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Transport properties of I, Te and Xe in thoria–urania SIMFUEL

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ABSTRACT

Diffusion properties for volatile fission products iodine and tellurium, and gaseous product xenon in a solid solution of thoria–2 mol% urania doped with fission products for simulating 2 at.% burnup were obtained by studying the release kinetics of the species from trace-irradiated fuel samples at different temperatures using post-irradiation annealing technique. Bulk diffusion coefficients for Xe, I and Te were evaluated in a well-defined powder sample of particle size in the range of 37–45 μm (25 $m^2\ kg^{-1}$ BET surface area) with 97% of theoretical density. Temperature dependences of the apparent diffusion coefficients of Xe, I and Te derived from this study could be expressed in the form of Arrhenius equations for the respective cases as $\ln D'_{\mathrm{I/Simfuel}}\ (\mathrm{s}^{-1}) = -(19{,}480 \pm 3300)/T - 9.3 \pm 2.2$ and $\ln D'_{\mathrm{Te/Simfuel}}\ (\mathrm{s}^{-1}) = -(31{,}234 \pm 3000)/T - 3.7 \pm 2.0$, $(1273 \leqslant T/K \leqslant 1773)$ and $\ln D'_{\mathrm{Xe/Simfuel}}\ (\mathrm{s}^{-1}) = -(22{,}755 \pm 1364)/T - 0.003 \pm 0.775$, $1700 \leqslant T/K \leqslant 1800$. For Xe diffusion the activation energy and frequency factor are 189 kJ mol^{-1} and 0.997 s^{-1}, respectively. For I and Te the activation energy values are 162 and 260 kJ mol^{-1}, respectively. The respective frequency factors for I and Te are 9.1×10^{-5} and $2.5 \times 10^{-2}\ s^{-1}$. On comparison with the reported data in pure urania and thoria matrices a lowering of activation energy for all three species was observed in case of the fission product doped matrix. On the other hand the frequency factor has increased only in the case for diffusion of Xe. This suggests different mechanisms of transport for Xe and volatile fission products I and Te in the fuel matrix.

1. Introduction

Safe operation of a nuclear reactor depends on the performance of its fuel-clad assembly. One of the important factors deciding the fuel performance is the distribution of the fission products generated within the fuel. Most of the fission products remain as dissolved state in the fuel while the others separate out as different phases. The gaseous and volatile fission products belong to the last category. The gaseous products xenon (Xe), and krypton (Kr) and the volatile products, iodine (I), tellurium (Te), cesium (Cs) and rubidium (Rb) get transported and redistributed in the fuel pin and ultimately accumulate at fuel-clad gap. The gaseous accumulations make significant change in gap conductance of heat energy while the reactive volatiles settlements deteriorate the mechanical property of clad. Detailed studies on their transport properties are necessary to understand the extent of their release from the matrix and these data help to judge the fuel performance under different irradiation conditions. The fission gases and volatiles are released by cumulative consequence of athermal and thermal processes. The athermal release by recoil and knock out processes in fission events and the thermally activated release through the combined effect of atomic diffusion to grain boundaries, grain growth and gas bubble formation and its migrations are well established in the case of conventional fuels [1]. Intragranular atomic diffusion, the primary step for the thermal release, is very specific for a fuel matrix. After a certain period of irradiation a steady state is attained with respect to the dissolution of the generated fission gases into bubbles and their resolution into the fuel matrix. Under such situation the transport of fission gases is totally governed by the intragranular diffusion phenomena. As for urania and plutonia based fuels, sufficient amount of data are reported on the diffusional transport properties of fission gases and volatiles [1,2] in these matrices. Such data are scanty for thoria based matrix envisaged as the fuel for advanced heavy water reactors (AHWR) in the third phase of the nuclear power generation programme in India. Thoria containing 3–4 mol% urania and plutonia will be used in AHWR fuel pins [3]. Transport properties of iodine, tellurium and xenon in the virgin fuel of thoria have been reported [4,5]. However, very little information exists about the influence of fission products incorporated in the matrix on the transport properties of I, Te and Xe [5]. At high burnup the oxide lattice undergoes significant change by the incorporation of the fission products as partially/fully dissolved states inside the fluorite phase, or as dispersed phases of oxide, metallic, or gaseous states. There is formation of significant concentrations of anionic vacancies in the oxide lattice due to substitution of trivalent yttrium and rare earths, and bivalent alkaline earths. Further, there is change of

