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Specific heat of UO_2-based SIMFUEL

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Abstract

The specific heats of SIMFUEL (simulated high-burnup UO_2-based fuel) with equivalent burnups of 3 and 8 at.% were measured between room temperature and 1400°C. The results from samples annealed at three different oxygen potentials showed only small changes with burnup and oxygen potential: the specific heat increased slightly with burnup and oxygen potential. An analytical expression describing specific heat as a function of burnup and oxygen-to-metal ratio (O/M; M represents the uranium and the dissolved metal atoms in the fluorite matrix) is proposed. Changes in the shape of plots of C_p as a function of temperature in the form of 'humps' for hyperstoichiometric UO_{2+x} could be related to the dissolution of the U_4O_9 phase observed by X-ray diffraction at room temperature. The plots of C_p as a function of temperature for SIMFUEL, preannealed under the same conditions, did not show the humps, and X-ray diffraction did not show any indication of U_4O_9 formation. © 1997 Elsevier Science B.V.

1. Introduction

Reliable thermophysical data of UO_2 fuel are required for normal reactor operating conditions and for reactor safety assessments. The specific heat of UO_2 is important in certain accident scenarios: e.g., fuel–coolant interactions, post-accident heat removal and loss-of-coolant accidents, for which the ability to store heat can be critical. In the case of an excursion, the specific heat directly affects the fuel behavior and determines the temperatures attained during the excursion, and therefore the Doppler feedback. Specific heat is also needed to convert thermal diffusivity to thermal conductivity, the former being commonly measured in out-of-pile tests, as was done in our earlier work on SIMFUEL [1–3].

The specific heat and enthalpy of UO_2 have been published in different papers (e.g., Ref. [4]) and these data were critically reviewed 10 years ago by Hyland and Ohse [5]. The available data were assessed and recommendations were made. However, that review does not treat the effect of fission-product buildup and deviation from stoichiometry on the heat capacity of irradiated fuel. C_p data on UO_{2+x} have been published before [6], and a proposal on how to allow for hyperstoichiometry is contained in the MATPRO fuel data collection [7]. There are also several papers by Naito, Matsui and co-workers [8–12] reporting specific-heat measurements on UO_2 doped with the rare earths Gd, La and Eu, or with Sc, Nb or Ti. These authors used direct-heating pulse calorimetry. In their latest paper [12], they report specific-heat values for a simfuel-like material, representing 10 at.% burnup. Their results showed an anomalous increase in specific heat at temperatures that decreased with impurity content (see also Naito [13]). Such an increase (e.g., by up to 25% at 1400 K), was not found in SIMFUEL [1,14] or in (U, Gd)O_2 [15] for the temperatures reported by the Nagoya group. Also, recent measurements of C_p on irradiated high-burnup fuel samples did not find any anomalous increase [16].

In the present paper, we review recent measurements of the specific heat of SIMFUEL at different burnups, and present new data from samples annealed in reducing or slightly oxidizing conditions. The results are analyzed and discussed in terms of the increase in simulated burnup and the deviation from stoichiometry. Analytical expressions for the dependence of specific heat on burnup and deviation from stoichiometry are proposed.

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2. Experimental

Simulated high-burnup UO_2-based fuel (SIMFUEL) replicates the composition, phase structure, and, to a certain extent, microstructure of irradiated high-burnup UO_2 fuels. The burnup is simulated by doping UO_2 with stable additives in appropriate amounts. Because gases and volatiles are not added, the microstructure does not contain the bubbles observed in irradiated fuel. We have previously reported the fabrication procedure of UO_2-based SIMFUEL with equivalent burnups of 1.5, 3, 6 and 8 at.% [17,18].

