due to oxygen pick-up from the vacuum environment maintained during annealing. As the molybdenum cell also did not develop any oxide scale in the experiments the oxygen potential inside the cell is taken to be below that of a $Mo(s)$–$MoO_2(s)$ biphasic mixture [8]. During the initial attainment of furnace temperature, the cell containing the sample was withdrawn in situ to place it
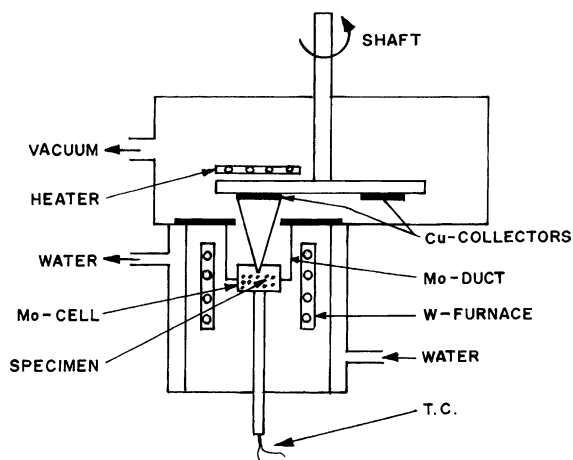

Fig. 1. Schematic diagram of the post-irradiation annealing apparatus.

outside the hot zone of the furnace. A thermocouple sheath supporting the cell was pulled downwards to accomplish the withdrawal. The cell temperature was monitored with the help of a calibrated Pt/Pt–13%Rh thermocouple held in an alumina sleeve and placed inside the sheath in close proximity of the cell-bottom. After the attainment of set temperature of the resistance furnace the cell was pushed inside the isothermal zone and the release kinetics of iodine and tellurium from the sample were followed. Typically the cell attained thermal equilibrium within two to three minutes which represent the extent of uncertainty of initiating the isothermal release kinetics. Volatile species released from the sample came out of the cell orifice as atomic beam and passed through a molybdenum tubular guide upwards to collect on hot collectors made of thin copper foils. The foils were separately heated at 650 K to facilitate chemical fixing of iodine and tellurium atoms received at the copper collectors [9]. The collectors held in array on a horizontal support were exposed to the geometrically defined atomic beam one at a time by a rotational shaft. The tubular guide receiving thermal radiation from the annealing furnace attained a temperature of 600 K and more at its top end in the experiments. Control experiments with standard iodine (silver iodide) and tellurium (Pd–Te alloy) sources showed that in the presence of the molybdenum guide tube the collection efficiencies of iodine and tellurium atoms released from the cell were augmented to 40% and 26%, respectively, from a value of 3% obtained in the absence of the guide. For the Te case the control experiments were carried out at the median of the working temperatures (1200–1800 K) of annealing study so that the data of 26% collection of Te obtained at 1500 K could be used over the entire temperature range

neglecting the uncertainty from varied condensation of the vapor in the guide tube.

The isothermal annealing period in the kinetic study was typically 6–8 h. Within this time period eight collectors were exposed to the atomic beam for monitoring the release kinetics. After the annealing experiment, all the copper collectors were assayed radiometrically for ^{131}I and ^{132}Te with the help of a high purity germanium detector coupled to 4 K multi-channel-analyzer. The radiometric assay involves the measurement of gamma activities of ^{131}I ($t_{1/2} = 8.02$ d) and ^{132}Te ($t_{1/2} = 76.3$ h) at 364 and 228 keV, respectively. The measured gamma activities of iodine and tellurium present in the collectors were compared with the total activities of these isotopes in the original sample used in the annealing experiment. The comparison was made after normalizing the measured activities to their respective values during the collection experiment. From the data of normalized activity data the fractional release of iodine and tellurium were obtained for the respective time of collections.