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morphology by microdispersed phases particularly the bubbles of gaseous fission products. The diffusion of atomic species can be influenced by the vacancies as well as the altered chemical environment due to the dispersed phases. Iodine and tellurium should have significant change in their diffusion characteristics by their chemical affinities to the metallic fission products. Xenon diffusion reportedly takes place through MO_2-trivacancy [2], or, tetravacancy complex of MO_2 and a cation [4]; substitutional vacancies of cation or anion are seen to have very little role [6,7]. Metal oxides like magnesia, niobia added for activated sintering and densification of the thoria based fuel can lead to formation of trivacancies by partial loss of the MgO component from the lattice during the high temperature treatment. The added oxides of alkaline earth fission products also lead to trivacancies in the simulated fuel lattice by their partial loss during the high temperature sintering [8]. The fuel lattice with the partial depletion of the oxide components is expected to have augmented diffusion.

In this study the diffusion data were generated for xenon and volatile fission products iodine, and tellurium in a solid solution of thoria–2 mol% urania doped with fission products for simulating 2 at.% burnup. Thoria used was predoped with magnesia for better sinterability. The kinetic data for the transport and release of the volatile species were obtained by using the post-irradiation annealing technique of the trace-irradiated fuel samples at different temperatures. In this technique the released fraction of the volatile components I and Te from irradiated fuel were collected on hot copper collectors where they were chemically fixed and radiometrically analyzed offline for the gamma activities of ^{131}I and ^{132}Te. For measurements on xenon transport the released gas at different temperatures was swept by helium into a charcoal trap cooled under liquid nitrogen. The gamma activity due to ^{133}Xe (81 keV, $t_{1/2}$ 5.27 days) adsorbed in the online trap was periodically counted with a gamma ray spectrometer.

2. Experimental

Powder samples of ThO_2–2 mol% UO_2 solid solution containing transition metal, rare earth and alkaline earth fission products were prepared as follows: Thoria powder of nuclear purity containing 600 ppm of Mg for better sinterability of the fuel pellet was used. The powder was co-grounded homogenously with weighed amount of urania and nine selected fission product elements in the form of their oxides, or carbonates, or in metallic forms (La_2O_3, Y_2O_3, CeO_2, ZrO_2, $Nd_2(CO_3)_3$,$7H_2O$, $BaCO_3$, $SrCO_3$, Ru and Mo). The elements were added to attain the fuel composition corresponding to a burnup of 20 GWD T^{-1}. The concentration of the elements calculated using the ORIGEN code [9] replicate the irradiated fuel. Elements with a similar chemical behavior were represented by a single element. Thus Nd and Ru additions were made to such extents that they respectively represent the trivalent rare earths (excluding La and Ce), and the metallic fission products (excluding Mo). The gaseous products Xe and Kr, and also the volatile fission products like alkali metals were not considered in the synthesis of simulated fuel. The added concentrations in milligrams of element per kilogram of fuel are listed in Table 1. The mixed powder was pressed in two stages to attain high green density, calcined at 1073 K under flowing argon atmosphere for several hours to decompose the carbonates to oxides and then sintered at 1900 K in flowing argon containing 8% hydrogen. The sintering operations were carried out in our laboratory using high temperature furnaces. Density of the sintered pellet measured by liquid displacement method was found to be about 97% T.D. The pellets were crushed to powder and then sieved to extract the particle size of the range 37–45 μm for the post-irradiation annealing experiments. The chemical analysis of Simfuel powder was carried out in Fuel Chemistry Division, BARC and the ICPMS analysis results agreed within 10–20% with the added amounts for all the elements except Ba and Mg, for which the agreement was within 43% and 28%, respectively. The large difference seen for Ba and Mg is taken to be due to evaporation loss of these elements. SEM-EDAX analysis was also carried out to see the grain morphology and overall homogenous distribution of the constituents. The BET surface area of the fuel sample was measured to be about 25 $m^2 kg^{-1}$. The radius of equivalent sphere having the same specific surface area worked out to be 12.5 μm. The derived radius was used in statistical treatment of the fuel sample of particle size 37–45 μm while analyzing the transport properties of Xe, I and Te.

Table 1
Simfuel composition.