To replicate the complex structure of high-burnup fuel, it is necessary to achieve a very fine and uniform dispersion of all added fission products, and to reach phase equilibrium during SIMFUEL preparation. This implies that SIMFUEL constituents must be mixed homogeneously on a submicrometer scale, and then heated to sufficiently high temperatures to achieve homogeneity on an atomic level by diffusion. Vacuum-dried, high-purity (99.999%) oxides are dry mixed with natural UO_2 powder. High-energy, wet attrition-ball milling is used to achieve a uniform fine dispersion. A spray-drying step serves to lock the selected composition (corresponding to burnups of 1.5, 3, 6 and 8 at.%) into granules. Conventional precompaction, granulation, pressing and sintering at 1700°C for two hours in flowing H_2 yields a structure typical of a fuel that has operated at high temperatures where solid phase precipitates and gas bubbles form.

Extensive characterization [17–19] has demonstrated the equivalence of the microstructure and phase structure of SIMFUEL to irradiated high-burnup fuel. All classes of fission products (except the gases and volatiles) are found in SIMFUEL. The UO_2 matrix contains fully or partially dissolved oxides (e.g., Nd, La, Ce, Y, Sr, Zr). Spherical metallic Mo–Ru–Pd–Rh precipitates are uniformly dispersed throughout the matrix, and a fine perovskite phase of the $(Ba,Sr)_2ZrO_3$-type precipitates at the grain boundaries. However, because Cs is too volatile to be retained in SIMFUEL composition, it is not added; consequently, possible oxygen buffering by cesium uranate cannot be investigated. Because of the advanced fabrication procedure and the extensive characterization, we regard SIMFUEL as a kind of a tradename for the final product fabricated in the above way. This SIMFUEL has provided valuable data on thermal conductivity degradation with burnup and deviation from stoichiometry [1–3]; the results have allowed prediction and modelling of thermal conductivity of irradiated fuel [20–22].

Unirradiated UO_2 and SIMFUEL samples with equivalent burnups of 3 and 8 at.% were measured using a Netzsch DSC 404 calorimeter. Specimens were annealed in reducing and slightly oxidizing conditions, to achieve various deviations from stoichiometry prior to the C_p measurements. The deviations from stoichiometry were quantified by the coulometric-titration technique [23]. Table 1 lists the designation of the specimens, the annealing conditions, and the measured deviations from stoichiometry. The O/M-ratios given in Table 1 use as metal, M, the sum of uranium and of the dissolved metallic fission products in the fluorite lattice.

The specific-heat measurements were made at a heating rate of 20°C/min in a high-purity argon (99.990% pure with an oxygen scrubber in the gas supply line) atmosphere with a flow rate of 50 ml/min. To avoid oxidation by trapped oxygen, the instrument was evacuated with a standard roughing pump and backfilled several times with argon prior to the tests. Baseline measurements (no sample) and measurements with sapphire (as reference) necessary to compute the specific-heat values from the raw data were performed under conditions identical to those that were used for the test specimens. Specific heats were calculated using the standard ratio method. Data were acquired in 25°C increments between 100 and 1400°C.

3. Experimental results and discussion

Table 2 lists the measured values of the specific heat between 100 and 1400°C. In general, the results show a small increase in the specific heat with burnup and deviation from stoichiometry for each temperature. The results are plotted as a function of temperature for the various

Table 1
Experimental conditions for sample preparation and designation of the specimens. The measured deviations from stoichiometry are also given

Sample ID	Equivalent burnup (at.%)	Annealing conditions (atmosphere, temp., time)	$\Delta\bar{G}(O_2)$ (kJ/mol)	Measured O/M-ratio
$UO_{2.000}$	0 at.% ($UO_{2.00}$)	4% H_2/Ar; 1500°C; 2 h	−540	2.000
$UO_{2.04}$	0 at.% ($UO_{2.04}$)	$CO_2/CO = 99/1$; 1220°C; 2 h	−220	2.035
$UO_{2.08}$	0 at.% ($UO_{2.08}$)	$CO_2/CO = 99/1$; 1380°C; 2 h	−195	2.084
$3S_{2.00}$	3 at.% SIMFUEL	4% H_2/Ar; 1500°C; 2 h	−540	1.997
$3S_{2.07}$	3 at.% SIMFUEL	$CO_2/CO = 99/1$; 1380°C; 2 h	−195	2.071
$8S_{2.00}$	8 at.% SIMFUEL	4% H_2/Ar; 1500°C; 2 h	−540	1.995
$8S_{2.03}$	8 at.% SIMFUEL	$CO_2/CO = 99/1$; 1220°C; 2 h	−220	2.026
$8S_{2.07}$	8 at.% SIMFUEL	$CO_2/CO = 99/1$; 1380°C; 2 h	−195	2.067