3. Results and discussion

At a given annealing temperature, the cumulative fractional release of iodine and tellurium over a time period was evaluated considering the data of the isothermal annealing runs. A fresh sample was used for each annealing temperature though some experiments were carried out to observe the release behavior in stepwise isothermal heating at successively higher temperatures. The typically observed release behavior of the two species in stepwise isothermal heating is shown in Fig. 2. It is clear from the figure that the release behavior of I and Te differs; Te release is in general higher than that of I at each of the temperatures indicated. The initial non-linear development of cumulative release as

Fig. 2. Typical release kinetics of iodine and tellurium from the thoria-2 mol% urania matrix.

shown by the dotted line, typically within 5 min, was due to 'burst release' [10] of iodine and tellurium from the superficial layers of the grains as exposed to the vacuum environment. Following the period of burst release, there is a linear growth of release of the species over a few hours. The growth then deviates from the linearity and practically reaches halt within another few hours. In general, the halt in the cumulative release of I appears earlier than that of Te at different annealing temperatures (Fig. 2). The cumulative releases of the species as they attained steady values were within 0.5–3% depending on the annealing temperatures. This observation was repeatedly made at all temperatures, and in fuel samples obtained from different batches of preparation. This early attainment of steady values is not expected unless the diffusion process changes over to a different mechanistic path of very high activation energy. Such change-over of the release behavior has not been reported. The possibility that some external factors caused the impediment of the diffusion was looked into. The possibilities like: (i) improper collection of the released species on hot copper targets due to coating of other vapors originating from annealing furnace, (ii) surface coating of the grains of fuel sample by pyrolysis of silicone oil-vapor back streaming from the diffusion pump were ruled out by separate experimentations with standard sources of iodine and tellurium vapors, and by surface analysis of heated samples and copper targets. Also, it was seen from the weight analysis of fuel samples before and after annealing experiments that the O/M ratio of the fuel remains constant with an uncertainty of ± 0.0005 during heating it in the molybdenum cell under high vacuum.

The early attainment of steady values of cumulative release of the volatile species appeared to be characteristic of the thoria-2 mol% urania matrix. An additional force inherently comes into play in the diffusion process leading to the deviation from the initial linear growth and near halting of the cumulative release at a value as low as 0.5%. The fact that the impediment in release occurred earlier for I, which is a more electronegative element than Te suggests that the force operative against the diffusion originates from ionic nature of the fission products in the host matrix; I is more likely to remain as anion than Te. The release of I^- species as I atom should be associated with a valency reduction of compensating the cation in the host lattice, or, with formation of a negatively charged vacany. Cations of alkali metal fission products such as Cs^+ need not be reduced and released along with the I atom. In fact, release rates of I in this study were significantly higher than reported release rates of Cs from a thoria rich matrix [11]. The cations that are more likely to be reduced as compensation for the atomic release are a minute fraction of higher valent uranium species such as U^{+5} or U^{+6} present in the slightly hyper-stoichiometric UO_2 component of the

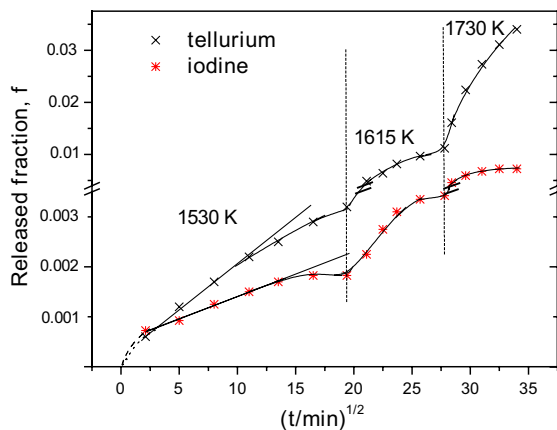cubic phase. Thus the overall release process of I(g) can take place by the reaction, $U_{lattice}^{n+} + I_{lattice}^{-} = U_{lattice}^{(n-1)+} + I(g)$, ($n = 5$ or 6) and following either of the two mechanistic paths: (i) I^- gets oxidized to I at lattice site and then diffuses out as neutral atoms, or, (ii) it diffuses out in the ionic form and gets released as I atoms leaving behind its electron at the boundary. The left-out electrons in turn come back inside the lattice under the internal electric field either to reduce the compensating cation, or to occupy a vacant site.