Elements	Concentrations (mg/kg of fuel at 20 GWD T^{-1} burnup) computed using ORIGEN-2 Code	Added concentrations (mg/kg of fuel)	Concentrations in the sintered Simfuel (97% T.D.)
Y	499	499	460
La	776	776	710
Nd	3383	3383	2850
Ce	1868	1868	1780
Zr	2723	2723	2700
Mo	1772	1772	1430
Ru	1294	1294	1250
Ba	791	791	450
Sr	973	973	850
Mg (sintering aid)		600	430

Typically one gram of the powder specimen in evacuated and sealed quartz capsules were irradiated in Apsara reactor of this research centre at a low burn up dose of about 5×10^{20} fissions m^{-3}. The sample temperature during irradiation was estimated to be less than 400 K. After irradiation, the specimens were cooled for a period of 10 days to allow the short-lived activities to decay. The powder specimen was transferred to the molybdenum Knudsen cell of the PIA experimental set up (Fig. 1a) for the study of the release behavior of the fission product iodine and tellurium from fuel materials. The detailed description of the equipment and experimental procedure are given elsewhere [10,11]. The annealing experiments were performed in the temperature range, 1273–1773 K. Released iodine and tellurium from the heated sample effused out from the cell-orifice upwards in high vacuum and passed through a heated duct of molybdenum to get collected on copper foils at 700 K as copper iodide and telluride, respectively.

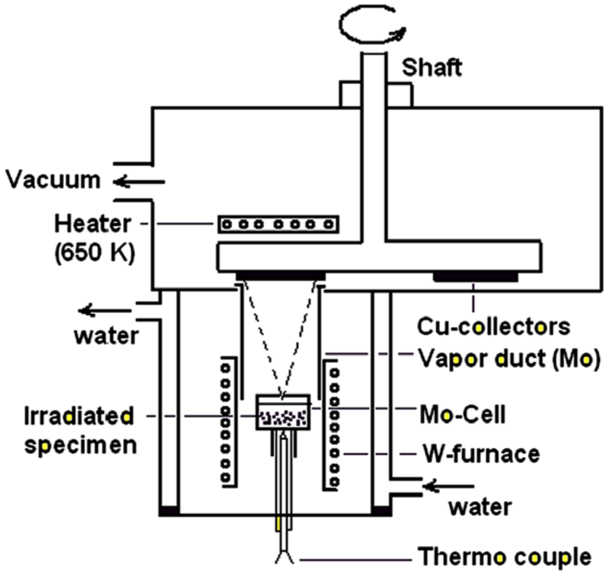

Fig. 1a. PIA apparatus for I and Te release study.

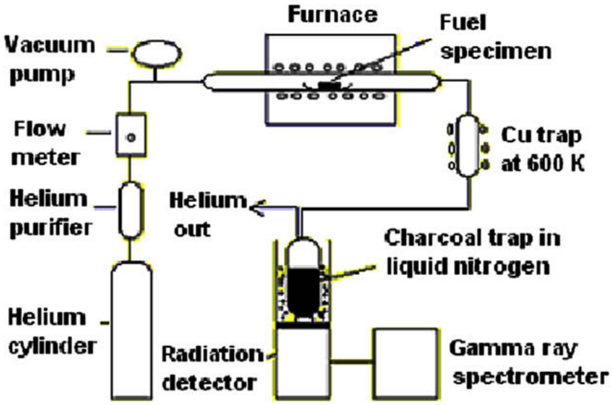

Fig. 1b. PIA apparatus for Xe release study.

The collection efficiencies for the two species were pre-calibrated in separate experiments using appropriate standards [10]. Isothermal annealing experiments were carried out typically over a period of 6 h. Within this period six to eight copper collectors were exposed to the atomic beam for monitoring the release kinetics. Radiometric analyses of ^{131}I and ^{132}Te in the collected deposits and in the fuel sample were carried out with the help of HPGe detector coupled to 4 K MCA. The two isotopes were selected for the analyses because of their suitable half-lives and gamma energies of 8.01d, 364 keV and 78 h, 228 keV, respectively. To get the fractional release the collected amount of ^{131}I/^{132}Te was divided by the total ^{131}I/^{132}Te present in the irradiated sample. The total amount was measured by the radiometric method.

For measurements of xenon release the irradiated specimens were transferred into the furnace of post-irradiation annealing apparatus where they were heated at different annealing temperatures and the released gases were swept out with purified helium. The setup used for gas release study was different from that for the volatiles and its construction is given in earlier publications [10] for Xe release from virgin fuel of thoria. A schematic of the apparatus is shown in Fig. 1b. The gas mixture swept through activated charcoal trap kept at liquid nitrogen temperature. The activity due to ^{133}Xe isotope adsorbed in the trap was periodically counted in situ with a gamma ray spectrometer. The ^{133}Xe is a gamma emitter with a photo peak at 81 keV and a half life of 5.27 days. The total ^{133}Xe present initially in the specimen was obtained by dissolving a known amount of the irradiated sample in conc. HNO_3 at 80 °C and trapping the Xe released and swept into a charcoal trap and recording the activity. The Xe adsorption efficiency of the trap was confirmed by using a second trap in the gas line and monitoring there the absence of Xe activity.