Table 2
Specific heat (in J/Kg) for stoichiometric and hyperstoichiometric UO_2 and SIMFUEL with equivalent burnups of 3 and 8 at.% (named 3S and 8S) and with different oxygen contents (see Table 1)

Temp. (°C)	$UO_{2.00}$	$UO_{2.04}$	$UO_{2.08}$	$3S_{2.00}$	$3S_{2.07}$	$8S_{2.00}$	$8S_{2.03}$	$8S_{2.07}$
100	0.262	0.269	0.279	0.263	0.273	0.267	0.280	0.279
200	0.282	0.284	0.286	0.282	0.287	0.284	0.295	0.289
300	0.297	0.299	0.301	0.298	0.300	0.301	0.306	0.307
400	0.304	0.312	0.320	0.304	0.313	0.310	0.323	0.321
500	0.310	0.333	0.355	0.309	0.317	0.316	0.328	0.325
600	0.315	0.331	0.348	0.316	0.323	0.319	0.334	0.330
700	0.318	0.326	0.335	0.320	0.326	0.322	0.342	0.337
800	0.320	0.329	0.337	0.323	0.331	0.327	0.341	0.340
900	0.325	0.326	0.328	0.328	0.337	0.333	0.345	0.343
1000	0.328	0.332	0.340	0.329	0.338	0.330	0.343	0.344
1100	0.331	0.338	0.350	0.330	0.343	0.333	0.342	0.355
1200	0.334	0.339	0.346	0.332	0.345	0.331	0.358	0.359
1300	0.338	0.344	0.353	0.334	0.351	0.332	0.365	0.368
1400	0.342	0.347	0.352	0.336	0.354	0.336	0.368	0.370

burnups and deviations from stoichiometry in Fig. 1 (eight plots grouped by increasing oxygen content, see Table 1).

The specific heat of hyperstoichiometric UO_{2+x} is slightly higher than the values measured for UO_2. Between 400 and 600°C, the specific heats of hyperstoichiometric $UO_{2.035}$ and $UO_{2.084}$ show a hump, which was confirmed in second runs on both samples of hyperstoichiometric UO_{2+x}, the ones for $UO_{2.035}$ being shown in Fig. 2. We attribute this hump to the dissolution of the U_4O_9 phase into the UO_{2+x} fluorite lattice, which occurs at temperatures above 400°C. The U–O phase diagram (see, for example, Ref. [24]) places the phase boundary between the phase field of $UO_2 + U_4O_9$ and the phase field of UO_{2+x} for the ratio $O/U = 2.08$ at $\simeq 500$°C. The U_4O_9 phase

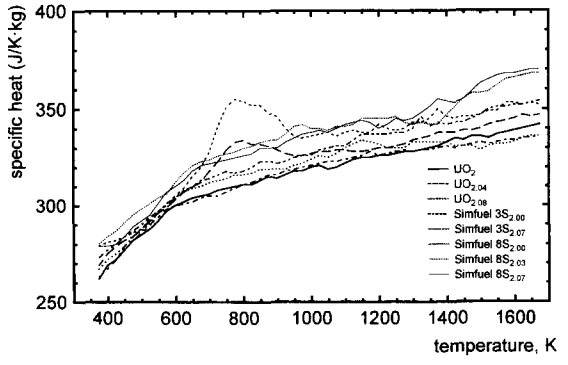

Fig. 1. Specific heat of UO_2 and SIMFUEL pre-annealed at three different oxygen potentials (see Table 1) as a function of temperature. The results are bundled within about 10% variation. The specimen designation is as in Tables 1 and 2, e.g., $8S_{2.03}$ stands for 8 at.% Simfuel with an O/M-ratio of 2.03 (M = U plus dissolved metallic fission products).