I release via the first mechanistic path depends on the local concentration of I atoms generated through the oxidation–reduction reaction. For release via the second path the diffusion of I^- has to take place against the internal electric field set-up due to its separation from the less mobile compensating cation. In spherical geometry of the grain, the radial electric field under the electrical potential $\varphi(r)$ is $\overline{E}_r \equiv -\partial\varphi/\partial\overline{r}$, which is positive in this case. With the I-release in progress, the concentration of left-out electrons (c^e) at the lattice boundary as well as the value of $\overline{E}_r$ grow up to a limit when inward drift flux of the electrons, $J_{in}^e \equiv (-e)\overline{E}_r u_r^e c^e$, due to its electric charge $(-e)$ and mobility u_r^e balances the net outward flux of I^-, $J_{out}^i \equiv -D\partial c^i/\partial\overline{r} - e\overline{E}_r u_r^i c^i$. J_{out}^i is constituted of the diffusion flow of the anion due to the radial gradients of its concentration c^i and the drift flow due to its mobility u_r^i under the field $\overline{E}_r$, respectively [12]. At the steady state limit of the flux balance, the rate of I release given by J_{out}^i reaches its minimum value, the minimum being decided by the mobility of electron and the anion, and also the ionic diffusivity in the lattice. The respective properties being temperature dependent the steady state can be disturbed with the increase in the annealing temperature. At the higher temperature, the annealing would result in the attainment of a new steady state after a spate of initial release as seen at the lower temperature.

Diffusion via the ionic path thus corroborates to the observed gradual impediment on the linear cumulative release of I atoms at each annealing temperature in stepwise heating (Fig. 2). The halt in release observed at each temperature suggests that the minimum flux of I(g) established at the steady state was below the overall sensitivity of assigning the fraction release ($\pm 5 \times 10^{-5}$) in the present measurements. For the lesser electronegative element Te, the path of ionic diffusion is less pronounced as evident from its release kinetics; the slowing down effect in Te release was less as compared to that of I. For Te, the other path of diffusion as atoms is more likely in comparison.

The observed pattern of the cumulative release of I and Te with time was analyzed with the help of Booth's model [13] taking into consideration the manifestation of the inherent electric field developed in the lattice during the diffusion process. Booth's model simulates the microstructure of the sample by a collection of

equivalent spheres having a surface per unit mass identical to that of the sample characterized by its BET surface. The radius, a, of the equivalent sphere of the model is correlated to the specific surface, S, of the sample of average grain density ρ as $a = 3/(\rho S)$. With an initially uniform distribution of the volatile fission product within the spheres, the model formulates the cumulative release of the species with time by using the diffusion equation in spherical geometry. The concentration of the diffusing species maintained null values at the spherical boundary, the cumulative released fraction for a species with diffusivity, D at a time period, t is expressed in the absence of any other driving force than the concentration gradient [12,13] as

$$f(t) = 1 - \frac{6}{\pi}\sum_{1}^{\infty}\frac{1}{n^2}\exp(-n^2\pi^2 D't), \qquad (1)$$

where $D' \equiv D/a^2$ is the apparent diffusion coefficient of the species. For samples with a fixed value of a, D' remains constant at a temperature. Under very short time approximation ($D't \ll 1$) the release is given by $f(t) = 6\sqrt{D't/\pi}$. The linear part of the plots of cumulative release versus (time)$^{1/2}$ observed in the first few hours in the case of I and Te release from the thoria-2 mol% urania matrix was thus interpreted as the constant $6\sqrt{D'/\pi}$ for the respective species. The apparent diffusion coefficients D' for the two volatile species evaluated thereof at different temperatures are plotted as logarithm of D' versus $1/T$ as shown in Fig. 3. The linear least-square fits of the plots are given by

$$\log D_I'\ (s^{-1}) = -(15\,000 \pm 1000)/T - 1.19 \pm 0.63, \qquad (2)$$

$$\log D_{Te}'\ (s^{-1}) = -(25\,600 \pm 1200)/T + 6.14 \pm 0.77. \qquad (3)$$
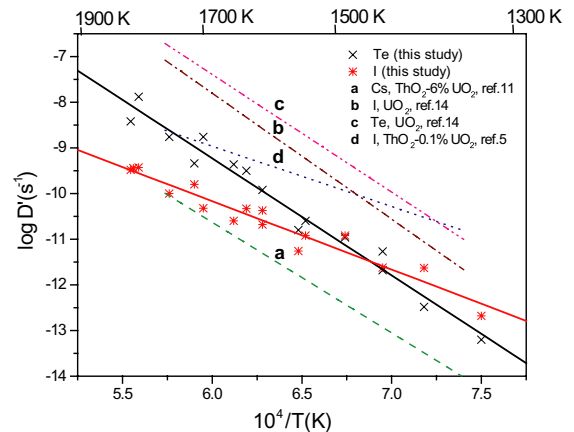

Fig. 3. Temperature trends of apparent diffusivities of iodine and tellurium in the thoria-2 mol% urania matrix.