The gamma spectrometry detectors were calibrated with ^{152}Eu (121.8, 344.3 and 778.9 keV) for ^{131}I and ^{132}Te and with ^{133}Ba (81 keV) for ^{133}Xe before every experiment. The energies were calibrated with a resolution of ±1 keV. Peaks of other products were found to be separated at least by 10 keV in the region of measurements of ^{131}I, ^{132}Te and ^{133}Xe. In each case the signal to noise ratio was kept high by placing the sample very near to the detector and shielding it with lead blocks to prevent intrusion of extraneous radiation.

3. Results and discussion

The release behaviors of ^{131}I and ^{132}Te were analyzed by plotting the cumulative fractions of these isotopes collected on copper foils as a function of $t^{1/2}$, where t is isothermal annealing time. The release behavior of fission gases in trace-irradiated fuel materials has been analyzed by the equivalent sphere model by Booth [12]. In this model, low values of released fraction, f, in the cases of long lived or stable isotopes is approximated by $f = 6(Dt/\pi a^2)^{1/2}$, where D is the lattice diffusion coefficient and 'a' is the radius of the equivalent spheres that statistically represent the specimen with their specific (BET) surface area identical to that of the specimen. Thus, when release is controlled by lattice diffusion in fuel materials, f versus $t^{1/2}$, or, f^2 versus t plots show straight lines, that is, linear release. In the present case of sintered Simfuel powder similar analysis provides the data on the release kinetics of I, Te and Xe isotopes that have comparatively long half-lives as compared to the experimental times.

Fig. 2 shows the typical nature of plot for the fractional release of ^{131}I and ^{132}Te from Simfuel powder specimen as a function of annealing time at 1773 K. The apparent diffusion coefficients D' ($=D/a^2$) were evaluated from the steady state part of the plots (indicated by dotted lines) at different temperatures in the range of 1273–1773 K. After initial burst release the cumulative release of iodine grew sluggishly over a small period and then attained the steady rate unlike the case of virgin fuel, where the iodine release in particular came almost to a halt after two hours annealing [10]. For tellurium, the steady growth of released fraction was attained soon after the burst release. The values of diffusion coefficient D ($\mathrm{m^2\,s^{-1}}$) of iodine and tellurium were calculated from the respective D' values by making use of the value of radius of equivalent sphere, $a \sim 12.5$ μm. The radius value was obtained from the specific surface area, $S = 25\ \mathrm{m^2\,kg^{-1}}$ from measured BET surface of the specimen of density, $\rho = 9700\ \mathrm{kg\,m^{-3}}$ ($a = 3/(\rho S)$).

The same procedure as in the case of iodine and tellurium was used to analyze the release behavior of Xe. Fig 3 shows a typical plot of fractional release of Xe versus square root of time from thoria–urania SIMFUEL. The total ^{133}Xe present initially in the specimen was obtained by dissolving a known amount of the irradiated sample in conc. HNO_3 at 80 °C and trapping the Xe released and swept into a charcoal trap and recording the activity. The Xe adsorption efficiency of the trap was confirmed by using a second trap in the gas line and monitoring there the absence of Xe activity. For the evaluation of apparent diffusivity D', the slope of the initial linear growth of Xe release up to the extent of 30–40% was considered.

The diffusion coefficients of iodine, tellurium and xenon in the Simfuel specimen were found to have temperature dependence as given by the Arrehenius relation $D = D_0 \exp(-Q/RT)$ where D_0/a^2 is frequency factor (D'_0), Q is the activation energy, R the

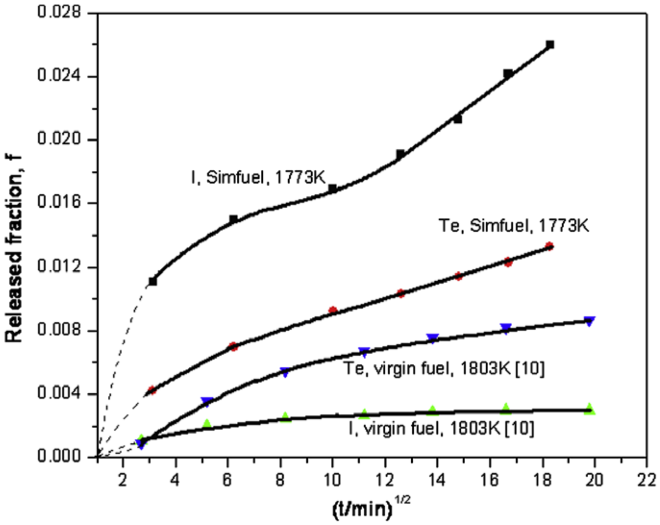

Fig. 2. Typical release plot of I and Te from Simfuel as compared to virgin fuel.

