ABSTRACT

The world, in particular India, has to tap nuclear energy to meet its ever increasing energy needs. The commercial nuclear reactors operating in the world today convert thermal energy produced during nuclear fission into electricity. The fuel used in these reactors is generally in the form of uranium dioxide contained in a metallic tube around which a coolant is passed to extract the thermal energy. Besides UO$_2$, the oxides, carbides, nitrides and the alloys of uranium and plutonium, are also used as fuels in reactors. The economics of power production depends on the performance of a fuel pin which in turn depends on the behaviour of the fuel during irradiation. Under the influence of large thermal gradients experienced by the fuel in a reactor, various reactions can occur among the elements produced by fission, known as fission products and the fuel materials, uranium and plutonium. Possible fuel-coolant as well as fuel-clad interactions also influence the performance of a fuel pin. Thermodynamic data on various fuel systems are therefore important to understand the fuel behaviour during irradiation and to predict the possible interactions. Uranium, clad in aluminium, and dispersions of UAl$_3$ in an aluminium matrix serve as fuels in many research reactors. Hence, calorimetric measurements were carried out on U-Al system to derive thermodynamic data which are of relevance to nuclear technology.

Fuel reprocessing is an important aspect of the nuclear fuel cycle. Nuclear fuel has to be reprocessed after irradiation in a reactor to separate the fuel materials,
uranium and plutonium, from fission products. The fuel materials, thus separated, will then be used for refabrication into fuel pins which will again be inserted in the reactor. Among the reprocessing methods, those employing non-aqueous reagents like molten salts and alloys are advantageous for metallic fuels. Salt transport is one such method in which liquid Cu-Mg alloys are used. Thermodynamic data of liquid Ce-Cu-Mg alloys are of importance in the separation of cerium, an important fission product, from the fuel materials by using the salt transport method. Hence, in the present work, thermodynamic studies on Ce-Mg, Ce-Cu and Ce-Cu-Mg alloys were carried out by using calorimetric measurements. Precipitation of uranium from liquid aluminium as uranium-aluminium intermetallic compounds has also been used as a non-aqueous reprocessing method. Thus thermodynamics of U-Al system is of interest in non-aqueous reprocessing also.

Rare earth metal alloys with marked compound-forming tendencies have chemical short range order in the liquid state and such alloys also tend to form amorphous alloys or glassy phases on rapid quenching. Glass forming abilities of alloys can be related to their thermodynamic properties. Hence thermodynamic data on the cerium alloys mentioned above will also be useful to predict whether they will form amorphous alloys on rapid cooling.

The integral enthalpies of mixing of liquid Ce-Mg alloys were calorimetrically measured in the temperature range of 998 - 1096 K covering the whole concentration range. The measured values showed asymmetric concentration dependence indicating the possible existence of chemical
short range order in the liquid alloy. The observed concentration dependence of the enthalpies of mixing is described by using an association model in which CeMg$_3$ associates are assumed to be present in the liquid alloy.

The enthalpy of formation of CeMg$_3$ at 298 K was determined by solution calorimetric measurements in which liquid magnesium was employed as the solvent. The value thus obtained was $-14.9 \pm 1.7$ kJ mol$^{-1}$. The enthalpy of fusion of CeMg$_3$ at its melting temperature, 1069 K, was calorimetrically measured as $11.7 \pm 0.7$ kJ mol$^{-1}$. The enthalpy of mixing of the liquid alloy with the composition, Ce$_{0.25}$Mg$_{0.75}$, computed by using the enthalpy of formation and the enthalpy of fusion of CeMg$_3$, is in agreement with the directly measured value. The partial enthalpy of solution of cerium in liquid magnesium at infinite dilution at 945 K, obtained from solution calorimetric measurements, was $-69.9 \pm 3.8$ kJ mol$^{-1}$.

The Gibbs free energy of the under-cooled liquid Ce-Mg alloy (computed by using the association model) at the estimated glass transition temperature indicated that Ce$_{0.65}$Mg$_{0.35}$ may possibly form a glassy phase on rapid cooling. However, it did not form any glassy phase due to kinetic factors.

The integral enthalpies of mixing of liquid Ce-Cu alloys were calorimetrically measured at 1095 K, 1130 K and 1473 K covering the whole concentration range. The measured values show asymmetric concentration dependence indicating the possible existence of chemical short range order in the liquid alloy. The observed dependence of the enthalpies of mixing on concentration as well as temperature is explained.
on the basis of an association model in which CeCu$_3^*$ associates are assumed to be present in the liquid alloy.

