HIGH TEMPERATURE THERMODYNAMIC PROPERTIES OF THE (U, AM)O_2 SOLID SOLUTIONS

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EXTENDED ABSTRACT

Studies on oxides of actinide elements such as thorium, uranium, plutonium and americium are of great interest in nuclear industry since most of these oxides are used or are planned to be used as nuclear fuels in various types of reactors [1] in the form of mixed oxides. The thermodynamic properties such as enthalpy and heat capacity of these materials are needed for reactor safety calculations. Furthermore studies of the temperature dependence of vapour pressure are essential in calculation of the thermodynamic functions in order to predict stable phases in any multi-component system.

The most abundant transuranium elements found in the high level waste of nuclear power reactor fuels are Am and Np [2]. Because the two elements can be transformed by fast neutrons into shorter-lived fission products, recycling these elements in fast reactors would improve the efficiency and reduce the long-term hazard. The solid solution of the uranium and americium oxides is a possible chemical form for recycling americium. To understand the stability of the system with respect to the temperature the thermodynamic properties of mixed oxides needs to be investigated.

One of the objectives of this study is to investigate the heat capacity of the (U, Am)O_2 solid solution system. In this purpose we are using a Setaram multi detector high temperature calorimeter (MDHTC), operated in drop mode and the heat capacity is obtained by derivation of the measured enthalpy increments over temperature [3]. The enthalpy increments of (U_{1-y}, Am_y)O_2 solid solutions were measured in the temperature range 400 – 1800 K and fitted using the least squares method.

The results of this study will be used to clarify if uranium and americium dioxides that form a continuous solid solution show an ideal behavior of the heat capacity (i.e. can be calculated by summing the proportional weights of their end-members) or if some excess contributions appear. The derived C_P curves of (U_{1-y}, Am_y)O_2 solid solutions, in the temperature range 298 – 1800 K, and the origin of the behavior will be discussed.

A Knudsen cell coupled with a mass spectrometer was used to perform vapour pressure measurements [4]. The vaporisation behaviour of (U_{1-y}, Am_y)O_2 solid solution samples has been studied in vacuum at high temperatures up to 2400 K. The evolution of the uranium and americium bearing species was also determined as a function of time, in order to evaluate the congruent vapour composition. Appearance potentials of the key molecular species were determined by varying the energy of the ionising electrons at constant temperature. The partial and the total vapour pressures of the oxides have been measured as a function of temperature. The dissociative ionisation contribution was evaluated with respect to the composition of the gaseous phase which under Knudsen conditions is in equilibrium with the condensed phase. The results on the vapour pressure of the (U_{1-y}, Am_y)O_2 samples will be discussed.

All the thermodynamic results obtained in this study are used for a consistent description of the ternary U-Am-O system and optimisation of the phase diagram.

REFERENCES

[1] C. Ganguly *IAEA-TECDOC*, 352, pp. 107-127 (1985).
[2] W. Bartscher and C. Sari, *Journal of Nuclear Materials*, 118, pp. 220-223 (1983).
[3] O. Beneš et al., *J. Chem.*, 49, pp. 651-655 (2011).
[4] P. Gotcu-Freis et al., *J. Chem. Thermodynamics* , 43, pp. 492-498 (2011).