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Minor actinides (MA: Am, Np, Cm) are created in the nuclear fuel through successive neutron captures occurring during irradiation. One of the options envisaged for reducing the long-term radiotoxicity of the nuclear waste is the transmutation of these elements in fast neutron reactors. In this frame, the attention is mainly focused on mixed uranium and americium dioxides $(U,Am)O_2$.
The possibility of using advanced fuels containing MA requires investigating their structural and thermodynamic properties, in order to foresee the in pile behavior. For instance, the thermal conductivity and the melting temperature are fundamental parameters to determine the safety limits of a fuel. In actinide dioxides, that generally admit a large existence domain, the thermal properties are affected by the Oxygen/Metal ratio (O/M). The latter also affects the chemical interaction between the fuel and the cladding. Therefore, a thorough knowledge of the existence domain of the dioxide phase is necessary.
The aim of this work is to develop a thermodynamic model of the U-Am-O ternary system through the semi-empirical CALPHAD method, which is based on the Gibbs energy assessment of each phase. Unfortunately, the experimental data on U and Am mixed oxides are rare, because of the scarcity and high radioactivity of americium [1], [2]. For this reason, an extensive experimental campaign on these compounds was carried out in collaboration with the JRC-Karlsruhe. $(U,Am)O_2$ samples with Am/(U+Am) ratios ranging from 0.1 to 0.7 were manufactured by powder metallurgy using the UMACS process [3].

Structural data, which are necessary to develop a reliable CALPHAD description of each phase, were obtained combining X-ray Diffraction (XRD) and X-ray Absorption Spectroscopy (XAS). XRD confirmed the maintaining of the fluorite-type structure, common to all the actinide dioxides. Nevertheless, XAS investigations highlighted a peculiar charge distribution, with Am reduced to trivalent state and U partially oxidized.
Thermodynamic data have been obtained through different techniques. Drop calorimetry was performed to measure enthalpy increments as a function of temperature and derive the heat capacities of $(U,Am)O_2$ with various Am contents. Melting temperature measurements were performed both under reducing and oxidizing conditions using a laser-heating technique. In order to obtain reliable data, various post-melting characterizations (XRD, XAS, Raman, SEM) were performed to determine the composition and the phases present in the samples after the measurements. The vaporization behavior of U-Am mixed oxides at high temperature (T>2000 K) was studied by Knudsen Cells Mass Spectrometry (KEMS). Finally, study of the oxygen pressure-temperature-composition equilibria were conducted by thermogravimetry in order to derive the oxygen potentials of $(U,Am)O_2$, whose knowledge is necessary

to foresee the O/M of these compounds under different conditions. Thanks to the new experimental data acquired on the U-Am-O system, a CALPHAD assessment will be performed and the resulting model will be integrated in the Thermodynamic of Advanced Fuel International Database (TAFID).

References

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