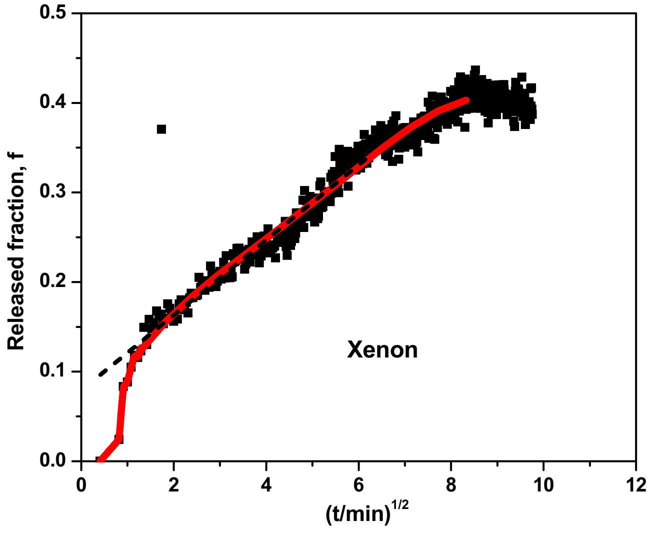

Fig. 3. Typical plot of Xe release from Simfuel at 1773 K.

gas constant and T is the absolute temperature. D'_0 refers to the jump frequency of the diffusing species across the characteristic length 'a' to another equivalent site. The more strongly a species is held at its site lower is the probability of its jump and therefore the frequency of jump (D'_0). Besides the jump frequency another important factor for reaching an equivalent site is the energy barrier (Q) encountered across the path. The exponential governed by Q decides the number of effective jumps. Fig. 4 shows the plot of log D' versus $1/T$ for the steady state release of both iodine and tellurium. The linear least square fits of the plots are respectively given by

$$\ln D'_{\mathrm{I/Simfuel}}(\mathrm{s}^{-1}) = -(19,480 \pm 3300)/T - 9.3 \pm 2.2$$

$$\ln D'_{\mathrm{Te/Simfuel}}(\mathrm{s}^{-1}) = -(31,234 \pm 3000)/T - 3.7 \pm 2.0$$

Thus, the apparent lattice diffusion coefficients of iodine and tellurium in Simfuel in the temperature range of 1273–1773 K can be expressed by the following relations, (1) and (2):

$$D'_{\mathrm{I/Simfuel}}(\mathrm{s}^{-1}) = 9.1 \times 10^{-5} \exp[(-162\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT}] \tag{1}$$

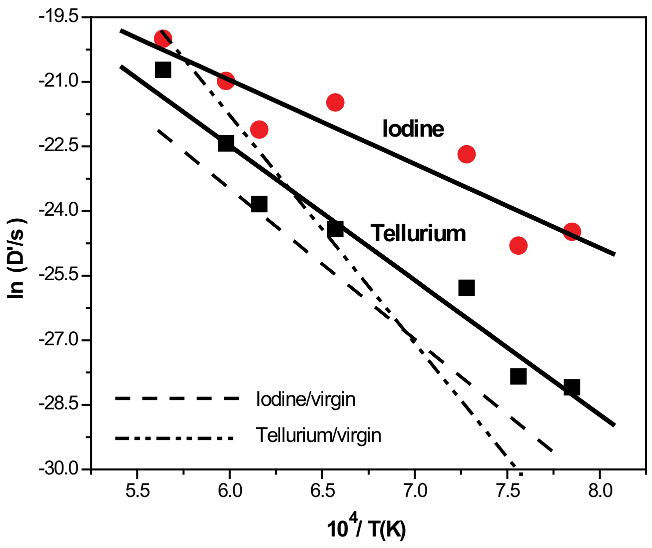

Fig. 4. Arrhenius plots of I and Te diffusions in Simfuel as compared to virgin fuel.

Table 2
Summary of kinetic parameters of I, Te and Xe.