The enthalpy of formation of the intermetallic compound, CeCu$_2$, at 298 K was determined from solution calorimetric measurements by employing liquid cerium as the solvent. The enthalpy of formation of CeCu$_2$ at 298 K thus obtained was $-18.7 \pm 1.9$ kJ mol$^{-1}$. The enthalpy of fusion of CeCu$_2$ at its melting temperature was also calorimetrically measured to be $11.3 \pm 2.8$ kJ mol$^{-1}$. The integral enthalpy of mixing of the liquid alloy with the composition, \( \text{Ce}_0.33\text{Cu}_0.67^* \), derived from the enthalpy of formation and the enthalpy of fusion of CeCu$_2$, is found to be in very good agreement with the value obtained by direct measurements.

The enthalpy increments of CeCu$_2$ were measured by drop calorimetry in the temperature range of 1039 - 1090 K. The heat capacity of liquid CeCu$_2$ in this temperature range was determined to be $44 \pm 2.5$ J mol$^{-1}$K$^{-1}$. The melting temperature and the enthalpy of fusion at the melting temperature were determined to be 1085 $\pm$ 4 K and 9.8 $\pm$ 1 kJ mol$^{-1}$ respectively.

Ce$_{0.72}$Cu$_{0.28}$ alloy was found to form a glassy phase on rapid cooling, as was indicated by the Gibbs free energy of the under-cooled liquid (computed by using the association model) at the glass transition temperature.

The integral enthalpies of mixing of liquid Ce-Cu-Mg alloys were calorimetrically measured in the temperature range of 998 - 1133 K. The measurements were carried out on the following concentration sections:

(a) \((\text{Cu}_{80}\text{Mg}_{20})_x \text{Ce}_{(1-x)}\)

(b) \((\text{Cu}_{67}\text{Mg}_{33})_x \text{Ce}_{(1-x)}\)
(c) \((\text{Cu}_{40}\text{Mg}_{60})_x\text{Ce}_{(1-x)}\)

(d) \((\text{Ce}_{33}\text{Cu}_{67})_x\text{Mg}_{(1-x)}\) and

(e) \((\text{Ce}_{72}\text{Cu}_{28})_x\text{Mg}_{(1-x)}\)

The observed concentration dependence of the measured enthalpies is explained by using association model computations in which the model parameters of the three binary systems were employed. The deviations of the computed values from the measured ones, observed in the case of concentration sections (b) and (c) given above, are explained on the basis of additional ternary interactions, among \(\text{Cu}_2\text{Mg}\) associates and unassociated free cerium atoms, that were not taken into consideration in the computations.

The computed values of the Gibbs free energies of the under-cooled liquid Ce-Cu-Mg alloys at the glass transition temperature show that these ternary alloys would possibly form a glassy phase on rapid cooling.

The integral enthalpies of formation of U-Al alloys were measured at 978 K, 1078 K and 1094 K. At 978 K, the measurements covered single phase liquid alloy as well as the two phase region containing the liquid alloy and the solid intermetallic compound, UAl\(_4\). From the measured values in the two phase region, the enthalpy of formation of UAl\(_4\) at 978 K, with reference to \(\alpha\)-uranium and solid aluminium, was determined to be \(-25.4 \pm 1.5\) kJ mol\(^{-1}\). At 1078 K and 1094 K, the measurements covered single phase liquid alloy as well as the two phase region containing the liquid alloy and the solid intermetallic compound, UAl\(_3\). From the measured values in the two phase region, the enthalpy of formation of UAl\(_3\) at 1086 K (mean of 1078 K and 1094 K), with reference to
α-uranium and solid aluminium, was determined to be $-29.9 \pm 2.2 \text{ kJ mol}^{-1}$. The enthalpies of formation of $\text{UAl}_4$ and $\text{UAl}_3$ at 298 K were determined by solution calorimetric measurements by using liquid aluminium as the solvent. The enthalpies of formation of $\text{UAl}_4$ and $\text{UAl}_3$ at 298 K thus obtained were $-25.3 \pm 2.7 \text{ kJ mol}^{-1}$ and $-29.5 \pm 2.1 \text{ kJ mol}^{-1}$ respectively. The enthalpies of formation of both the compounds at 298 K are in agreement with the respective enthalpies of formation at higher temperatures confirming the validity of Neumann-Kopp's rule for both of them. The partial enthalpy of solution of uranium in liquid aluminium at infinite dilution at 980 K was determined to be $-153.7 \pm 7.1 \text{ kJ mol}^{-1}$. 