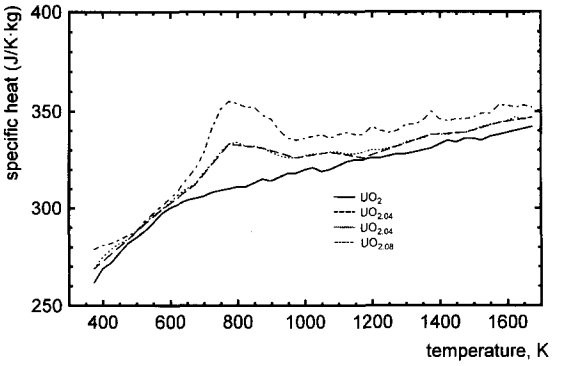

Fig. 2. Specific heat of hyperstoichiometric $UO_{2.04}$ and $UO_{2.084}$ (two runs on the same specimen) showing an increase between 400 and 700°C caused by the U_4O_9 dissolution which does not occur for $UO_{2.00}$.

precipitated in hyperstoichiometric UO_{2+x} during sample preparation; X-ray diffraction at room temperature showed it as broad, low intensity reflections toward lower Bragg angles (Fig. 3a). X-ray diffraction of SIMFUEL samples annealed under the same conditions did not exhibit the

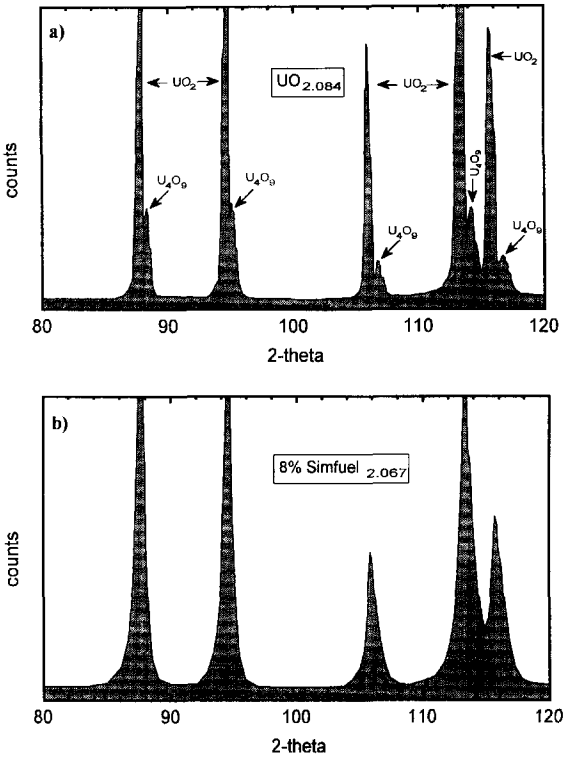

Fig. 3. Diffraction patterns at room temperature and at high Bragg angles from: (a) $UO_{2.084}$ indicating the presence of U_4O_9 along with the UO_2, and (b) 8 at.% burnup SIMFUEL annealed at the same oxygen potential of -195 kJ/mol without detectable U_4O_9 presence.

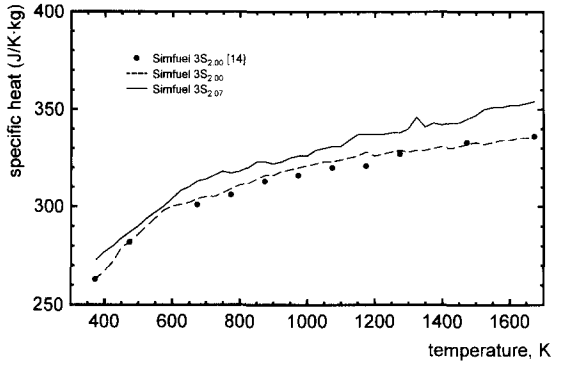

Fig. 4. Specific heat of 3 at.% SIMFUEL compared with earlier results [14] for various temperatures between 100 and 1400°C.