Fuel type and data generated	D_0 ($\mathrm{m}^2\ \mathrm{s}^{-1}$)	Q (kJ mol^{-1})
I release from virgin fuel [10]	$(23 \pm 20) \times 10^{-12}$	287 ± 19
I release from Simfuel [This study]	$(6 \pm 6) \times 10^{-14}$	162 ± 27
Te release from virgin fuel [10]	$(6 \pm 6) \times 10^{-4}$	490 ± 23
Te release from Simfuel [This study]	$(16 \pm 12) \times 10^{-12}$	260 ± 25
Xe release from Simfuel [This study]	$(20 \pm 13) \times 10^{-11}$	189 ± 11

$$D'_{\mathrm{I/Virgin\ fuel}}(\mathrm{s}^{-1}) = 6.4 \times 10^{-2} \exp[(-286\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT}], \tag{1a}$$

$$D'_{\mathrm{Te/Simfuel}}(\mathrm{s}^{-1}) = 2.5 \times 10^{-2} \exp[(-260\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT}], \tag{2}$$

$$D'_{\mathrm{Te/Virgin\ fuel}}(\mathrm{s}^{-1}) = 1.4 \times 10^{6} \exp[(-491\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT}]. \tag{2a}$$

The corresponding expressions for the diffusion coefficients of iodine and tellurium can be obtained by using the relation, $D(\mathrm{m}^2\ \mathrm{s}^{-1}) = D'\ (\mathrm{s}^{-1}) \times 1.6 \times 10^{-10}$. For comparison, the results of virgin fuel of thoria–urania reported earlier [10] are also included (relations (1a) and (2a)). The kinetic parameters for the different cases are summarized in Table 2. It is seen that in simulated fuel lattice, both the volatile species, I and Te, encounter less barrier of energy in their diffusion paths. This can be due to the presence of anionic vacancies in the fuel, the vacancies being formed by the substitution of trivalent rare earths and bivalent alkaline earths in the MO_2 fluorite lattice. Results of reported studies [13] in fact suggest that iodine diffuses through anionic vacancies. The reported Q value [5] for self diffusion of anion in thoria is about 270 kJ mol^{-1}. As electronegative elements, both the species form compounds with many fission products elements. Iodides and tellurides of Cs/Rb, and tellurides of Ru, Rh and Pd are quite stable at elevated temperatures [1]. Tellurium's greater affinity in metallic components of the Simfuel, is reflected in its larger drop in the frequency factor as compared to that of iodine. The jump frequency of Te dropped by about eight orders of magnitude whereas that of iodine by about three orders only. The diffusion is chemically driven. The opposing effects of jump frequency and activation barrier energy have been reflected in the kinetic coefficient D'. At higher temperature (~1600 K), the kinetic coefficient of tellurium has therefore fallen below that in virgin fuel (Fig. 4). As for iodine, this effect is not manifested within the experimental temperature range. There is little information on iodine and tellurium diffusion in simulated fuel matrix of thoria based fuel. The reported results [14] on the release kinetics of ion implanted iodine in Simfuel of thoria can at best be considered for qualitative analysis of the release behavior from reactor irradiated fuel because ion implanted matrix does not truly represent the case of irradiated fuel materials where the concentration of the volatile products as well as radiation induced defects are uniformly distributed in the matrix. Fig. 5 shows the Arrhenius plot for the apparent diffusion coefficient of Xe, $D'_{\mathrm{Xe/Simfuel}}$, in the thoria–urania Simfuel in the measured range of temperatures (1713–1801) K. D' values were derived from the steady state release of the gas. The linear least square fit of the plot is given by $\ln D'_{\mathrm{Xe/Simfuel}}\ (\mathrm{s}^{-1}) = -(22,755 \pm 1364)/T - 0.003 \pm 0.775$. The variation of the apparent diffusion coefficient could be expressed by the relation $D'_{\mathrm{Xe/Simfuel}}\ (\mathrm{s}^{-1}) = 0.997\ \exp[(-189\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT})]$. The powder specimen being represented by spheres of radius 12.5 μm, the temperature dependent actual diffusion coefficient is given by $D_{\mathrm{Xe/Simfuel}}\ (\mathrm{m}^2\ \mathrm{s}^{-1}) = 1.5 \times 10^{-10}\ \exp[(-189\ \mathrm{kJ\ mol}^{-1})/\mathrm{RT})]$.

