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High-Temperature Heat Capacity of (U,Am)O_{2±x} Oxides

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Context and Objectives

In the frame of **minor actinide recycling** in sodium cooled fast reactors, $(U,Am)O_2$ are promising transmutation targets. Data on their thermal properties are mandatory to predict the behavior of these compounds in reactor under both normal and accidental conditions. For instance, the **heat capacity** (C_p) plays a crucial role by determining the quantity of heat that can be accumulated in the material. Several studies have been reported on the enthalpy increments and the heat capacity of UO_2 from room temperature (RT) up to its melting, but very few experimental data exist for Am binary oxides and U-Am mixed oxides. Measurements of the enthalpy increments from room temperature of AmO_2 were performed by Nishi *et al.* [1], but these were limited to 1080 K. For mixed uranium-americium dioxide, only one set of high temperature enthalpy increments has been reported in the literature, by Vălu *et al.* [2]. In this work, we extended the investigation of the $(U_{1-y}Am_y)O_{2±x}$ system to higher americium contents: five compositions with Am/(Am+U) ratio equal to 0.3, 0.4, 0.5, 0.6 and 0.7 were investigated.

Experimental set-up & procedure



The experiments were performed under purified Argon (oxygen content ~1 ppm) atmosphere for the samples with Am/(Am+U)≤0.5 and under air for the highest Am contents, in order to try to keep the O/M ratio close to the stoichiometric value of 2.0.

The enthalpy increments for the five $(U_{1-\gamma}, Am_{\gamma})O_{2\pm x}$ compounds were measured between 470 and 1750 K . The results are represented in Fig.2 (a) and (b), with a comparison to the literature data.

The two binary dioxides UO_2 and AmO_2 and the mixed compounds share a similar **enthalpy** trend with temperature. However, in the mixed dioxides with Am/(Am+U)>0.4, the enthalpy increments seem generally higher than those of UO_2 and AmO_2 for T>1100 K.

The **heat capacity** functions of the $(U_{1-y}, Am_y)O_{2\pm x}$ oxides were derived using a linear regression of all the enthalpy data. A **Maier-Kelley** polynomial relation was used for the fit:

$$C_p = a + b \cdot T + c \cdot T^{-2}$$

Experimental Results



Heat Capacity functions





of the Drop calorimeter



Discussion and comparison to thermodynamic CALPHAD model



The experimental enthalpies $H_{meas}(T) = H(T) - H(298.15)$ are compared to the ideal values obtained applying the **Neumann-Kopp** rule $H_{NK}(T)$. For AmO₂, the extrapolation of the data fit by Nishi et al. [1] is used for T>1100 K. The resulting difference $\Delta(H_{meas}-H_{NK})$ is represented as a function of the temperature Fig. 4. The difference is randomly distributed around the zeroline for the U_{0.68}Am_{0.32}O_{2±x} compound ^(b) and it can then be neglected. On the contrary, clear shifts toward positive values are observed above 1000 K for the compositions with higher Am other content. Moreover, the shifts increase with the temperature. The systematic nature of the phenomenon indicates the presence of an *excess contribution*.



The **Am-O CALPHAD model** of Epifano et al. [3] was adopted to perform thermodynamic calculations. The H(T) of AmO_{2-x} was computed as a function of T, including in the calculation a gas phase with $pO_2=0.21$ atm, hence simulating air. The results are shown in Figure 5(a). In Figure 5(b), the variation of the composition of the AmO_{2-x} phase with temperature is illustrated.

Under air, the $Am^{+4} \rightarrow Am^{+3}$ reduction and the **O vacancy formation** start at ~1100 K. This causes the departure from the linearity of the H(T) function. Indeed, all the measured H(T) for the mixed (U,Am)O₂ samples are comprised

Fig. 4: Comparison to the Neumann-Kopp additivity rule



Conclusions and perspectives

Drop calorimetry measurements were performed in the 470 < T < 1750 K range and H increments data for $U_{0.68}Am_{0.32}O_{2±x}$, $U_{0.61}Am_{0.39}O_{2±x}$, $U_{0.51}Am_{0.49}O_{2±x}$, $U_{0.42}Am_{0.58}O_{2±x}$ and $U_{0.32}Am_{0.68}O_{2±x}$ were reported for the first time. The experimental data were fitted in order to derive the Cp functions. The obtained enthalpy data are higher than those of UO_2 and AmO_2 for T>1100 K and Am/(Am+U)>0.39. However, the available experimental data for AmO_2 are limited to 1080 K and the enthalpy function was extrapolated above this temperature. This extrapolation is not appropriate because it does not keep into account the effect of the **oxygen vacancy formation**, that occurs in AmO_{2-x} for T>1100 K even under pure O_2 . This leads to an increase of the enthalpy values, as confirmed by the thermodynamic computations presented in this work, which were in very good agreement with the experimental trend. Therefore, the oxygen vacancy formation is responsible for the high enthalpy values measured for the compositions with high Am content [4]. In fact, a reduction similar to that of AmO_2 can be supposed at high temperature. For further improvement of the interpretation of the results, the effect of O vacancies on the heat capacity needs to be further quantified.

[1] T. Nishi et al., J. Nucl. Mater. 414 (2011) 109-113.
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