U_4O_9 formation (Fig. 3b); consequently, their specific-heat dependence on temperature did not show a protuberance between 400 and 600°C.

Our previous specific-heat data [1,3] were included in papers presenting thermal diffusivity-thermal conductivity data. The present results for SIMFUEL with an equivalent burnup of 3 at.% are compared to the previously published data [14] in Fig. 4. The former and the latter results are in good agreement (within 3%). Fig. 5 shows the results of specific heat for 8 at.% burnup SIMFUEL samples annealed at oxygen potentials of −265, −220 and −195 kJ/mol.

All SIMFUEL specimens (except for samples $3S_{2.00}$ and $8S_{2.00}$ annealed in reducing conditions) showed an increase in specific heat with increasing temperature, and had the same trend as UO_2. The increase was most pronounced below 600°C. However, the two SIMFUEL samples annealed in reducing conditions ($3S_{2.00}$ and $8S_{2.00}$) showed a different trend at temperatures above 900°C: the specific heat did not increase significantly with increasing temperature. Consequently, the C_p values of these samples were lower than those of UO_2 above ≃ 1200°C. This behavior suggests a slight oxidation process. Such an oxidation is possible since a few part-per-millions (ppm) oxygen are probably present in the test gas and the samples were initially slightly hypostoichiometric (see Table 1).

The effect of simulated burnup on the specific heat is inconspicuous. The specific heat increased marginally with burnup. The changes in specific heat caused by simulated fission products follow the simple Kopp–Neumann rule as was shown earlier [1]. For deviation from stoichiometry, the effect on specific heat is more prominent (see, for example, Ref. Fig. 5).

The present results can be used to express the burnup and oxygen-to-metal (O/M) ratio dependence of the specific heat for UO_2 fuel. Currently, MATPRO [7] suggests the following analytical expression for the C_p of UO_{2+x}:

$$C_p = \frac{k_1\Theta_E^2\exp(\Theta_E/T)}{T^2(\exp(\Theta_E/T)-1)^2} + k_2T + \frac{yk_3E_D}{2RT^2}\exp(-E_D/RT),$$

where C_p is the specific heat (J/K kg), T is the temperature (K), $R = 8.314$ (J/K mol); y is the O/M ratio, Θ_E the Einstein temperature (535.3 K), E_D is the formation energy for Frenkel defects, taken in MATPRO to be 157.7 kJ/mol, in order to allow for the defect contribution to C_p and its increase above ≃ 1300°C and k_1, k_2 and k_3 are empirical constants of 296.7 J/K kg, 0.0243 J/K^2 kg and 8.745×10^7 J/kg, respectively for unirradiated UO_2. As there were no specific heat measurements available on irradiated or simulated fuel at that time, it was suggested that irradiation would not directly affect the specific heat of UO_2.

The new SIMFUEL results indicate that the burnup effect caused by fission products (except gases and volatiles) is rather small. This is in agreement with calculations performed for SIMFUEL using the Kopp–Neumann rule [25]. It can also be incorporated in the analytical expression of the specific heat by modifying the constant k_2 accordingly. Taking into account the measured O/M ratio, the present and earlier SIMFUEL data yield

$$k_2' = k_2(1 + 0.011\beta),$$

where $k_2 = 0.0243$ J/K^2 kg is the constant from the MATPRO expression and β is the numerical value of burnup expressed in at.%. This revised analytical expression for the specific heat takes into account the burnup and O/M ratio dependence, and is more suitable for irradiated fuel.

