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Heat capacity, thermal conductivity and thermal diffusivity of uranium–americium mixed oxides

O.S. Vălu [a,b], D. Staicu [a], O. Beneš [a], R.J.M. Konings [a,b,*], P. Lajarge [a]

[a] European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany
[b] Delft University of Technology, Faculty of Applied Sciences, Mekelweg 15, 2629 JB Delft, The Netherlands

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ABSTRACT

The enthalpy increments of $(U_{1-y}, Am_y)O_{2-x}$ mixed oxides with $y = 0.0877$ and 0.1895 and $x = 0.01$–0.03 were measured using drop calorimetry in the temperature range 425–1790 K and the heat capacity was obtained as differential of the obtained enthalpy increments with respect to temperature. The thermal diffusivity was measured using the laser flash technique from 500 to 1550 K. The thermal conductivity was calculated from the measured thermal diffusivity, density and heat capacity. Measured enthalpy increments of the $(U_{1-y}, Am_y)O_{2-x}$ solid solutions are very close to the end members, indicating no excess contribution. The derived heat capacities for the two intermediate compositions are slightly higher than that of UO_2 and in a good agreement with literature data of AmO_2 up to 1100 K. For the thermal conductivity of (U, Am)O_{2-x} mixed oxides a correlation using the classical phonon transport model in crystal structures is proposed.

1. Introduction

The most abundant transuranium elements found in the high level waste from reprocessed nuclear power reactor fuels are Am and Np. Within the realm of partitioning and transmutation, these long-lived minor actinides and Pu should be recycled in fast reactors, in which they are transmuted to short lived fission products. Thus the long term hazard is alleviated. The solid solution formed by uranium and americium oxides is a possible target for recycling americium in fast neutron reactors. For this reason the synthesis and the thermodynamic properties of the (U, Am)O_{2-x} mixed oxides need to be investigated.

In order to understand the behavior of nuclear fuel during irradiation it is mandatory to have clear information about the thermodynamic properties of the fuel material in its pristine state. The heat capacity and thermal conductivities of the (U, Am)O_{2-x} solid solution are essential for the reactor design and safety calculations. There is a significant number of publications on the synthesis and characterization of (U, Am)O_{2-x} solid solutions [1–4], but very few thermophysical properties studies [5,6].

In this work, $(U_{1-y}, Am_y)O_{2-x}$ solid solutions with $y = 0.0877$ and 0.1895 and $x = 0.01$–0.03 were considered. A high temperature calorimeter operated in drop mode was used for the determination of the enthalpy increments in the 425–1790 K temperature range (shown in Fig. 1). From these results the heat capacity was derived. The thermal diffusivities were measured using the laser flash method in the 500–1550 K temperature range, and by combining the results with the heat capacity, the thermal conductivity was obtained. An additional goal of this study was to determine possible excess contributions in these thermodynamic properties, as this will allow developing models that reliably interpolate between measured compositions. Experimental data on the thermodynamic properties of these compounds have never been reported in literature, and the results obtained in this study bring a significant contribution to a better description of the (U, Am)O_{2-x} system and can be used for benchmarking theoretical calculations.

2. Experimental work

2.1. Sample preparation

Samples of (U, Am)O_{2-x} targets were prepared with two ^{241}Am contents (8.77 and 18.95 mol%) and were characterized by Vespa et al. [1]. Porous beads (in this case UO_2) were synthesised by a sol–gel process [7,8] and which were then introduced into the Minor Actinide handling facility, where they were infiltrated with an Am solution. The Am nitrate solution was prepared by dissolution of the oxide. A key step of the process is the infiltration, and it is essential that the porous beads do not dissolve in the Am nitrate solution. For UO_2 porous beads, however, this can

* Corresponding author at: European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany. Tel.: +49 7247 951391; fax: +49 7247 95199391.
E-mail address: rudy.konings@ec.europa.eu (R.J.M. Konings).

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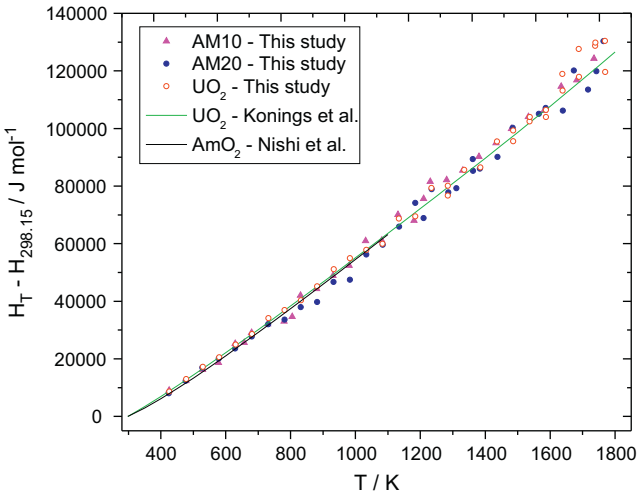

Fig. 1. The enthalpy increments of the UO_2 end-member, AM10 and AM20 intermediate compositions measured in this study together with enthalpy equations of AmO_2 obtained by Nishi et al. [14] and UO_2 assessed by Konings et al. [13].

become problematic. Adjustment of the free nitrate concentration of the Am solution was required to hinder the dissolution of the beads and to avoid Am precipitation from solution. Thus, the acid concentration was kept low (<3M HNO_3) during the dissolution of the Am oxide.

