Abstract

Solid solutions of the oxides, carbides and nitrides of uranium and plutonium or their alloys find applications as fast reactor fuels. Uranium-thorium mixed oxides are candidate fuels for advanced thermal reactors based on $^{232}$Th-$^{233}$U fuel cycle. Starting from a fuel of uniform chemical composition, in general, a variety of fission products are produced during irradiation. The chemical states of U, Pu and the fission products in the fuel, as a function of the irradiation time and radial position, are important data. For predicting the chemical state of these elements in the fuel during irradiation, thermodynamic data are needed. For a safe and reliable operation of a reactor, the fuel must be compatible with the metal cladding used to contain the fuel as well as the coolant used for removing the fission generated heat energy. Thermodynamic properties of a nuclear fuel have a key role to play in understanding the compatibility of the fuel with the coolant and cladding. Among the thermodynamic properties of a system, heat capacity determines the evolution of all the other properties as a function of temperature. Further, especially in the case of nuclear fuel, heat capacity data have an added importance of being the key parameter to determine the thermal conductivity data from the experimentally measurable thermal diffusivity data. Thermal conductivity derives its importance from the fact that it determines the maximum power that can be extracted from unit length of the fuel element during its operation.

Uranium-plutonium mixed carbides have been successfully irradiated up to a burn-up of 155 GWd/t in the Fast Breeder Test Reactor at the Indira Gandhi Centre for Atomic Research, Kalpakkam. Uranium-plutonium mixed oxides have been chosen as the fuel for the 500 MW(e) Prototype Fast Breeder Reactor under construction in Kalpakkam. Uranium-plutonium mixed nitrides are candidate advanced fuels for future fast breeder reactors. The third stage of Indian nuclear energy programme aimed at exploiting the large reserves of thorium for future generation of power using advanced reactors will be based on $^{233}$U-$^{232}$Th fuel cycle. Thermal breeder reactors using uranium-thorium mixed oxides or thorium-plutonium mixed oxides are expected to be employed in the third stage. Hence in the present investigations, heat capacity and enthalpy increment measurements were carried out on the following nuclear fuel materials using calorimetric methods with a view to determining their thermodynamic properties.
1. Uranium-plutonium mixed oxides, \((U,Pu)O_2\)
2. Uranium-plutonium carbides and nitride, \((U,Pu)C\) and \((U,Pu)N\)
3. Uranium-thorium mixed oxides, \((U,Th)O_2\)

Fuel materials containing plutonium are radioactive as well as highly toxic and hence they have to be handled in glove boxes maintained under a negative pressure with respect to the ambient. Further, uranium-plutonium mixed carbides and nitrides used in this study are quite sensitive to oxygen and moisture as well as pyrophoric in nature especially in a finely divided state. Therefore a leak-tight glove box system having a carefully controlled inert atmosphere is an essential requirement for handling and carrying out measurements on them. An argon atmosphere glove box facility maintained at a negative pressure of 20 to 40 mm water column with respect to the ambient was designed and set up and a high temperature drop calorimeter was incorporated in the glove box for carrying out calorimetric studies on Pu bearing fuel materials.

Enthalpy increments of uranium-plutonium mixed oxides, \((U_{0.70}Pu_{0.21})O_2\), \((U_{0.72}Pu_{0.28})O_2\), \((U_{0.60}Pu_{0.40})O_2\), \((U_{0.55}Pu_{0.45})O_2\), \((U_{0.45}Pu_{0.55})O_2\) and \((U_{0.35}Pu_{0.65})O_2\) were measured in the temperature range 1011-1776 K, 1009-1771 K and 1025-1771 K, 993-1803 K, 960-1782 K and 956-1797 K, respectively by employing inverse drop calorimetric method. Thermodynamic functions such as heat capacity, entropy and Gibbs energy function were computed from measured enthalpy increments in the temperature range 298-1800 K. The results indicate that the enthalpy increments and heat capacity of \((U,Pu)O_2\) solid solutions in the temperature range 298-1800 K obey the Neumann-Kopp’s rule.

Enthalpy increment measurements have been carried out on Mark-I and Mark-II fuels of FBTR in the temperature range 1021-1759 K and 1018-1765 K, respectively. The present study provides the first experimental enthalpy data for hyperstoichiometric Mark-I \((U_{0.30}Pu_{0.70})C_{1+x}\) and Mark-II \((U_{0.45}Pu_{0.55})C_{1+x}\) fuels of FBTR, in the temperature range 1021-1759 K and 1018-1765 K, respectively. This study also provides for the first time data for the thermodynamic functions, heat capacity, entropy and Gibbs energy function in the temperature range 298-1800 K for Mark-I and Mark-II fuels of FBTR.

Uranium–plutonium mixed nitride \((U,Pu)N\) is a candidate advanced fuel for fast reactors. Enthalpy increments measurement on \((U_{0.45}Pu_{0.55})N\) were carried out in
the temperature range of 1025–1775 K. This study presents the first measurements of the enthalpy increments and heat capacity of (U0.45Pu0.55)N.

Urania-thoria solid solutions, namely, (U0.10Th0.90)O2, (U0.50Th0.50)O2 and (U0.90Th0.10)O2 were prepared by co-precipitation method and characterised by X-ray diffraction. A “Multi-detector” High Temperature Calorimeter (MHTC-96) of M/s. SETARAM, France was employed for enthalpy increment measurements of the above urania-thoria solid solutions in the temperature range 480-1800 K. The results indicate that the enthalpy increments and heat capacity of (U,Th)O2 solid solutions in the temperature range 298-1800 K obey the Neumann-Kopp’s rule.

Heat capacity measurements of (U0.10Th0.90)O2, (U0.50Th0.50)O2 and (U0.90Th0.10)O2 were also carried out by using a heat flux type Differential Scanning Calorimeter in the temperature range of 298-800 K. The heat capacity data from DSC are in agreement with those from drop calorimetric measurements within ± 4%. In this study, calorimetric measurements on uranium-thorium mixed oxides cover a wide range of temperatures as well as compositions.