Fig. 6 shows the temperature dependence of C_p for UO_2 (and $UO_{2.10}$ and $UO_{2.20}$) suggested by MATPRO,

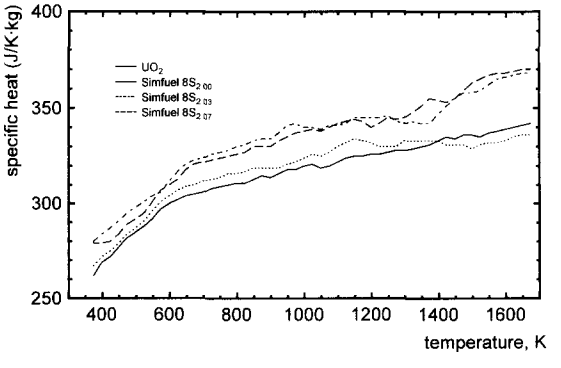

Fig. 5. Specific heat of hyperstoichiometric SIMFUEL with an equivalent burnup of 8 at.% as a function of temperature for different deviations from stoichiometry compared with the values measured for $UO_{2.00}$.

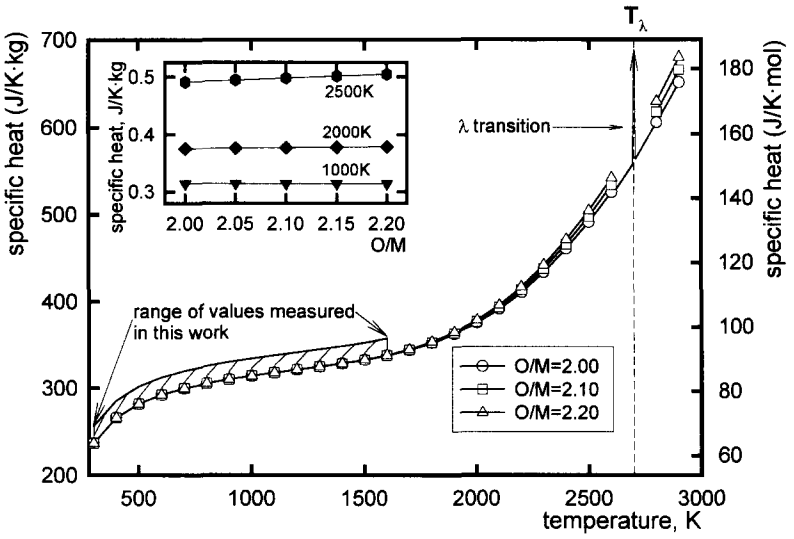

Fig. 6. Specific heat of UO_2, $UO_{2.1}$, and $UO_{2.2}$ as recommended by MATPRO [7] (circles, squares and triangles spaced at 100 K intervals) with the present results for UO_2, 3 and 8 at% SIMFUEL with different oxygen contents shown in a band. The peak in C_p at the λ-transition [26,27] is also indicated.

together with the present data in a band. Included is also the region in C_p values where the λ-transition occurs in UO_2 at $\simeq$ 2670 K as it was measured with a sophisticated laser heating technique developed at the institute for transuranium elements [26,27]. The significant effect of hyperstoichiometry reported in early work by Affortit and Marcon [6] and the anomaly in the T-dependence for UO_2 containing impurities or fission products reported more recently by Naito, Matsui and co-workers [8–13] were not observed in our study. Recent preliminary measurements [28] with 8% burnup SIMFUEL using laser heating at high temperatures (2000 K), confirmed the absence of such an anomaly in SIMFUEL.

4. Conclusions

In summary, the specific heat measurements on UO_2 and SIMFUEL have shown:

- the specific heat of SIMFUEL has a temperature dependence that is similar to that of UO_2;
- the specific heat increases slightly with the burnup, as predicted by the Kopp–Neumann rule;
- higher oxygen contents increase the specific heat, but only slightly;
- the dependence on burnup and on deviation from stoichiometry can be expressed by slightly modifying the coefficients used for the analytical expression recommended for UO_2.

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