Some data are available on the diffusivity of Xe in pure urania, and thoria–urania solid solutions [4,5]. Data on SIMFUEL are absent. Matzke [6] has studied the Xe diffusivity through urania matrix by ion implantation technique and found the temperature dependence of diffusivity to be $D_{\mathrm{Xe}}(\mathrm{m}^2\ \mathrm{s}^{-1}) = 5.01 \times 10^{-14}$

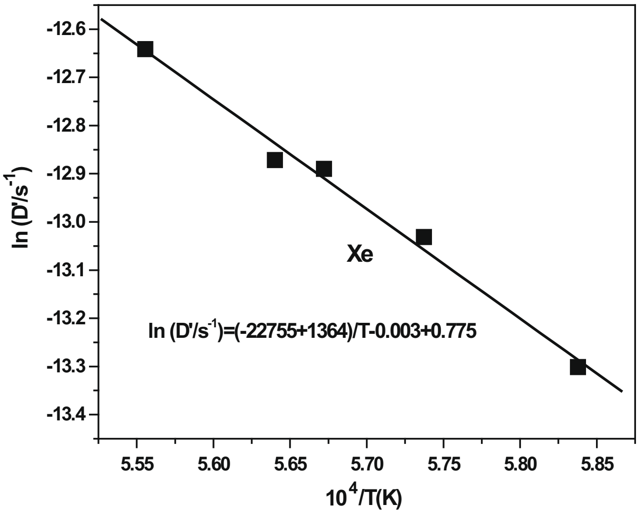

Fig. 5. Arrhenius plots of Xe diffusion in Simfuel.

exp[(−335 kJ mol^{-1})/RT)]. Reported data by Naik et al on xenon release from thoria–1% urania [5] (90% T.D, particle size 35–45 μm) irradiated at the dose of 5.5×10^{21} fission m^{-3} indicate that the gas migration occurs through interstitial motion of Xe atoms with activation energy around 239 kJ mol^{-1} and a frequency factor of 0.009 s^{-1}; the data corroborates to the diffusion coefficient D_{Xe} (m^2 s^{-1}) = 1.4×10^{-12} exp[(−239 kJ mol^{-1})/RT)]. Powder specimen used by Naik et al. had nearly same specific surface area as in the present case. Naik et al. have also shown that the presence of dissolved fission products have insignificant influence on the diffusivity of xenon through the fuel matrix. Shiba [4] have reported xenon release from (Th, U)O_2 kernels with grain size of 10 μm and density approximately 99% T.D. and irradiated at the low dose of 10^{21} fission m^{-3}. Their reported data resulted in diffusion coefficients to be expressed as D_{Xe} (m^2 s^{-1}) = 2.6×10^{-5} exp[(−478 kJ mol^{-1})/RT)]. Shiba et al. explained the observed high barrier energy by invoking that Xe transport occurred through tetra vacancy mechanism [15], that is, a cationic vacancy joining with the normally envisaged neutral trivacancy out of a missing MO_2 molecule in the fluorite lattice. The mechanism involves high energy because the cation vacancy formation and migration together control the movement of Xe-trivacancy complex.

Intercomparison of the present result of Xe diffusion in thoria based Simfuel with those of the reported ones summarized above shows that the derived Q value of 189 kJ mol^{-1} is below the reported values that range from 239 kJ mol^{-1} to 478 kJ mol^{-1}. It is rather closer to the theoretically predicted activation energy of about 2.1 eV for Xe migration involving trivacancies [2] (Schottky trios) in the fluorite MO_2 lattice. Incidentally, the transport of Xe was carried out in the same setup using the procedure led by Naik et al. who noted Q value of 239 kJ mol^{-1} in their low density of thoria–1%urania specimen (90% T.D.). In the presently used higher density fuel (~97% T.D.), the proximity of the derived activation energy to that predicted by trivacancy mechanism is possibly because of the formation of significant concentration of trivacancies in the oxide lattice by evaporation of doped magnesium oxide ($[MgO]_{fluorite} = Mg(g) + ½\,O_2(g)$), barium and strontium oxides during long time sintering of the fuel pellet at high temperature. Further, one can compare the frequency factor of 0.997 s^{-1} of this result with the value of 0.009 s^{-1} reported by Naik et al. who worked with specimen having nearly same characteristic dimension ($a \sim 12.5$ μm). The presently observed significant rise in the frequency factor corroborates to the presence of augmented concentrations of trivacancies in the Simfuel. The combined effect of higher jump frequency and lower barrier energy is evidenced in attaining very high release of Xe within short annealing time. Fig. 3 shows that the cumulative release is more than 40% within an hour of annealing of the irradiated Simfuel powder specimen at the temperature of 1773 K.