Following infiltration, the beads were dried and then calcined in Ar at 800 °C for 2 h to convert the Am nitrate to oxide. A single infiltration cycle was used to produce a sample with ~10 mol% Am. For the higher 20 mol% Am content, the infiltration and calcination steps were repeated once. After the calcination step, the beads were compacted into disks in a bi-directional press, and sintered under humidified Ar/H_2 atmosphere at 1650 °C for 8 and 24 h, for the 10 and 20 mol% samples, respectively. The density of the 20 mol% sample was 93% of the theoretical density (%TD), whereas for the 10 mol% Am concentration, sintered disks reached a value of 87% of TD.

After production, the actual Am content was determined by a calorimetric method [9] measuring the decay heat of ^{241}Am, the results of which are provided in Table 1. More information about the sample preparation of the uranium–americium mixed oxides can be found in the study of Vespa et al. [1]. The notations defined in Table 1 were used in the text and graphs.

2.2. Experimental procedure

2.2.1. Drop calorimetery

The enthalpy increment measurements performed in this study were made with a Setaram Multi Detector High Temperature Calorimeter (MDHTC – 96 type) operated in drop mode. The temperature scale of the calorimeter was calibrated using high purity (⩾99.95%) standard materials (In, Zn, Sn, Pb, Al, Ag and Au). In order to measure active samples, the calorimeter was enclosed in a glove-box keeping most of the electrical parts outside in order to minimize the nuclear waste after the operational lifetime of the calorimeter [10] and more importantly easing repairs during its operation.

The samples, as solid fragments, were introduced in a sample holder which is positioned on top of the detector. The furnace was programmed to reach the desired temperature at which the measured heat flow signal is stabilized during 7 h. After this period the samples were dropped from ambient temperature into the calorimeter which is programmed to maintain a constant temperature. Each drop was repeated every 25 min which was sufficient to restabilize the temperature and the heat flow signals. Before and after each sample, a reference material was dropped to determine the sensitivity (signal vs heat ratio) of the detector. As reference material we used small pieces (150–200 mg) of platinum 99.995%. The system records the energy which is necessary to heat up the sample from the room temperature to the programmed temperature. The details of the instrument were described in our previous study [11] to which we refer for more details.

2.2.2. Thermal diffusivity

The thermal diffusivity measurements were carried out using a shielded laser flash device [12]. The samples were disks with a thickness of about 1.5 mm, and with a diameter of 5 mm. The faces were checked to ensure that they were plane parallel, without defects. The samples were heated to the measurement temperature in a high frequency furnace, in the temperature range from 500 to 1550 K. The thermal diffusivity measurements were performed under a static atmosphere of 10^{-3} mbar of nitrogen initially containing 0.1% of oxygen. This atmosphere is usually used to avoid reduction of $(U, Pu)O_2$ samples, without any oxidation of the UO_2 phase present in the samples. Preliminary tests consisting of oxygen potential determinations before and after the thermal diffusivity measurements have shown that under these conditions the oxygen content of fresh stoichiometric UO_2 and $(U, Pu)O_2$ fuels was not modified, enabling us to conclude that this arrangement would be suitable for the $(U, Am)O_{2-x}$ too.

The measured thermogram at each temperature was carefully inspected to ensure that heat transfer conditions were standard. The precision of the individual thermal diffusivity measurements was always better than 2%, and the overall accuracy is about 5%, due to sample thickness variations.

3. Results and discussion

3.1. Enthalpy increment measurements

Enthalpy increment measurements of ceramic $(U_{1-y}Am_y)O_{2-x}$ with $y = 0.0877$ and 0.1895 were performed in the temperature range 425–1765 K. In addition the UO_2 end-member was measured and compared with literature data, obtaining a good agreement. The measured enthalpy increments of UO_2 are given in Table 2, while enthalpy increments of AM10 and AM20 are listed in Tables 3 and 4 respectively. The samples weight ranged between 46.6 and 142.9 mg for the 10% Am content sample, 43.7–94.2 mg for the 20% Am content sample and 107.6–157.2 mg for UO_2, respectively. For all experiments, high purity helium gas was used as carrier gas with a flow rate of 2.8 l/h. Helium was selected for its good thermal conductivity. Fig. 1 shows all measured enthalpy increments together with literature data of the end members UO_2 from Konings et al. [13] and AmO_2 from Nishi et al. [14]. For each measured temperature the corresponding enthalpy increment value represents the mean of all performed measurements at that temperature.

The experimental enthalpy increment values of both intermediate compositions were fitted using the least square method into an Maier–Kelly empirical temperature relationship with a constraint, $H_T - H_{298.15} = 0$ at $T = 298.15$, using the Origin software. The enthalpy increment fits are shown in Fig. 2.

Fig. 1 shows a comparison of the obtained enthalpy increments of the UO_2, AM10 and AM20 intermediate compositions together with the enthalpy equations of AmO_2 obtained by Nishi et al. [14] and UO_2 assessed by Konings et al. [13] from all available literature. Even if Nishi's study only reaches 1100 K we observed that our results match with the AmO_2 values and follow the curve of the UO_2 up to 1800 K. From this comparison it is difficult to distinguish an independent behavior of one single component and we conclude that the enthalpy of UO_2 and AmO_2 are very similar for the temperature range 300–1800 K. Furthermore, the obtained enthalpy increments of the two intermediate compositions follow

Table 1
$(U, Am)O_{2-x}$ notations, compositions and fabrication data.

Notation	Nominal composition Am/(U+Am) (mol%)	Actual composition[a] Am/(U+Am) (mol%)	Sintering under Ar/H_2	Disk density (% TD[b])
AM10	10	8.77	1650 °C, 8 h, 1500 ppm H_2O	87
AM20	20	18.95	1650 °C, 24 h, 2400 ppm H_2O	93

[a] Composition measured by calorimetry [9].
[b] TD = theoretical density, determined from gravimetry and geometry.