For the sake of intercomparison, the reported results of release kinetics of I, Te and Cs from thoria and urania-based matrices are included in Fig. 3, which shows that the temperature trend of the diffusion coefficient of iodine obtained in this study is similar to that reported by Naik et al. for the thoria-0.1 mol% urania matrix. The higher value of the reported data of the apparent diffusion coefficient, D'_I could be due to the usage of the less dense matrix ($\approx$90% T.D.) with smaller radius of the equivalent spherical particle ($a = 9.4$ μm) in their experiment. The lowering of D'_I values with the increase in the matrix-density is reported by Naik et al. [5] from their release study in the thoria-0.1 mol% urania matrix with the two different densities and the a values: 90% T.D. ($a = 9.4$ μm) and 79% ($a = 0.23$ μm). Fig. 3 also shows that the transport coefficients for both the species, I and Te, are significantly lower in the thoria matrix as compared to those reported in the urania matrix [14]. In Fig. 3, it is evident that below 1780 K, the transport coefficient of Cs reported for the thoria based fuel matrix [11] remains lower than that of I obtained in this study.

The result of this study indicates that the diffusion of Te significantly differs from that of I; the diffusion coefficient of Te has steeper rise with temperature resulting in its higher release rate as compared to that of I above 1460 K. The activation energies, E, of diffusion of the two species calculated from the Arrhenius plots are 286 kJ mol^{-1} for iodine and 491 kJ mol^{-1} for tellurium. The corresponding jump frequencies, i.e., the values of D'_0 are 6.4×10^{-2} s^{-1} and 1.38×10^6 s^{-1}, respectively. The E-value for iodine is somewhat higher than that of 249 kJ mol^{-1} for the thoria-0.1%urania matrix [5], and significantly lower than that of 481 kJ mol^{-1} for the polycrystalline UO_2 matrix [14], though both the reported data were also derived from release studies of trace-irradiated polycrystalline samples. Since such an irradiated sample does not show the presence of fission gas bubbles, the kinetic data generated by post-irradiation annealing experiment should corroborate to the property of single atom/ion diffusion in the grains and grain boundaries. In fact, the E(I) value of this study can be compared with the value of 270 kJ mol^{-1} reported for the oxygen diffusion inside the thoria matrix [15]. It suggests that both the anion vacancies and interstitials contribute to the iodine diffusion inside the lattice like the case of oxygen as reported [16]. As for the Te-diffusion the present data suggest that the species follow a different mechanistic path of diffusion. The high value of 491 kJ mol^{-1} for E(Te) is in agreement with the reported value of 481 kJ mol^{-1} for the Te diffusion in the polycrystalline UO_2 matrix [14]. It is interesting to find that the E(Te) value compares well with the activation energy of 478 kJ mol^{-1} for the Xe diffusion in the ThO_2–6 mol% UO_2 matrix reported from the study of release kinetics of trace-irradiated samples [17]. The high value of acti-

vation energy possibly corroborates to the diffusion of Te-species using a tri-vacancy complex consisting of one Th and two O vacancies in the fluorite lattice of ThO_2 as reported in the case of Xe diffusion [17]. However, such corroboration remains speculative in the absence of a detailed analysis of the diffusion behavior of the two chemically different species, Te and Xe.

4. Conclusion

From post-irradiation annealing study of a trace-irradiated fuel sample of dense powder (>95% T.D. and particle size 37–45 μm) of ThO_2–2 mol% UO_2, the transport properties of iodine and tellurium were derived and the properties were found to be different in the two species; with temperature increase, the extent of Te release was more than that of I. Further, the release of both the species from the thoria matrix were observed to be quite less as compared to those reported from pure urania.

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