As expected, the diffusional transport coefficients of iodine, tellurium and xenon are quite different from those of the urania based fuel matrix. The transport properties were obtained for the evaluation of thermal release of these species from thoria–urania fuel of advanced heavy water reactor. Though the athermal part of release generally dominate in the normal operating temperatures of the PWR fuel, the thermally activated part becomes significant at higher temperatures during power ramp situation. The evaluation of thermal release involves solving transport equation that describes concentration evolution in time considering the rates of atom generation, atomic diffusion under variable boundary due to grain growth, release of diffused atoms in gas bubble and resolutions of atoms into the lattice. The diffusion flux expressible with the presently generated data will complement the evaluation. Rich experience available for thermal as well as athermal release from urania fuels will set the guideline. As for the release during off-normal situation of the nuclear reactor, the reported information of augmented release [16] from urania due to its lattice expansion from oxidation and therefore O/M rise would require reconsideration in the case of thoria rich fuel. This is so as oxygen incorporation in thoria fuel will be insignificant due its poor affinity for oxidation as well as oxygen transport. As a result, the release during off-normal situation will be mostly governed by the gas in plenum, where the accumulation takes place cumulatively over the irradiation period.

4. Conclusions

Transport properties for xenon and volatile fission products iodine, and tellurium in a solid solution of thoria–2 mol% urania doped with fission products for simulating 2 at.% burnup were obtained by studying the release kinetics of the species from trace-irradiated fuel samples at different temperatures using post-irradiation annealing technique. Bulk diffusion coefficients for Xe, I and Te were evaluated in a well-defined powder sample of particle size in the range of 37–45 μm (25 m^2 kg^{-1} BET surface area) with 97% of theoretical density. In all the three cases lowering of activation energy for diffusion was observed as compared to the case of diffusion in virgin thoria–urania matrix. This decrease can be attributed to the increase in vacancy concentration in the doped fuel matrix. The frequency factors were also significantly lowered in case of I and Te, more so for Te, which indicates its greater affinity as compared to I, for metallic constituents present in the fuel matrix. However, for Xe the frequency factor is found to increase in the present study as compared to the virgin fuel matrix. This increase might be due to its higher mobility owing to the increase of neutral trivacancies generated by evaporation of alkaline earth oxides from the doped fuel matrix. This leads to an augmented release of Xe from the Simfuel matrix as compared to the virgin fuel.

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References

[1] H. Bailly, D. Menessier, C. Prunier (Eds.), The Nuclear Fuel of Pressurized Water Reactors and Fast Reactors-Design and Behavior, Intercept Ltd., 1999.

[2] H.J. Matzke, Diffusion processes in nuclear fuels, in: R.P. Agarwala (Ed.), Diffusion Processes in Nuclear Materials, Elsevier Science, Publishers, North-Holland, 1992.

[3] R.K. Sinha, A. Kakodkar, Nucl. Eng. Des. 236 (2006) 83.

[4] K. Shiba, Diffusion processes in thoria and thorium-based oxides with emphasis on fission fragments irradiation effects, in: R.P. Agarwala (Ed.), Diffusion Processes in Nuclear Materials, Elsevier Science, Publishers, North-Holland, 1992.

[5] M.C. Naik, Diffusion controlled and burst release of gaseous and volatile fission products from UO_2 and ThO_2, in: R.P. Agarwala (Ed.), Diffusion Processes in Nuclear Materials, Elsevier Science, Publishers, North-Holland, 1992.

[6] H.J. Matzke, Nucl. Appl. 2 (1966) 131.

[7] H.J. Matzke, J. Nucl. Mater. 21 (1967) 190.

[8] J.P. Hiernaut, T. Wiss, J.Y. Colle, H. Thiele, C.T. Walker, W. Goll, R.J.M. Konings, J. Nucl. Mater. 377 (2008) 313.

[9] B. Krishna Mohan, Physics aspects of advanced heavy water reactor, in: Ann. Prog. Rep., 1998–1999, BARC/1999/I/007.

[10] K.N.G. Kaimal, A.S. Kerkar, A.N. Shirsat, D. Das, A. Datta, A.G.C. Nair, S.B. Manohar, J. Nucl. Mater. 317 (2003) 189.

[11] K.N.G. Kaimal, A.S. Kerkar, A.N. Shirsat, D. Das, A. Datta, A.G.C. Nair, S.B. Manohar, Conf. INS (INSAC 2001), Indore, 10–12 October 2001, p. 7.

[12] A.H. Booth, G.T. Rymer, Report CRDC- 720, 1958.

[13] M.C. Naik, A.R. Paul, K.N.G. Kaimal, J. Nucl. Mater. 96 (1981) 57.

[14] H.J. Matzke, R.A. Verrall, J. Nucl. Mater. 182 (1991) 261.

[15] R.W. Grime, AEA-InTec-0195, 1990.

[16] F.C. Iglesias, B.J. Lewis, P.J. Reid, P. Elder, J. Nucl. Mater. 270 (1999) 21.